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Suspect and Nontarget Screening for Contaminants of Emerging Concern in an Urban Estuary

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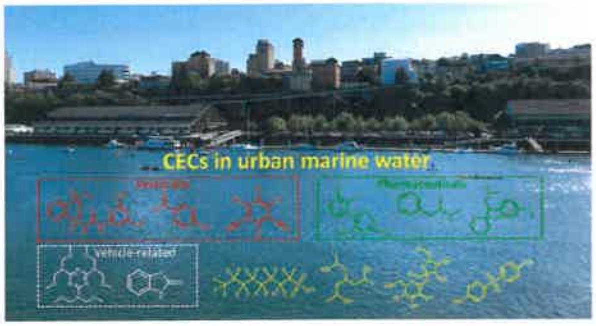
ABSTRACT: This study used suspect and nontarget screening with high-resolution mass spectrometry to characterize the occurrence of contaminants of emerging concern (CECs) in the nearshore marine environment of Puget Sound (WA). In total, 87 non-polymeric CECs were identified; those confirmed with reference standards (45) included pharmaceuticals, herbicides, vehicle-related compounds, plasticizers, and flame retardants. Eight polyfluoroalkyl substances were detected; perfluorooctanesulfonic acid (PFOS) concentrations were as high as 72−140 ng/L at one location. Low levels of methamphetamine were detected in 41% of the samples. Transformation products of pesticides were tentatively identified, including two novel transformation products of tebuthiuron. While a hydrodynamic simulation, analytical results, and dilution calculations demonstrated the prevalence of wastewater effluent to nearshore marine environments, the identity and abundance of selected CECs revealed the additional contributions from stormwater and localized urban and industrial sources. For the confirmed CECs, risk quotients were calculated based on concentrations and predicted toxicities, and eight CECs had risk quotients >1. Dilution in the marine estuarine environment lowered the risks of most wastewater-derived CECs, but dilution alone is insufficient to mitigate risks of localized inputs. These findings highlighted the necessity of suspect and nontarget screening and revealed the importance of localized contamination sources in urban marine environments.



INTRODUCTION

Estuaries are critical natural habitats for many marine organisms; they also benefit humans by providing transportation, fisheries, and other critical ecosystem services.[1] With 22 of the 32 largest global cities located on estuaries,[2] human activities from urban areas disturb both the ecological function and water quality of nearshore marine environments. Estuarine marine waters and other nearshore habitats are typically contaminated by wastewater effluent, industrial discharge, stormwater runoff, aquaculture, and agricultural sources of pollution.[3] Among such complex mixtures, contaminants of emerging concern (CECs) are commonly detected,[4−6] and the concern over their impacts on marine wildlife is growing,[7,8] as many CECs have been implicated in adverse biological effects even at low concentrations.[9,10]

CECs broadly include pharmaceuticals, personal care products, pesticides, industrial additives, and other unregulated anthropogenic chemicals.[11] Extensive efforts in water quality monitoring have identified hundreds of CECs in natural and engineered aquatic systems,[12,13] but given the large diversity of chemical pollution, the specific anthropogenic chemicals produced, used, and discharged to aquatic environments remain uncertain.[14,15] In nearshore marine environments, multiresidue analyses have detected CEC classes such as pharmaceuticals, UV filters, flame retardants, and pesticides.[4,16−19] However, these studies primarily employed targeted analyses focusing on preselected groups of CECs, especially those compounds associated with wastewater effluent.[4,20] CECs from other sources or those not previously monitored represent significant opportunities for unanticipated adverse effects linked to water quality.[14]

Suspect and nontarget screening techniques represent emerging methods to enhance our understanding of CEC profiles in environmental systems.[21] Using high-resolution mass spectrometry (HRMS) and advanced data analyses, many chemicals can be detected in complex matrices with limited pre-existing knowledge. Detected compounds can be prioritized using data-driven and/or experiment-driven strategies[15] and subsequently identified,[22] as exemplified by reports of unexpected or previously unknown contaminants in

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water,[23−26] soil,[27] sediment,[28] biological tissue,[29,30] household dust,[31,32] and aerosols.[33] Although HRMS methods have been widely applied to wastewater and freshwater systems, few studies have applied such methodologies to marine waters and urban estuaries.,[34,35] and the results from suspect and nontarget screening remain preliminary.[36] Further, despite their important ecological functions, CEC risks to estuarine ecologies are not well understood. Thus, there is an urgent need for application of broad, holistic screening approaches to these estuarine systems to characterize CECs and evaluate their potential impacts on water quality.

To address such concerns, we investigated Puget Sound as a representative urban estuary and used suspect and nontarget screening to comprehensively characterize water quality at 18 nearshore marine locations. Puget Sound is the second largest estuary in the United States and is highly impacted by humans. Notably, the current regional population (~4 million) is expected to grow to 5.8 million by 2050, increasing pollution pressures on ecological health. CECs are documented in Puget Sound surface waters and organisms[4] and pose threats to culturally and economically significant species such as Southern Resident Killer Whale and salmonids.[37−39] The objectives of this study were to (1) characterize CEC occurrence in a representative human-impacted estuary; (2) identify priority contaminants for future management; and (3) investigate major CEC sources based on the contaminant profiles and dilution factor analysis. The results updated the knowledge on the contamination of urban marine environments and provided insights for the future practice of environmental monitoring and contamination control.

■ MATERIALS AND METHODS

Chemicals. Acetic acid (99.7%), ammonium acetate (HPLC grade, 97.8%) were purchased from VWR Scientific (Radnor, PA). Ammonium fluoride (99.9%) was purchased from Sigma Aldrich (St. Louis, MO). HPLC-grade solvents, including *n*-hexane, dichloromethane (DCM), acetone, ethyl acetate (EA), and methanol, were purchased from Fisher Scientific (Pittsburgh, PA). Deionized (DI) water was produced by a Nanopure water purification system (Thermo Barnstead Nanopure Diamond UV, Dubuque, IA). A complete list of reference standards is provided in the Supporting Information (SI).

Water Sampling and Extraction. Eighteen sampling sites were selected based on land use, proximity to primary contaminant sources (e.g., wastewater and urbanized areas), and existing data from marine water[40] and biological monitoring programs[41] (Figure 1). The sites were expected to be broadly representative of the range of conditions in the nearshore environment. In 2018, five sampling campaigns were conducted to evaluate wet and dry weather conditions: April 17th and October 30th (wet; 0.7 and 1.1 inch of antecedent rainfall, respectively); May 9th, June 18th, and August 22nd (dry). Detailed sampling and site information is provided in Table S1. Samples were collected in precleaned 4 L amber glass bottles without headspace. Field blanks were collected by bringing DI water to the sites and exposing to ambient air while collecting marine water samples. Samples were transported to the laboratory on wet ice, stored at 4 °C, and extracted within 24 h of collection.

Triplicates of each samples were extracted by established methods with modifications.[42,43] Precleaned micro glass beads (0.5 g; Filter Aid 400, 3M, MN) were added to solid phase extraction (SPE) cartridges (200 mg, 6 mL Oasis HLB, Waters, MA) to prevent clogging. Cartridges were preconditioned (5 mL methanol, 25 mL DI water; 5−10 mL/min). Water samples (1 L) were loaded onto SPE cartridges at 5−10 mL/min. Cartridges were rinsed with 10 mL of DI water, dried (15 min, N_2), and eluted with methanol (four 2.5 mL aliquots). Eluates were concentrated to 1 mL under N_2 and spiked with a set of 16 isotopically labeled internal standards (ISTDs; Table S2).[43] Method (laboratory DI) and field blanks were extracted identically and used for quality control and blank correction.

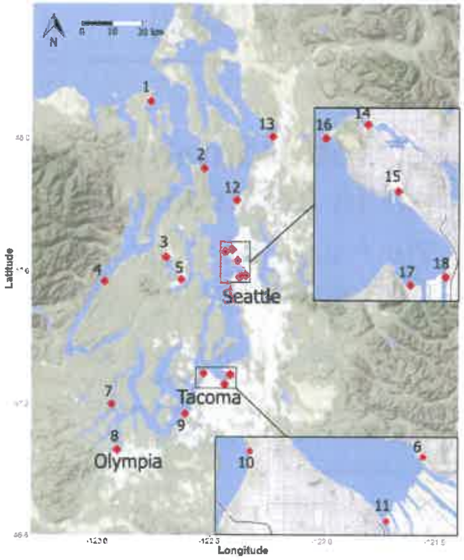

Figure 1. Sampling site locations in Puget Sound. Sampling sites: 1. Port Townsend Water Street, 2. Point No Point, 3. Silverdale, Dyes Inlet, 4. Hood Canal Holly, 5. Evergreen Rotary Park, 6. Commencement Bay Skookum, 7. Hammersley Inlet, 8. Budd Inlet, West Bay, 9. Saltar's Point, 10. Salmon Beach, 11. Commencement Bay Thea Foss, 12. Edmonds Ferry, 13. Everett Boat Launch, 14. Salmon Bay, Commodore Park, 15. Smith Cove, Terminal 91, 16. West Point South, 17. Joe Block Park, and 18. Jack Perry Memorial Park.

Instrumental Analysis. Processed extracts were analyzed using an Agilent 1290 Infinity ultrahigh-performance liquid chromatography (UHPLC) system coupled to an Agilent 6530 quadrupole time-of-flight HRMS (Santa Clara, CA) with electrospray ionization in both positive and negative modes (ESI+/−), with full scan HRMS data acquired at the range of m/z 100−1700. For structure identification, MS/MS data was acquired (m/z 50−1700, collision-induced dissociation at 10, 20, and 40 eV) by data-dependent acquisition using lists of preferred precursors based on initial MS-only screening. UHPLC separation used a reversed-phase C18 analytical column (Agilent ZORBAX Eclipse Plus 2.1 mm × 100 mm, 1.8 μm) with a C18 guard column (2.1 mm × 5 mm, 1.8 μm). For ESI+, the mobile phase (0.4 mL/min) consisted of 5 mM ammonium acetate and 0.1% acetic acid in each of water (A) and methanol (B) using a gradient of 5% B at 0−1 min, 50% B at 4 min, 100% B at 17−20 min, 5% B at 20.1 min; stop time 22.5 min; and post-time 2 min. For ESI−, the mobile phase consisted of 1 mM ammonium fluoride in water (A) and methanol (B),[31] using the same gradient.

For quality assurance and quality control (QA/QC), a check-tune including mass calibration was performed before each analytical run, and mass accuracy was corrected via continuous infusion of purine and HP-921 calibrants. Solvent blanks and ISTD controls were analyzed every 12 samples, and triplicate method blanks and field blanks were analyzed alongside samples. The retention time (RT), mass accuracy, and abundance of ISTD controls were used for performance evaluation of each analytical run. The RT deviation and mass error of the ISTDs in all samples were <0.2 min and <5 ppm, respectively. Response (peak area) variations of ISTDs were <15% within each analytical batch and 65−170% across different analytical batches, and these reflected a combination of instrumental variations and matrix effects. Additional instrumental parameters and QA/QC procedures are described in Du et al.[43]

Data Prioritization and Identification. The data analysis workflow[42,43] uses MassHunter Profinder (B.08.00) for nontarget feature extraction and alignment across samples, with features prioritized in Mass Profiler Professional (B.13.00, MPP) by replicate filters and blank subtraction (Figure S1). Features with peak area >5000, occurring in all replicates, and present at peak area 5-fold greater than solvent, method, and field blanks were retained. Formula assignment, suspect screening, and feature identification were performed in MassHunter ID Browser (B.07.00) and MassHunter Qualitative Analysis (B.08.00). We used two databases for suspect screening: (1) an in-house database with molecular formula and RT for ∼1100 compounds (CUW database) that includes chemicals from EPA's ToxCast library[42,44] and a range of wastewater and stormwater-derived contaminants and (2) a larger formula only database adapted from the merged NORMAN Suspect List Exchange Database.[45] Molecular features matching exact mass (<5 ppm), isotope pattern, and RT (<0.3 min) of the CUW database or matching exact mass and isotope pattern with high formula scores (>85, full score 100) via the NORMAN database were integrated into MS/MS preferred lists. Features not matched to either database but with high formula scores (>90) and heteroatoms (N, P, S, F, Cl, Br, I) were also prioritized for MS/MS.

To achieve a more comprehensive nontarget screening, additional priority features were identified through a parallel workflow using XCMS Online (Table S3).[46] Nontarget features were prioritized based on the following criteria: present in all replicates, average peak area >50 000, fold change (vs field blanks) >5, $p < 0.01$ (Welch's t-test), and maximum peak height >10 000 and were added to MS/MS preferred lists. A comparison of the results of the parallel workflows is shown in Figure S2, and the effect of data reduction criteria can be seen. While the two workflows generated similar overall numbers of features for the same sample group (June, site 15), approximately 10−20% additional unique features were identified using both methods compared to a single method alone.

MS/MS spectra were extracted in MassHunter Qualitative Analysis and matched against mzCloud[47] and EU MassBank.[48] The confidence level of identification was based on Schymanski et al.[22] The highest confidence (Level S1) identifications were achieved by matching the RT and MS/MS with reference standards, while level S2a was assigned by matching at least two major fragment ions with MS/MS libraries. The MS/MS spectra of features that did not match the library spectra were compared to in silico fragmentation spectra of PubChem compounds using MetFrag[49] (R package ReSOLUTION[50] and MetFragCL2.4.4) and CSI:FingerID[51] (SIRIUS 4.0.1). Matches with similarity scores of at least 0.8 for MetFrag or 50% for CSI:FingerID were examined individually, and the most probable structure was assigned as level S2b. If the putative structures shared a common functional group but similarity scores were below cutoffs or the exact location of the functional group was uncertain, level S3 identification was assigned. For example, tolyl diphenyl phosphate ($C_{19}H_{17}O_4P$) presented clear substructures of phenyl [C_6H_5] and tolyl [C_7H_7] groups in MS/MS spectra, but its identity remained uncertain because of the ambiguous methyl position of the tolyl group. Similarly, some long-chain amine and amide surfactants, such as *N*,*N*-dihexyl-1-decanamine and octyldimethylamine oxide, remained level S3 due to structural uncertainties or low scores from in silico fragmentation.

Level S1 compounds were quantified by 4-point external standard calibration curves and normalized to injection internal standards (Table S2). This semiquantitative method normalizes based on variation of instrumental response and matrix effects but does not explicitly account for extraction recovery, so estimated concentrations are likely underestimated.

Risk Assessment. Risk assessment employed risk quotients (RQ, eq 1) calculated for level S1 CECs by comparing maximum measured environmental concentrations to lowest predicted-no-effect concentrations (PNECs) for marine organisms (from NORMAN ecotoxicology database,[52] Table S4). RQ > 1 implies a potential risk to marine species based on single compound exposure.

$$\mathrm{RQ} = \text{max concentration}/\text{lowest PNEC} \quad (1)$$

Salish Sea Model. Cumulative distribution patterns of wastewater effluent were evaluated with the Salish Sea Model (SSM), a three-dimensional hydrodynamic and biogeochemical model of Puget Sound capable of resolving interbasin exchange and biogeochemical response to pollution from 99 wastewater outfalls and runoff from 161 watersheds. Model hydrodynamics use the finite-volume community ocean model (FVCOM)[53] with an unstructured grid framework.[54,55] For this study, model hydrodynamics included a 13 month simulation period (Jan 01, 2012 to Jan 25, 2013), with hydrodynamic inputs of tidal forcing from the open ocean, river, and wastewater flows, and meteorological conditions from 2012/13.

To simulate and track the cumulative transport of wastewater-derived contaminants, the SSM was run with all 99 point sources having a fixed model tracer concentration of 100 units. The synthetic tracer was modeled as a neutrally buoyant and conservative dye, representing an unreactive contaminant. To achieve pseudo-steady-state conditions, the SSM was run for three cycles, with final dye concentration across the model domain of each cycle being used as the initial conditions for the subsequent cycle. The final modeled dye concentration represented the cumulative WWTP effluent concentration considering dilution and transport but not degradation. The relationship between modeled wastewater dye concentrations and detected contaminants was investigated by comparing model predictions at 11 sampling sites with measured contaminant concentrations. Data for dry weather sampling (May, June, and August) was used to avoid potential dilution effects of precipitation, which could not be modeled. A 14 day mean and standard deviation of the dye concentrations were calculated for each sample location and date (Table S6). Linear regressions between measured abundances and predicted dye concentrations were performed in *R* (3.5.1), and *F*-tests assessed statistical significance. To avoid overprediction and account for model outputs in grid cells that included both the sample location and a WWTP outfall, a 10 000-replicate bootstrap was performed to incorporate site-specific variability, and *p*-values were determined from 95% quantile of the bootstrap.

Table 1. Detection Characterization of 87 Non-Polymeric CECs Identified by Suspect and Nontarget Screening in Puget Sound Marine Waters

name	formula	RT[a] (min)	m/z	confidence level	DF (%)[b]	conc.[c] (ng/L)	compound group
		Negative Mode					
perfluorooctanesulfonic acid	$C_8HF_{17}O_3S$	9.21	498.9290	S1	10	1.8−140	PFAS
perfluorohexanesulfonic acid	$C_6HF_{13}O_3S$	7.03	398.9462	S1	6	2.1−43	PFAS
perfluorobutanesulfonic acid	$C_4HF_9O_3S$	5.06	298.9430	S1	13	0.2−4.4	PFAS
perfluorooctanoic acid	$C_8HF_{15}O_2$	8.09	412.9656	S1	4	2.0−7.1	PFAS
perfluoroheptanoic acid	$C_7HF_{13}O_2$	6.91	362.9697	S1	4	2.3−3.8	PFAS
perfluorohexanoic acid	$C_6HF_{11}O_2$	5.77	312.9734	S1	4	3.8−14	PFAS
perfluoropentanoic acid	$C_5HF_9O_2$	5.04	262.9774	S1		1.0−2.6	PFAS
sucralose	$C_{12}H_{19}Cl_3O_8$	4.24	395.0072	S1	96	8.8−400	food additive
bisphenol S	$C_{12}H_{10}O_4S$	4.76	250.0305	S1	26	0.5−14	plasticizer or flame retardant
4-((4-Isopropoxyphenyl)sulfonyl)phenol	$C_{15}H_{16}O_4S$	7.45	291.0710	S3	13		plasticizer or flame retardant
4-nitrophenol	$C_6H_5NO_3$	4.85	139.0267	S1	87	1.6−18	herbicide or fungicide
2,4-dinitrophenol	$C_6H_4N_2O_5$	3.51	183.0053	S1	69	1.4−15	herbicide or fungicide
2-methyl-4,6-dinitrophenol	$C_7H_6N_2O_5$	4.33	197.0211	S2a	27		herbicide or fungicide
4-hydroxyquinoline	C_9H_7NO	3.64	144.0453	S1	97	0.5−3.4	other
2-hydroxyquinoline	C_9H_7NO	4.83	144.0453	S2a	97		other
hydroxyacridine	$C_{13}H_9NO$	5.85	194.0617	S2b	5		other
salicylic acid	$C_7H_6O_3$	2.59	137.0250	S1	5	2.5−4.6	food additive
vanillin	$C_8H_8O_3$	4.27	151.0401	S1	17	1.6−35	food additive
N-butylbenzenesulfonamide	$C_{10}H_{15}NO_2S$	6.67	212.0750	S1	22	0.8−37	plasticizer or flame retardant
2-mercaptobenzothiazole	$C_7H_5NS_2$	5.60	165.9789	S1	27	3.0−170	vehicle-related
benzothiazole-2-sulfonic acid	$C_7H_5NO_3S_2$	3.54	213.9643	S1	23	47−820	vehicle-related
8-hydroxy-5-quinolinesulfonic acid	$C_9H_7NO_4S$	3.88	224.0027	S2b	3		other
benzotriazole	$C_6H_5N_3$	4.13	118.0403	S1	37	2.2−6.3	vehicle-related
5-methylbenzotriazole	$C_7H_7N_3$	4.99	132.0561	S1	49	0.4−27	vehicle-related
2-cyclohexylethyl hydrogen sulfate	$C_8H_{16}O_4S$	5.03	207.0686	S2b	14		other
2,2′-bis(chloracetoxy) ethyl sulfone	$C_8H_{12}C_{12}O_6S$	4.31	304.9649	S2b	1		other
triclopyr	$C_7H_4Cl_3NO_3$	5.49	253.9185	S1	4	37−180	herbicide or fungicide
4-hydroxy-chlorothalonil	$C_8HCl_3N_2O$	5.66	244.9083	S1	6	0.2−19	herbicide or fungicide
1-amide-4-hydroxy-chlorothalonil	$C_8H_3Cl_3N_2O_2$	4.02	262.9188	S3	1		herbicide or fungicide
hydroxybenzaldehyde	$C_7H_6O_2$	3.93	121.0293	S2b	67	1.8−140	other
		Positive Mode					
lamotrigine	$C_9H_7N_5Cl_2$	4.71	256.0151	S1	83	0.1−10	pharmaceutical
venlafaxine	$C_{17}H_{27}NO_2$	5.38	278.2118	S1	9	1.2−4.5	pharmaceutical
O-desvenlafaxine	$C_{16}H_{25}NO_2$	4.43	264.1950	S1	37	0.2−5.7	pharmaceutical
N-desvenlafaxine	$C_{16}H_{25}NO_2$	4.51	264.1950	S2a	37		pharmaceutical
lidocaine	$C_{14}H_{22}N_2O$	4.31	235.1082	S1	6	1.2−3.7	pharmaceutical
methamphetamine	$C_{10}H_{15}N$	3.83	150.1272	S1	41	0.3−2.0	pharmaceutical
metoprolol	$C_{15}H_{25}NO_3$	4.63	268.1894	S1	1	1.5	pharmaceutical
tris(1-chloro-2-propyl)phosphate	$C_9H_{18}Cl_3O_4P$	8.79	327.0077	S2a	10		plasticizer or flame retardants
tris(2-chloroethyl)phosphate	$C_6H_{12}Cl_3O_4P$	5.99	284.9612	S1	27	0.6−6.2	plasticizer or flame retardants
tris(2-butoxyethyl) phosphate	$C_{18}H_{39}O_7P$	12.76	399.2508	S1	23	0.5−35	plasticizer or flame retardants
tolyl diphenyl phosphate	$C_{19}H_{17}O_4P$	12.00	341.0935	S3	3		plasticizer or flame retardants
phenyl di(*p*-tolyl) phosphate	$C_{20}H_{19}O_4P$	12.86	355.1093	S3	4		plasticizer or flame retardants
tebuthiuron	$C_9H_{16}N_4OS$	6.15	229.1126	S1	4	50−110	herbicide or fungicide
tebuthiuron TP1	$C_8H_{14}N_4OS$	5.34	215.0980	S2b	3		herbicide or fungicide
tebuthiuron TP2	$C_7H_{13}N_3S$	5.58	172.0905	S2b	5		herbicide or fungicide
tebuthiuron TP3	$C_6H_{11}N_3S$	4.85	158.0741	S2b	4		herbicide or fungicide
metsulfuron-methyl	$C_{14}H_{15}N_5O_6S$	5.25	382.0814	S1	4	11−81	herbicide or fungicide
rimsulfuron	$C_{14}H_{17}N_5O_7S_2$	5.85	432.0645	S1	4	7.6−36	herbicide or fungicide
diuron	$C_9H_{10}Cl_2N_2O$	7.25	232.0169	S1	4	0.5−1.1	herbicide or fungicide
fluridone	$C_{19}H_{14}F_3NO$	8.00	330.1110	S1	8	0.4−9.0	herbicide or fungicide
propamocarb	$C_9H_{20}N_2O_2$	3.19	189.1593	S1	9	0.5−1.1	herbicide or fungicide

Table 1. continued

name	formula	RT[a] (min)	m/z	confidence level	DF (%)[b]	conc.[c] (ng/L)	compound group
		Positive Mode					
2,6-dichlorobenzamide	$C_7H_5Cl_2NO$	3.93	189.9819	S1	18	0.2−27	herbicide or fungicide
N-octyl-2-pyrrolidone	$C_{12}H_{23}NO$	10.38	198.1844	S2a	8		surfactant
hexa(methoxymethyl)melamine	$C_{15}H_{30}N_6O_6$	6.75	391.2293	S1	28	**1.0−28**	vehicle-related
diphenylguanidine	$C_{13}H_{13}N_3$	4.27	211.1124	S1	22	0.9−93	vehicle-related
dicyclohexyl urea	$C_{13}H24N_2O$	8.42	224.1882	S1	5	0.9−1.8	vehicle-related
triisopropanolamine	$C_9H_{21}NO_3$	1.02	192.1596	S1	22	0.1−7.7	other
N-ethyl-*p*-toluenesulfonamide	$C_9H_{13}NO_2S$	5.69	200.0740	S2a	28		plasticizer or flame retardants
hexylamine	$C_6H_{15}N$	3.44	102.1078	S2a	6		surfactant
N-butyl-pentanamine	$C_9H_{21}N$	5.69	144.1747	S2b	3		surfactant
N-butyl-hexylamine	$C_{10}H_{23}N$	5.58	158.1903	S2b	9		surfactant
dicyclohexylamine	$C_{12}H_{23}N$	4.81	182.1899	S2a	13		vehicle-related
butyl-dimethyl-tetradecylazanium	$C_{20}H_{43}N$	13.54	298.3471	S2b	10		surfactant
N,*N*-dihexyl-1-decanamine	$C_{22}H_{47}N$	13.47	326.3783	S3	22		surfactant
N-butyl-3-pentanamide	$C_9H_{19}NO$	7.71	158.1538	S3	12		surfactant
N,*N*-diethyl-2-cyclohexene-1-carboxyamide	$C_{11}H_{19}NO$	3.28	182.1529	S2b	38		surfactant
N,*N*-dimethyloctanamide	$C_{10}H_{21}NO$	3.44	172.1695	S2b	1		surfactant
octyldimethylamine oxide	$C_{10}H_{23}NO$	6.20	174.1852	S3	23		surfactant
N,*N*-dimethyldodecylamine *N*-oxide	$C_{14}H_{31}NO$	11.35	230.2480	S1	26	0.3−45	surfactant
N,*N*-dimethyltetradecanamine *N*-oxide	$C_{16}H_{35}NO$	13.39	258.2794	S2b	27		surfactant
N-[3-(dimethylamino)propyl]dodecanamide	$C_{17}H_{36}N_2O$	10.32	285.2895	S3	13		surfactant
N-octadecyl butanamide	$C_{22}H_{45}NO$	12.07	340.3576	S2b	1		surfactant
olivetol	$C_{11}H_{16}O_2$	7.48	181.1225	S3	1		food additive
DEET	$C_{12}H_{17}NO$	7.22	192.1385	S1	4		other
caffeine	$C_8H_{10}N_4O_2$	3.98	195.0894	S1	1	22	food additive
1-cyclohexylpyrrolidin-2-one	$C_{10}H_{17}NO$	6.23	168.1383	S1	1	18	surfactant
ammonium perfluorooctanesulfonate	$C_8H_4F_{17}NO_3S$	10.08	534.9983	S3	4		PFAS
12-amino-1,7-bis(sulfanyl)dodecan-6-ol	$C_{12}H_{27}NOS_2$	4.85	266.1599	S2b	3		surfactant
1-[5-(1-aminoethyl)-2-methylsulfanyl-4-propylsulfanylphenyl]ethanamine	$C_{14}H_{24}N_2S_2$	2.58	285.1451	S3	50		other
caprolactam trimer	$C_{18}H_{33}N_3O_3$	4.38	340.2562	S3	5		other
diisononyl phthalate	$C_{26}H_{42}O_4$	17.39	419.3160	S1	10	**10−150**	plasticizer or flame retardants
isononyl decyl phthalate	$C_{27}H4_4O_4$	17.60	433.3319	S2b	13		plasticizer or flame retardants
isononyl undecyl phthalate	$C_{28}H_{46}O_4$	17.86	447.3483	S2b	15		plasticizer or flame retardants
N,*N*-dimethylpurin-1-amine	$C_7H_9N_5$	3.98	164.0927	S2b	4		other
1-[[2-hydroxy-3-(2-hydroxypropylamino)propyl]amino]hexan-2-ol	$C_{12}H_{28}N_2O_3$	3.22	249.2175	S2b	1		other
2-methylbenzimidazole	$C_8H_8N_2$	2.96	133.0765	S2b	8		pharmaceutical
N-phenyl acrilamide	C_9H_9NO	5.04	148.0757	S2b	4		other

[a]RT = retention time. [b]DF = detection frequency, calculated from 78 samples. [c]Bold figures indicate the concentrations above lowest PNEC.

RESULTS AND DISCUSSION

Occurrence and Environmental Relevance of Identified CECs. Overall, we identified 87 non-polymeric (Tables 1 and S4) and 118 polymeric contaminants (Table S5) in the 78 nearshore marine water samples. Among the 87 non-polymeric contaminants, 45 were confirmed with reference standards (level S1), 30 matched MS/MS libraries (level S2a) or in silico fragmentations (level S2b), and 12 were tentatively identified (level S3) via MS/MS and functional groups (adduct form, MS/MS fragments, and SMILES in Table S4). The major detected contaminant classes were herbicides, pharmaceuticals, vehicle-related compounds, plasticizers, and flame retardants (Figure 2). Of the 75 compounds identified at level S1 or S2, only 11 were reported previously in the study area,[4] illustrating the value of HRMS screening in water quality characterization.

Herbicides, Fungicides, and Their Transformation Products (TPs). Ten herbicides, four herbicide TPs, and two fungicide TPs were identified in nearshore marine waters, and this class has inherent potentials for adverse exposure effects and biological risks.[56] Although many pesticides are transformed or degraded under environmental conditions, their TPs can be bioactive,[57,58] and some may revert to the parent compounds.[59] Typically, dilution of nonpoint runoff entering estuaries is expected to mitigate risk potentials, so herbicides or fungicides are commonly excluded from CEC evaluations in marine environments.[4] However, concentrations of pesticides and TPs in some samples were more than 10 ng/L or even 100 ng/L (e.g., triclopyr and tebuthiuron) in the Puget Sound nearshore.

The urea herbicides tebuthiuron, diuron, metsulfuron-methyl, and rimsulfuron were detected in ~5% of samples (Table 1), and they typically occurred at single sites during each sampling

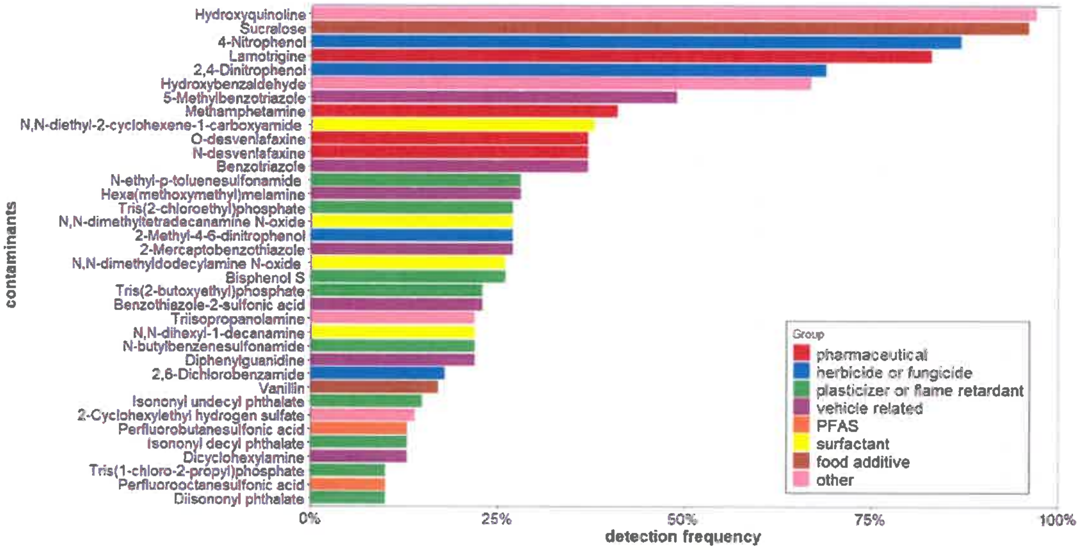

Figure 2. CECs detected in Puget Sound nearshore marine water, with detection frequency above 10% (n = 78, only including compounds with identification levels S1 and S2).

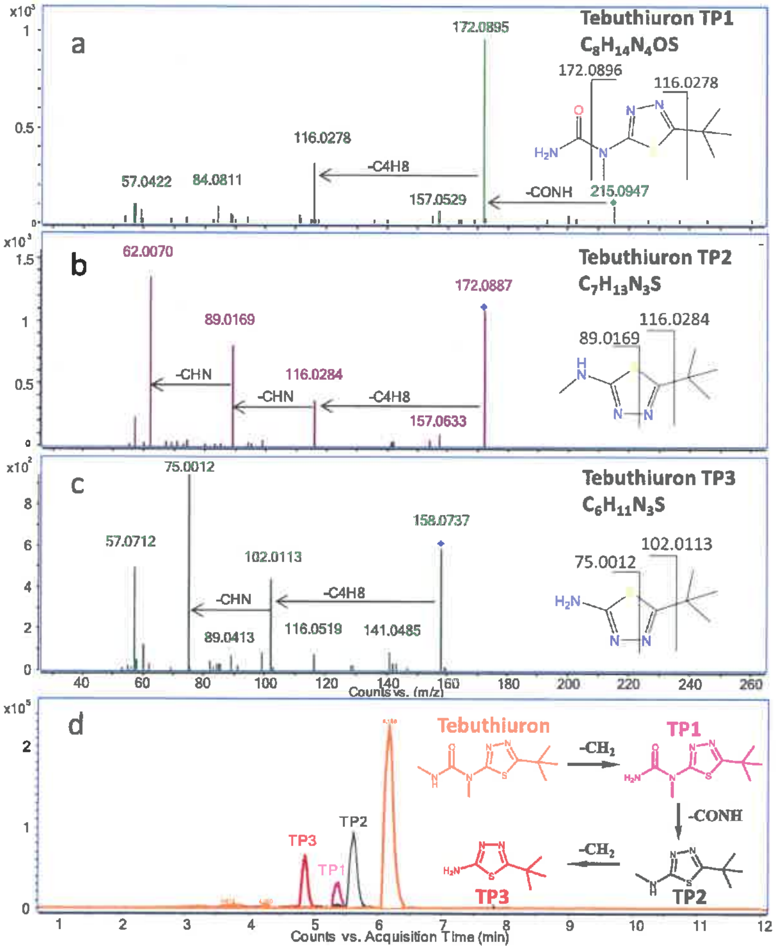

Figure 3. MS/MS spectra and CSI:FingerID calculated results for TP1, TP2, and TP3 (a–c) and chromatograms and proposed transformation pathway (d) of tebuthiuron and related transformation products.

event, suggesting that their presence was associated with specific applications; they were not widespread in the study area. For example, metsulfuron-methyl and rimsulfuron consistently co-occurred (site 9 in April; site 15 in May, June, and August), indicating their likely co-application via commercial formulations that contain both compounds (e.g., Negate 37WG).

Tebuthiuron (50−110 ng/L) was consistently detected at site 15 in dry sampling dates. It can be transported to receiving waters >100 days after application,[60] although its environmental fate remains unclear. The occurrence of three features (*m/z* 215.0980, 172.0905, and 158.0741), each with putative thiadiazole substructures, was correlated with the occurrence of tebuthiuron at site 15. These were assigned formulas $C_8H_{14}N_4OS$, $C_7H_{13}N_3S$, and $C_6H_{11}N_3S$, respectively (spectra and isotope patterns are shown in Figure S3a−c). For these three features, in silico fragmentation with CSI:FingerID indicated thiadiazole substructures in their top 5 predicted structures. MS/MS spectra (Figure 3a−c) included common fragments of *m/z* 57.0451 [C_4H_9], 89.0169 [$C_2H_5N_2S$], and 116.0277 [$C_3H_6N_3S$] and indicated neutral losses of $-C_4H_8$ and −CHN. Based on these common structural units and their co-occurrence, we propose that the smaller compounds were potential tebuthiuron TPs (level S2b, Figure 3d). Tebuthiuron TP1 ($C_8H_{14}N_4OS$) was previously reported as a product of the hydroxy radical-mediated transformation of tebuthiuron.[61] To the best of our knowledge, the other proposed TPs ($C_7H_{13}N_3S$ and $C_6H_{11}N_3S$) are novel. This example, especially the conservation of predicted substructures across related features, demonstrates how in silico fragmentation enables structural elucidation and the identification of novel compounds. The proposed transformation pathway in Figure 3d was based on the detections and similar biotransformation reactions.[62] In addition, the concentrations of tebuthiuron (50−110 ng/L) were similar to exposure concentrations resulting in endocrine disrupting effects in fish (100 ng/L),[63] indicating a potential for contaminant-derived endocrine impacts in these marine waters. The three tebuthiuron TPs comprised approximately 40% of total group peak areas. Assuming that these TPs have a response factor similar to that of the parent compound, the total concentrations of this group would be 83−180 ng/L. The TPs could be potentially bioactive, especially TP1, which shared more substructures with tebuthiuron.

Chlorothalonil is a broad-spectrum fungicide heavily used in the US for crop and vegetable agriculture.[64] It was recently banned in the EU because of high toxicity to fish, amphibians, and insects;[65,66] the TP 4-hydroxy-chlorothalonil is even more toxic and persistent.[67] Although chlorothalonil was not detected directly (not ESI amenable), two TPs, 4-hydroxy-chlorothalonil (Figure S3d, level S1, 0.2−19 ng/L) and 1-amide-4-hydroxy-chlorothalonil (Figures S3e and S4b, level S3 due to ambiguous amide location), were present at sites 11 and 15. As both sites were in urbanized areas close to marinas, an unconventional application such as an antifouling paint ingredient may best explain chlorothalonil detection.[68] Likewise, triclopyr, an herbicide used in lakes and beaches to control invasive algae,[69] was only detected at site 14 (37−180 ng/L). As site 14 is downstream of Lake Washington, a freshwater lake within a highly urbanized watershed (see Figure 1), we speculate that applications within the Lake Washington watershed best explain its occurrence.

The additional five detected herbicides and TPs are expected to represent low risk to ecosystems and public health based on available toxicological information and observed concentrations. 2,6-Dichlorobenzamide, a persistent and mobile TP of the herbicide dichlobenil that is commonly detected in soil, groundwater, and surface waters,[70] was detected in 18% of samples at 0.2−27 ng/L. Fluridone, an aquatic herbicide used for controlling noxious weeds and algae, also occurred at the site receiving the lake outflow (site 14). 4-Nitrophenol (1.6−18 ng/L), 2,4-dinitrophenol (1.4−15 ng/L), and 2-methyl-4,6-dinitrophenol (S2a) are structurally related compounds used as herbicides and intermediates for pesticide production. Their acute toxicities were observed at levels much higher than these measurements (e.g., 500−940 ng/L PNEC),[71] indicating limited potential for adverse effects to marine aquatic organisms.

Pharmaceuticals. Eight pharmaceuticals and their metabolites were detected in the marine nearshore, generally at concentrations <10 ng/L. Lamotrigine, *O*-desmethylvenlafaxine, and *N*-desmethylvenlafaxine were detected in 83, 37, and 37% of samples, respectively, while venlafaxine, lidocaine, and metaprolol were present in <10% of samples. The anticonvulsant lamotrigine is typically persistent and pervasive in surface waters[72] and was the most frequently detected pharmaceutical. Observed lamotrigine concentrations (0.1−10 ng/L) were lower than reported concentrations in freshwater environments (17−1000 ng/L).[72,73] Venlafaxine (1.2−4.5 ng/L) and *O*-desmethylvenlafaxine (0.2−5.7 ng/L) occurred at low levels, and both *N*- and *O*-desmethylvenlafaxine are known human or bacterial metabolites of venlafaxine.[74]

Methamphetamine was detected in 41% of samples at ∼0.3−2.0 ng/L. Although methamphetamine is reported in wastewater influent[75] and effluent,[76] its occurrence in surface water is rarely reported in the United States.[77] Its detection here helps confirm the ubiquity of drugs of abuse throughout anthropogenic receiving waters.[78] Methamphetamine can disturb the neurotransmitters and alter the physiological functions of *Caenorhabditis elegans* at 50 ng/L[79] and influence aquatic microbial communities at 1.6−34 ng/L,[80] indicating some potential for adverse impacts from methamphetamine exposures in marine ecosystems.

Perfluoroalkyl Substances (PFASs). Seven legacy PFASs were detected, including three perfluorosulfonic acids and four perfluorocarboxylic acids. Perfluorobutanesulfonic acid (PFBS) and perfluorooctanesulfonic acid (PFOS) both occurred in ∼15% of the samples, but detections were confined to sites 6, 11, and 15. At site 15, all seven PFASs were consistently detected across seasons, and PFOS concentrations (72−140 ng/L) exceeded EPA health advisory levels for drinking water (70 ng/L). These concentrations were higher than those reported in a previous survey in the Puget Sound (1.5−41 ng/L),[81] probably because the current study included nearshore sites adjacent to highly urbanized and industrialized drainages.

Vehicle-Related Contaminants. Vehicle-related contaminants, including the roadway tracers benzotriazole, 5-methylbenzotriazole, 2-mercaptobenzothiazole, and benzothiazole-2-sulfonic acid (BTSA)[82] and the stormwater contaminants 1,3-diphenylguanidine (DPG) and hexa(methoxymethyl)melamine (HMMM),[42] were frequently detected. Due to their reported use and transport profiles, these compounds were expected to occur more frequently and at a higher abundance during wet weather sampling compared to dry weather sampling. However, 5-methylbenzotriazole (0.4−27 ng/L) and benzotriazole (2.2−6.3 ng/L) occurred more frequently in dry weather (56 and 60%) than wet weather (0 and 27%), implying contributions from non-stormwater sources (e.g., wastewater or atmospheric deposition).[83,84] Despite similar detection frequencies in dry (25%) and wet (17%) conditions, BTSA concentrations were significantly higher (Welch's *t*-test, $p = 0.023$) during storms (370−820 ng/L) than dry weather (47−190 ng/L). Likewise, DPG and HMMM were detected more frequently on wet (46 and 58%) than dry (10 and 13%,) sampling dates (Figure S5), and the maximum concentrations for both were observed on wet

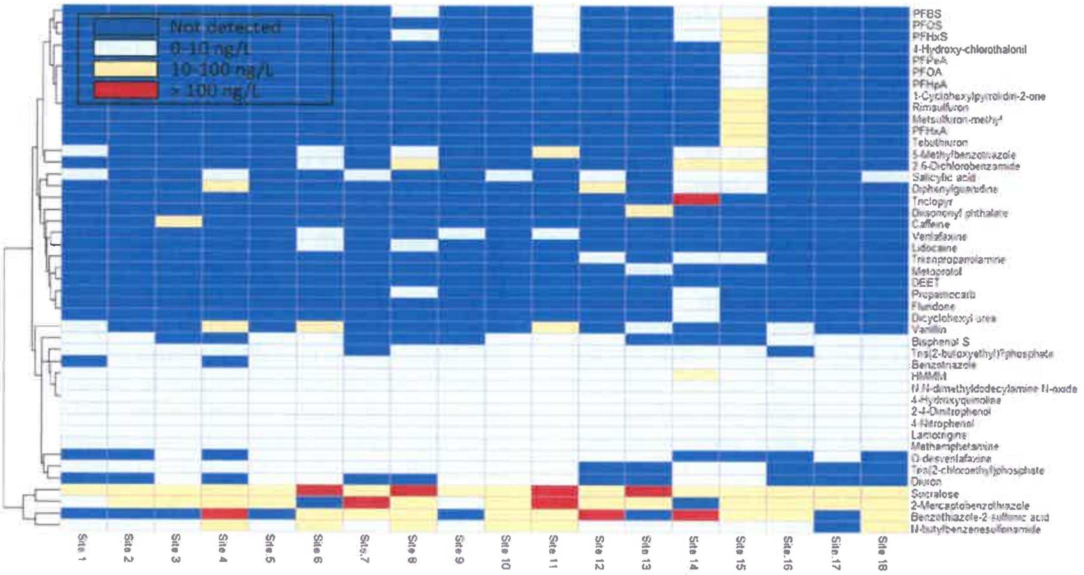

Figure 4. Hierarchical cluster analysis based on median concentrations on dry sampling dates (using Ward's method and Euclidean distance) of CECs identified at level S1.

dates (93 and 28 ng/L, respectively). These indicated a clear impact of stormwater pollution on marine receiving waters.[35]

Plasticizers and Flame Retardants. Plasticizers and flame retardants are widely detected in environmental matrices, and many can induce adverse biological effects.[85] The plasticizers *N*-ethyl-*p*-toluenesulfonamide (Et-*p*-TSA) and bisphenol S (BPS) were detected in 28 and 26% of samples, respectively. Et-*p*-TSA (S2a), previously identified in surface and groundwaters as wastewater-derived,[83] is widely used in polymeric resins and printing inks. Although little is known about its toxicity, Et-*p*-TSA is included on screening lists of predicted endocrine disruptors (e.g., EPA's Endocrine Disruptor Screening Program). BPS (0.5−14 ng/L) is an increasingly used structural analogue of and substitute for bisphenol A (BPA), with similar potential for endocrine disruption in aquatic organisms.[86] In addition, we tentatively identified 4-((4-isopropoxyphenyl)-sulfonyl)phenol ($C_{15}H_{16}O_4S$, S3), a BPS derivative and likely novel contaminant not previously reported in the environment. The MS/MS spectra included the substructure $C_{12}H_8O_4S$ and one fragment $C_6H_4O_3S$ of BPS, suggesting the structural similarity (Figure S4a). Two organophosphate esters that are widely used as flame retardants and detected at high abundances in surface water[64] and exposed organisms,[87] tris(2-chloroethyl)-phosphate and tris(2-butoxyethyl)phosphate, were detected in 27 and 23% of samples, respectively. Phthalate plasticizers such as isononyl undecyl phthalate and isononyl decyl phthalate were found in15 and 13% of the samples, respectively.

Surfactants. A suite of 118 non-polymeric and polymeric surfactants was identified in these samples (Table S5). Non-polymeric surfactants were mostly amine or amide compounds such as *N*,*N*-dimethyldodecylamine *N*-oxide and *N*,*N*-diethyl-2-cyclohexene-1-carboxyamide. Polymeric surfactants included groups of glycol polymers such as polyethylene glycols, polypropylene glycols, nonylphenol ethoxylates, and octylphenol ethoxylates. Confirmation of their identities was based on mixed technical standards. Exact concentrations of each component of the technical standard were not known, so environmental concentration could not be determined. Although these surfactants are environmentally ubiquitous[26] and previous reports have indicated toxicological relevance of certain surfactants,[42,88] their structural diversity, lack of pure standards, and varied sources limit our ability to fully evaluate their implications for nearshore marine water quality.

Other Ubiquitous CECs. Other CECs were also prioritized based on their high detection frequency (Figure 2). For instance, hydroxyquinolines, the most frequently detected compounds (97%, 0.5−3.4 ng/L), are used as antimicrobials, agrochemicals, and precursors for pharmaceuticals;[89] 2-hydroxyquinoline is a metabolite of microbial degradation of quinoline. Hydroxyquinolines are tautomers of quinolones, increasing their environmental stability. Sucralose, an environmentally persistent artificial sweetener with low removal rates in wastewater treatment, was also near ubiquitous (96%, 8.8−400 ng/L). Its occurrence suggests widespread wastewater impacts to marine waters in this region.[40]

Prioritization of CECs Based on Concentration and Toxicity. For all of the level S1 contaminants (45), we used the estimated environmental concentrations and the lowest PNEC to calculate RQ (eq 1). Note that for many compounds, only limited or incomplete ecotoxicological and PNEC data exists, implying that overall actual risks are likely to exceed estimated risks for these complex and poorly characterized contaminant mixtures.

Eight contaminants had RQ > 1: PFOS, BPS, 2-mercaptobenzothiazole, venlafaxine, fluridone, metsulfuron-methyl, diisononyl phthalate, and HMMM. PFOS had the highest RQ (2150) because the highest detected concentration (140 ng/L) was far above the lowest PNEC (0.065 ng/L).[52] This stringent PNEC was derived from the tolerable daily intake (TDI) with a high bioaccumulation factor (700). Bioaccumulation and adverse effects of PFOS in marine animals have been reported,[7,30] making its detection especially concerning because Puget Sound habitats are used by endangered marine mammals such as the Southern Resident Killer Whale. Further monitoring, source apportionment, and source control for compounds with high bioaccumulation potentials, such as PFOS, are necessary to protect sensitive ecosystems.

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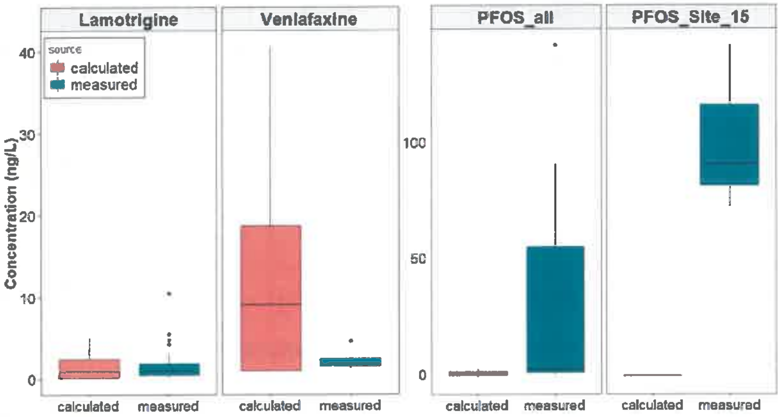

Figure 5. Comparison of calculated and measured concentrations of lamotrigine, venlafaxine, and PFOS in marine waters. Calculated concentrations were based on dilution factors from the Salish Sea hydrodynamic model and previously reported concentrations in wastewater effluent.[4,92]

Venlafaxine was the only wastewater-derived CEC with RQ > 1. Although detected at only three sites (sites 6, 8, and 11), concentrations were above or close to the lowest PNEC (3.8 ng/L) on multiple days. Herbicides also were prioritized in this assessment, as metsulfuron-methyl and fluridone have RQ > 1. Although fluridone was safe for humans and mammals,[90] its RQ (1.6) suggests potential risk to fish and other aquatic life. Since many of these herbicides are used in urban and residential areas or transported from freshwater, such nonpoint sources might induce substantial contamination at unexpected sites that are not routinely monitored.

Notably, for all CECs with RQ > 1, detection frequencies were below 30% and problematic occurrences were localized to a few sites (e.g., sites 8, 11, 14, and 15), albeit on multiple sampling dates. For instance, metsulfuron-methyl was detected twice at site 15 (May and June) at concentrations (81 and 11 ng/L) above the lowest PNEC (1 ng/L). Such patterns imply that ecological risk might be dependent on site-specific CEC contamination profiles (Figure 4) and not generalizable across the entire study area. This suggests that identifying such pollutant "hot spots" for CECs remains challenging and may require focused investigations to identify areas of concern. Result outcomes may not easily be scalable to regional and national applications. We suggest that the further development and utilization of regional hydrodynamic models, as demonstrated here, could be essential in focusing future monitoring and that source characterization (e.g., wastewater effluent, surface water runoff, etc.) based on nontargeted HRMS methods may prove essential in meeting the challenges of characterization and source identification, which is crucial for risk management.

Source Analysis Based on Measurements and the SSM Model. Three approaches were used to evaluate potential source pathways for selected CECs detected in this study: evaluation of temporal patterns, comparison of predicted vs measured spatial patterns, and comparison of predicted vs measured concentrations at specific sites.

Temporal and Spatial Pattern of CECs. The comparison of dry (May, June, and August) and wet (April and October) samples suggests that freshwater dilution and stormwater transport may dominate water quality outcomes. We used the numbers of detected suspects (matching CUW database) as a surrogate for the diversity of CECs. The median counts of detected suspects were lower in wet (<15 suspects per site) versus dry (>15 suspects) sampling dates (Figure S6b) despite the fact that the CUW database is biased toward stormwater pollutants, indicating that precipitation often dilutes many contaminants to nondetect levels. Using the nontarget data (Table S7), we assessed the median number of features detected across all sites for each sampling event and median total peak area across all sites for each sampling event (Figure S6c,d). Although the detected features were not limited to anthropogenic contaminants, there were more features and higher total abundance in dry weather samples compared to wet weather samples. The lower numbers of features and peak areas in April and October reflected the dilution effect from the surface water runoff. All samples were collected ~0.5 m below the water surface, a region likely to be in the lower density freshwater lens most impacted by freshwater inputs and surface water dilution. The Puget Sound region has a Mediterranean climate (rains in the winter and dry in summer). Runoff events in the fall contain a higher mass of stormwater contaminants that accumulated on surfaces during the dry summer period, and the spring stormwater, after continual runoff through the rainy season, is cleaner. These are also reflected in Figure S6, where peak areas and feature numbers were lowest in April and slightly higher in October. Samples collected during rain events did have higher concentrations and detection frequencies of vehicle-related contaminants (Figure S5), indicating the importance of transportation-derived CECs and stormwater flows to water quality degradation in estuarine environments.

For the four most frequently detected CECs (4-hydroxyquinoline, sucralose, lamotrigine, and 4-nitrophenol), we assessed their potential source pathways by comparing the spatial patterns of effluent predicted by the SSM with measured concentrations (Table S8) using a simple linear regression. A strong relationship between the predicted and measured concentrations would suggest that wastewater effluent was an important pathway. Among these CECs, sucralose and lamotrigine were well correlated ($R^2 > 0.5$, $p < 0.05$) with model outputs, providing a line of evidence that wastewater effluent was a primary contributing pathway and supporting the notion that these CECs can be effective wastewater tracers, as reported elsewhere[40,73] However, 4-hydroxyquinoline and 4-nitrophenol were poorly correlated ($R^2 < 0.5$, $p > 0.3$) with model outputs, suggesting that other sources and pathways (e.g., dry season runoff and industrial discharge) were important for specific CECs.

The spatial distribution and profile of the contamination hot spots also provide insights into the potential sources (Figure 4).

Site 8 was the most heavily impacted by wastewater effluent as indicated by the relatively high predicted SSM dilution factor 0.54–0.74% and highest concentrations of multiple WWTP tracers, but the median number of suspect detections were lower there compared to sites 6, 11, and 15 (Figure S6a). In these three sites, typical wastewater-derived CECs were quite diluted but herbicides, PFASs, and plasticizers were abundant, with several compounds occurring at concentrations > PNECs (e.g., metsulfuron-methyl and PFOS at site 15 and BPS at site 11). The unique occurrence of non-wastewater-derived herbicides is apparent at some sites, such as tebuthiuron in site 15 and triclopyr in site 14 (Figure 4). These results highlighted the values of HRMS-based methods.

Dilution Calculation Using SSM and Wastewater Effluent Data. The SSM output provided predicted dilution factors that were used to estimate concentration ranges for selected contaminants. If the CECs were predominantly via wastewater, the measured concentrations would be comparable to (or lower than) the estimated concentrations. Comparisons were made for lamotrigine, venlafaxine, and PFOS.

Lamotrigine and venlafaxine have been reported as tracers of municipal wastewaters[91] and so measured environmental concentrations were expected to vary consistently with SSM predictions. SSM output indicated that the dilution factor of WWTP effluent in the marine sampling sites ranges from 0.04 to 0.74% (Table S6). Assuming that lamotrigine and venlafaxine concentrations in local WWTP effluents reflect reported values (2100–5800 and 210–650 ng/L, respectively),[92] expected marine concentrations (solely based on dilution) would be 0.9–41 ng/L lamotrigine and 0.1–4.8 ng/L venlafaxine (Figure 5, calculated), which are consistent with the measured concentrations across sites (0.1–10 ng/L for lamotrigine and 1.2–4.5 ng/L for venlafaxine, Figure 5, measured), further suggesting the importance of WWTP effluent as the primary source pathway of these compounds and their utility as wastewater tracers in nearshore marine environments.

PFASs are not completely removed through traditional wastewater treatment processes; the concentration of PFOS is typically in the range of tens to hundreds ng/L.[93−96] Based on the measured PFOS concentration in effluent of a local WWTP (460 ng/L)[4] and the modeled dilution factor at site 15 (0.12–0.17%, Table S6), the estimated concentrations of wastewater-derived PFOS would be 0.55–0.78 ng/L—significantly lower (Welch's *t*-test, $p = 0.039$) than observed (72–140 ng/L) (Figure 5). Thus, WWTP effluent cannot explain the high concentrations of PFOS at site 15. Similarly, the median measured PFOS concentration across all sites (4.3 ng/L) was higher than the predicted median (1.8 ng/L), suggesting that the PFOS concentrations could not be fully explained by wastewater effluent alone and that other local sources are likely important to the marine nearshore. Unlike the wastewater-derived CECs, contaminants from localized sources could undergo less dilution and occur at high concentrations at specific sites. The time series of samples also suggests that localized impacts are persistent and can lead to chronic exposure risks in marine ecosystems. Thus, nearshore marine surface waters in urban and peri-urban regions seem to be affected by both spatially variable but relatively continuous wastewater-derived CECs and contaminants from localized sources linked to urbanization and industrial land uses.[97]

Environmental Implications. Characterizing CEC occurrence and risk in urban and peri-urban estuarine environments is critical to protect their valuable ecological function. Suspect and nontarget HRMS screening revealed a complex contamination profile consisted of wastewater- and stormwater-derived CECs, pervasive plasticizers, and industrial chemicals and supported the identification of novel compounds (e.g., tebuthiuron TPs and the BPS derivative) in human-impacted receiving waters. As expected, wastewater effluent impacts estuarine water quality, with lamotrigine and sucralose detection frequencies >80%. However, both model predictions and measured concentrations indicated extensive dilution of WWTP-related compounds. Furthermore, the eight CECs prioritized for their toxicological relevance were neither pervasive in the study area nor wastewater-derived, indicating the importance of strong localized pollution sources such as stormwater inputs. These sources clearly merit significant attention as important drivers of ecological risk from CEC exposure in nearshore marine waters. Also, the novel and prioritized CECs reported here should guide biomonitoring and toxicology studies to more fully evaluate their potential to cause adverse biological impacts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b06126.

NORMAN ecotoxicology database; 87 non-polymeric and 118 polymeric contaminants; MS/MS fragments, and SMILES (XLSX)

Semiquantification using external calibration curve and internal standards; information for marine water sampling sites and date sampled; isotope-labeled internal standard mixture for qTOF analysis; workflow for data prioritization and identification; isotope patterns of tebuthiuron TPs and chlorothalonil TPs; MS/MS spectra for level S3 tentatively identified contaminants (PDF)

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Notes

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