Non-target and Suspect Screening of Contaminants of Emerging Concern in lower Columbia River

Columbia River Basin Restoration Program (CRBRP) Grant Program
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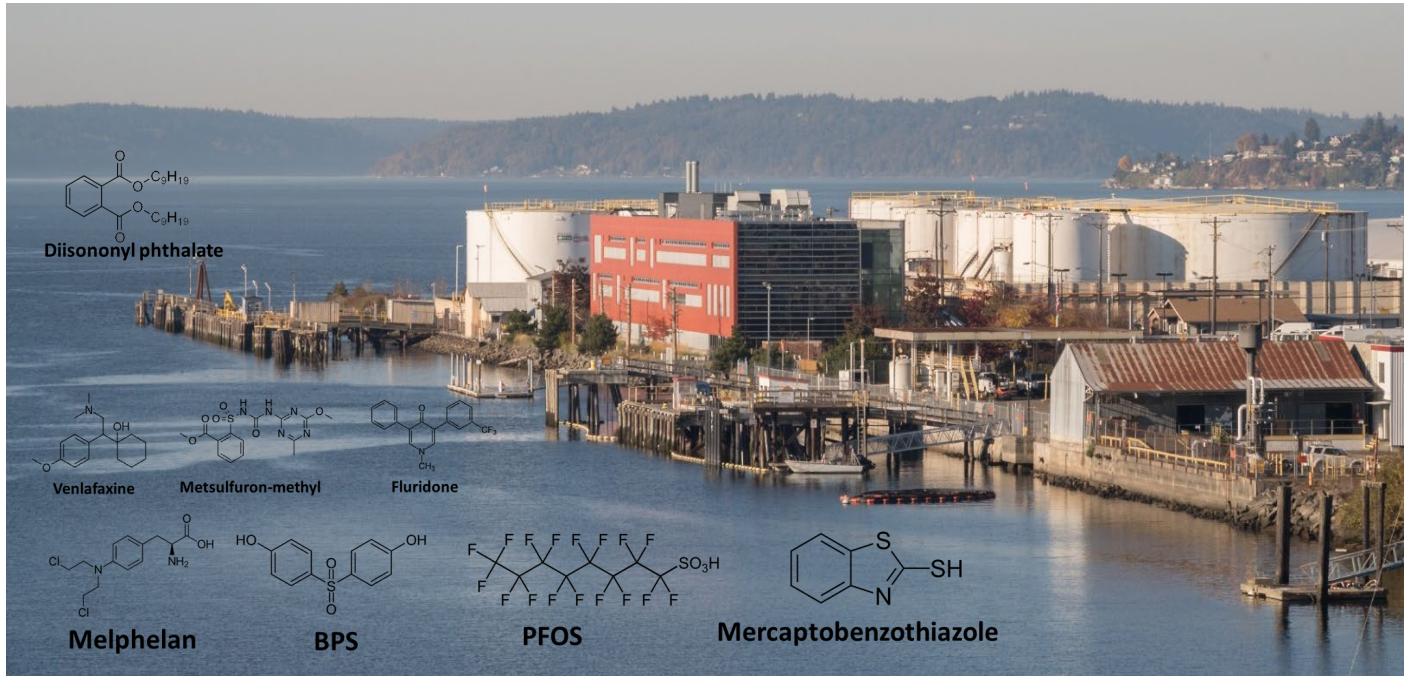
Project:

Characterize the occurrence of Contaminants of Emerging Concern in the Lower Columbia River using High Resolution Mass Spectrometry methods

Evaluate ecotoxicological context in order to understand if there is a potential to harm exposed biota



Tian et al, ES&T, 2019

Motivation:

- CECs are in the environment. Some have been associated with environmental harm.
  - Endocrine disruption, reduced survival, pre-spawn mortality syndrome
- Improving our understanding of CECs is a priority of ecosystem recovery programs

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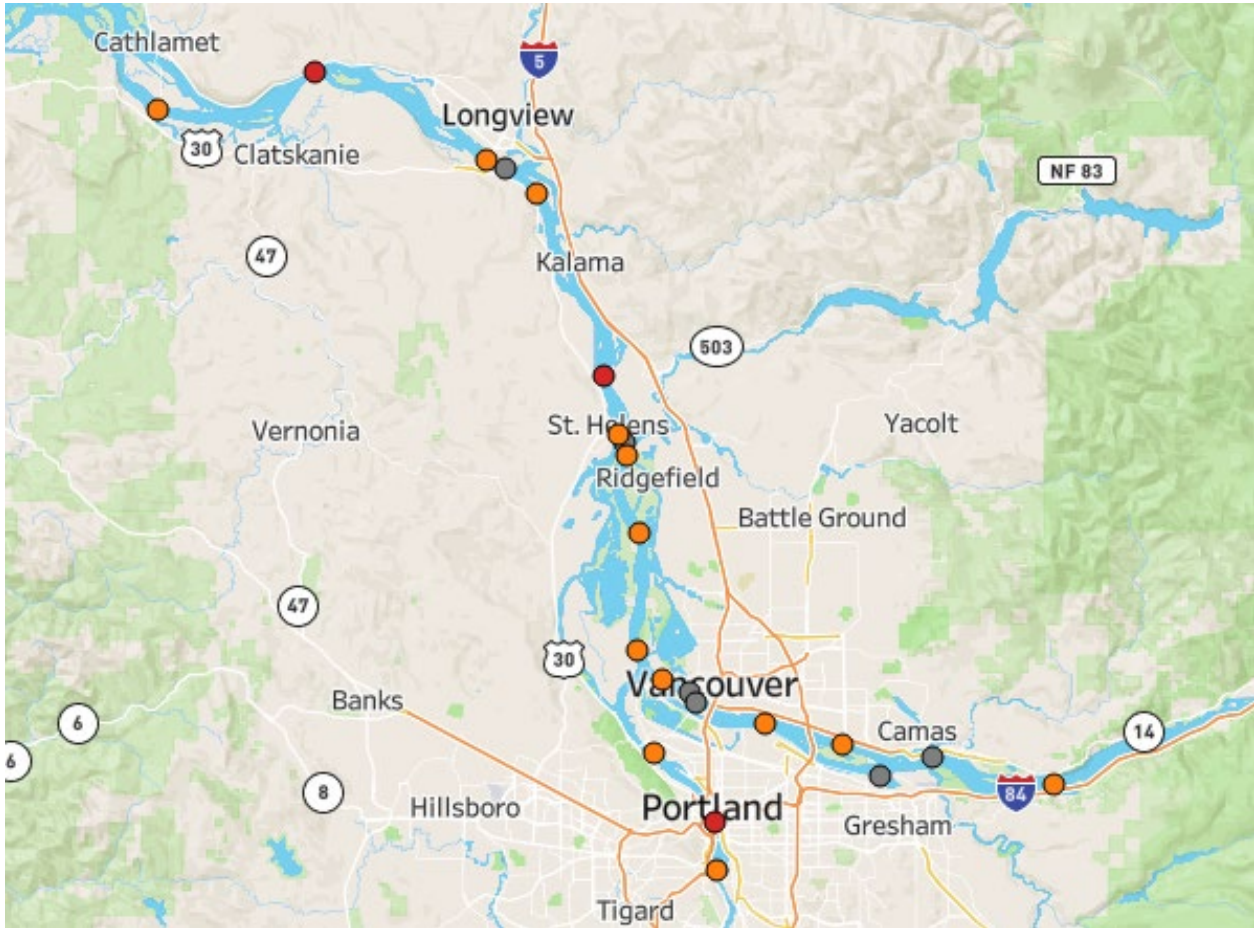
Monitoring



- 16 sampling locations
  Selected in consultation with USGS Oregon Water Science Center in order to characterize potential areas of impact based on past monitoring or inputs
- Four sampling events
  Two – February and March
  Two – August and September

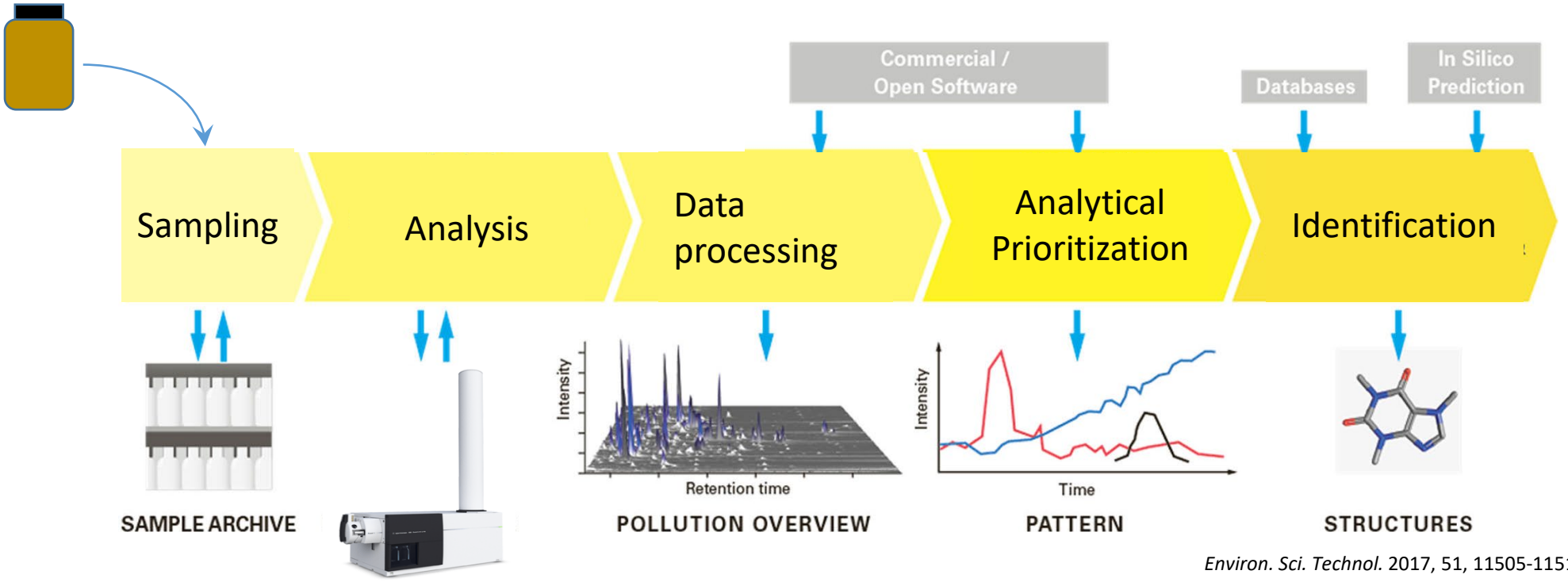
Note: Selected WWTP outfall locations are shown for reference only. WWTP effluent will not be sampled under this project.

Columbia River Sampling

Analysis

Non-target screening based on high resolution mass spectrometry

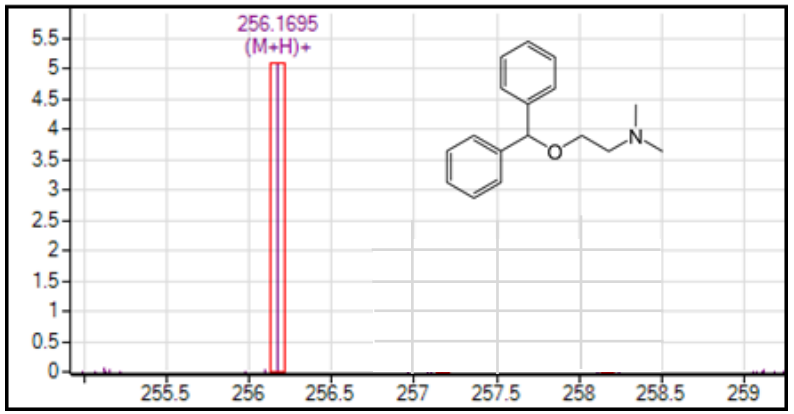
- Detect 100s-1000s of unique compounds in a given sample without a priori knowledge of compound IDs
- Analytical prioritization based on replication and occurrence patterns



Environ. Sci. Technol. 2017, 51, 11505-11512 (with modification)

HRMS Data – fragmentation (MS/MS)

Diphenhydramine



MS only

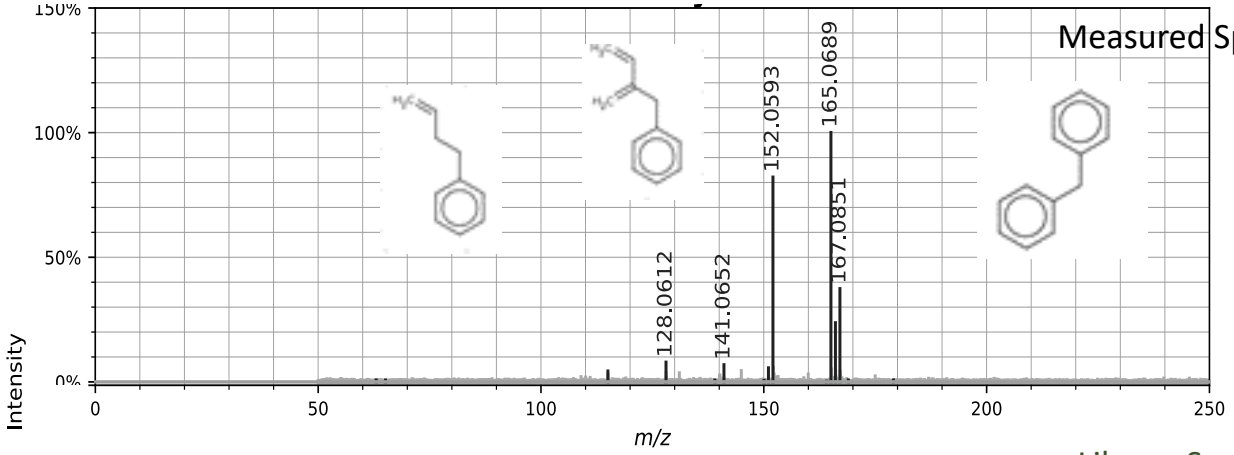
Accurate Mass of Compound

$C_{17}H_{21}NO$

(Five Compounds with Same Formula)

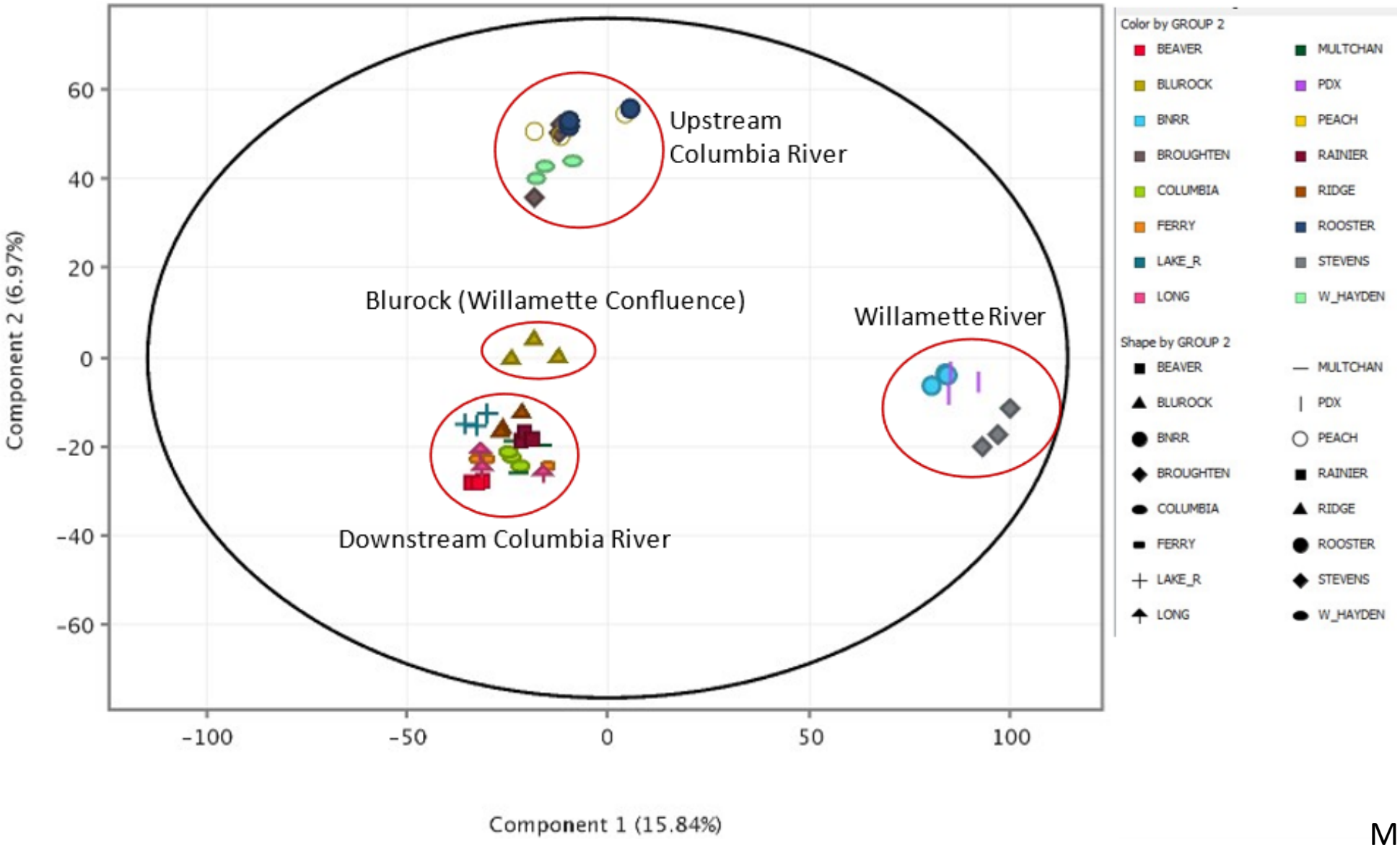
MSMS

Increase Confidence of Identification



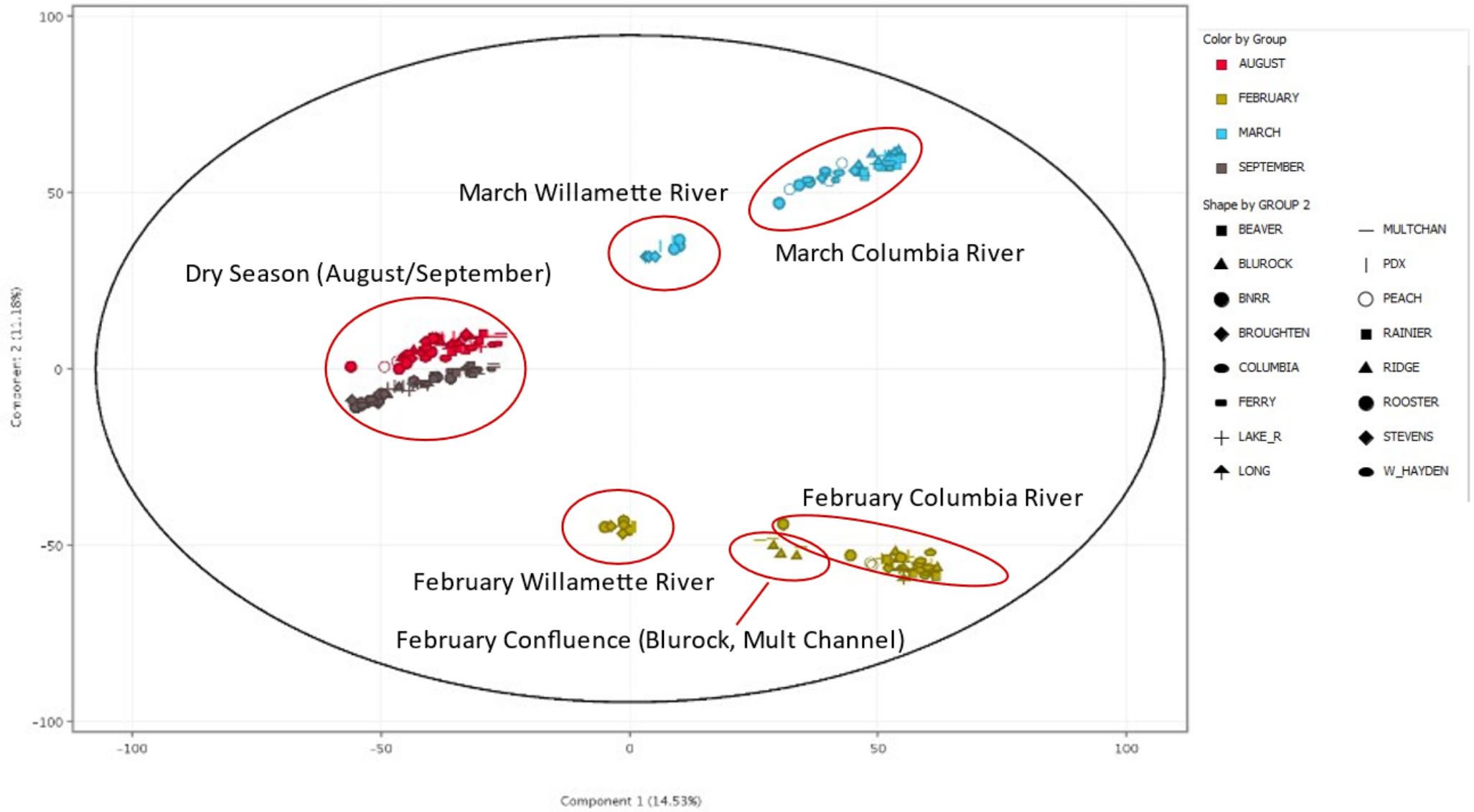
Library Spectra

Clear geographic trends in sample similarity



March 2021 ESI+

Seasonal differences were more complex



All Samples ESI+

Compound Identification

- Identified ~120 unique anthropogenic compounds across samples
- Had analytical standards to semi-quantify ~ 20 compounds
- 5 compounds had RQ >1 potential to cause harm

Compound Name	CEC Category	PNEC (µg/L)
Bis(2-ethylhexyl) phthalate	Phthalates	0.0048
Erucamide	Industrial	0.0071
Dimethyldioctadecylammonium	Commercial	0.0072
Docosahexaenoic acid	Commercial	0.012
Hexa(methoxymethyl)melamine	Industrial	0.017
Octadecanamide	Industrial	0.020
N,N'-Diphenyl-p-phenylenediamine	Industrial	0.029
Oleamide	Commercial	0.037
Venlafaxine	Pharmaceutical	0.038
4-Cholesten-3-one		0.038
Linolenic Acid		0.042
Carbamazepine	Pharmaceutical	0.050
Fexofenadine	Pharmaceutical	0.053
Metribuzin	Pesticide (Current use)	0.058
Diuron	Pesticide (Current use)	0.070
Palmitamide	Commercial	0.074
Benzyldimethyltetradecylammonium	Industrial	0.074
Benzyldodecyldimethylammonium	Commercial	0.078
Fludioxonil	Pharmaceutical	0.100

Tris(2-butoxyethyl) phosphate

- Replacement flame retardant used in foams
- Present in house dust and WWTP effluent
- Evidence of bioactivity (ToxCast) and endocrine disruption (Liu et al., 2016)
- TBOEP exposure of zebrafish decreases the average number of egg production, as well as hatching success and survival rates in offspring (Xu et al., 2017)
- Median concentration 40 ng/L; RQ >10

Venlafaxine

- Antidepressant
  (serotonin and norepinephrine reuptake inhibitors (SNRI).
- Primary metabolite (O-Desmethylvenlafaxine) is also present
- #33 in most prescribed drug list (~2.5M people taking drug)
  #2 by mass (48,363 kg in 2018; Gould et al., 2021)
- May affect reproductive success and individual fitness
- Identified as High Priority in Puget Sound system (James et al., 2023)
- Median concentration 3 ng/L; RQ >10

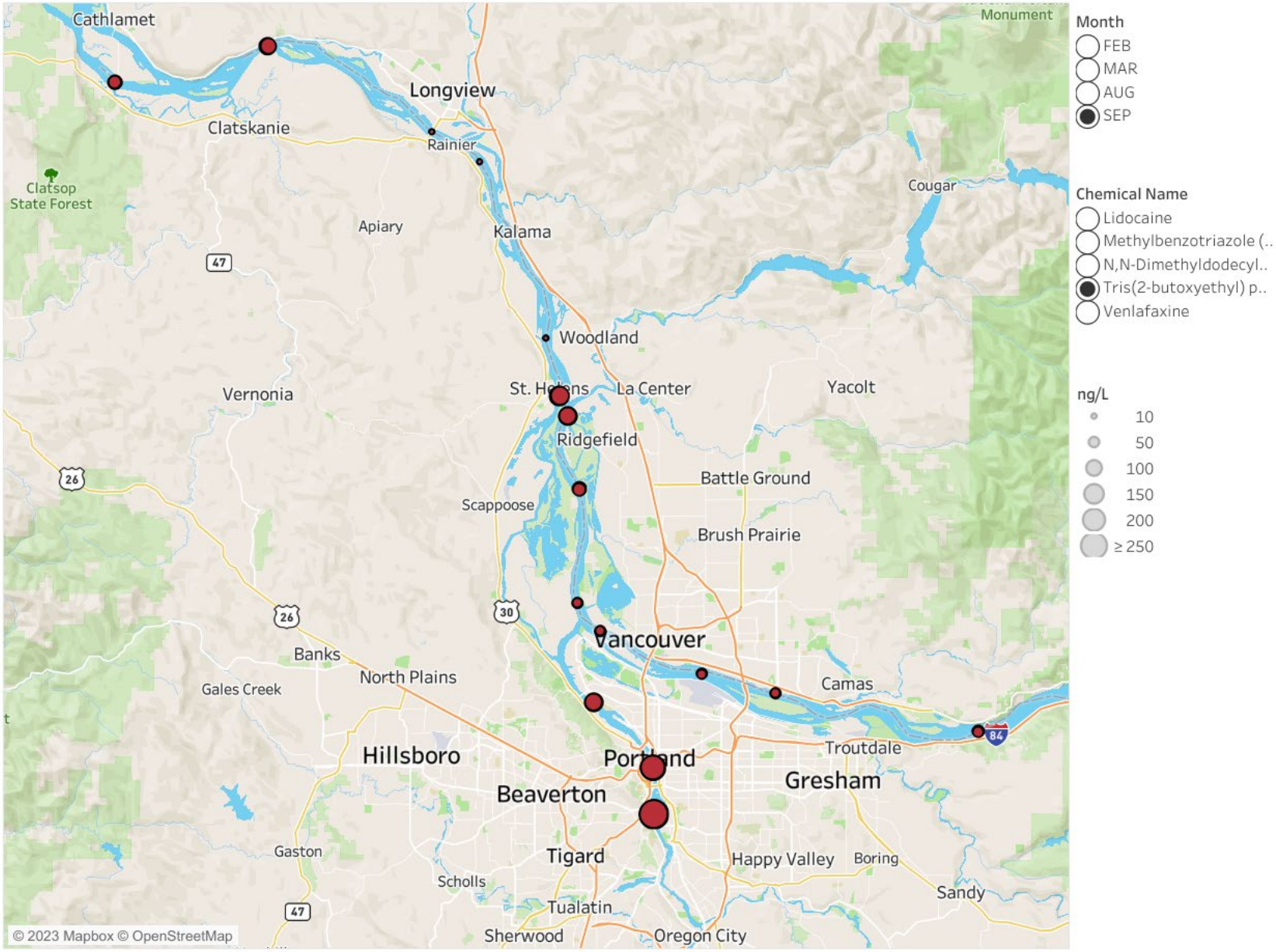
N,N-dimethyldodecylamine N-oxide (Lauramine Oxide)

- Surfactant, widely used in household and commercial cleaners.
- High production volume chemical: up to 20 million lbs annually
- Presents a high risk to aquatic life due to the mass released into the environment annually from normal use of household products (Nakamura et al., 2008).
- Median concentration 30 ng/L; RQ >1

Lidocaine

- Local anesthetic.
- Has been detected in surface waters (Baker et al., 2021) and WWTP effluents (Rúa-Gómez & Püttmann, 2011).
- Not much is known about long-term exposure effects at environmentally relevant concentrations.
- Metabolites such as 2,6-xylidine are also of concern.
- Median concentration 6 ng/L; RQ >1

TBOEP Detections By Month



Next Steps

- Follow up monitoring of focused locations within lower Columbia system
- Additional ecotoxicological screening and information
- Coordinate with environmental resource managers in region to understand data/information needs

Thank You

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Data Analysis

- System wide based on broad comparative analysis

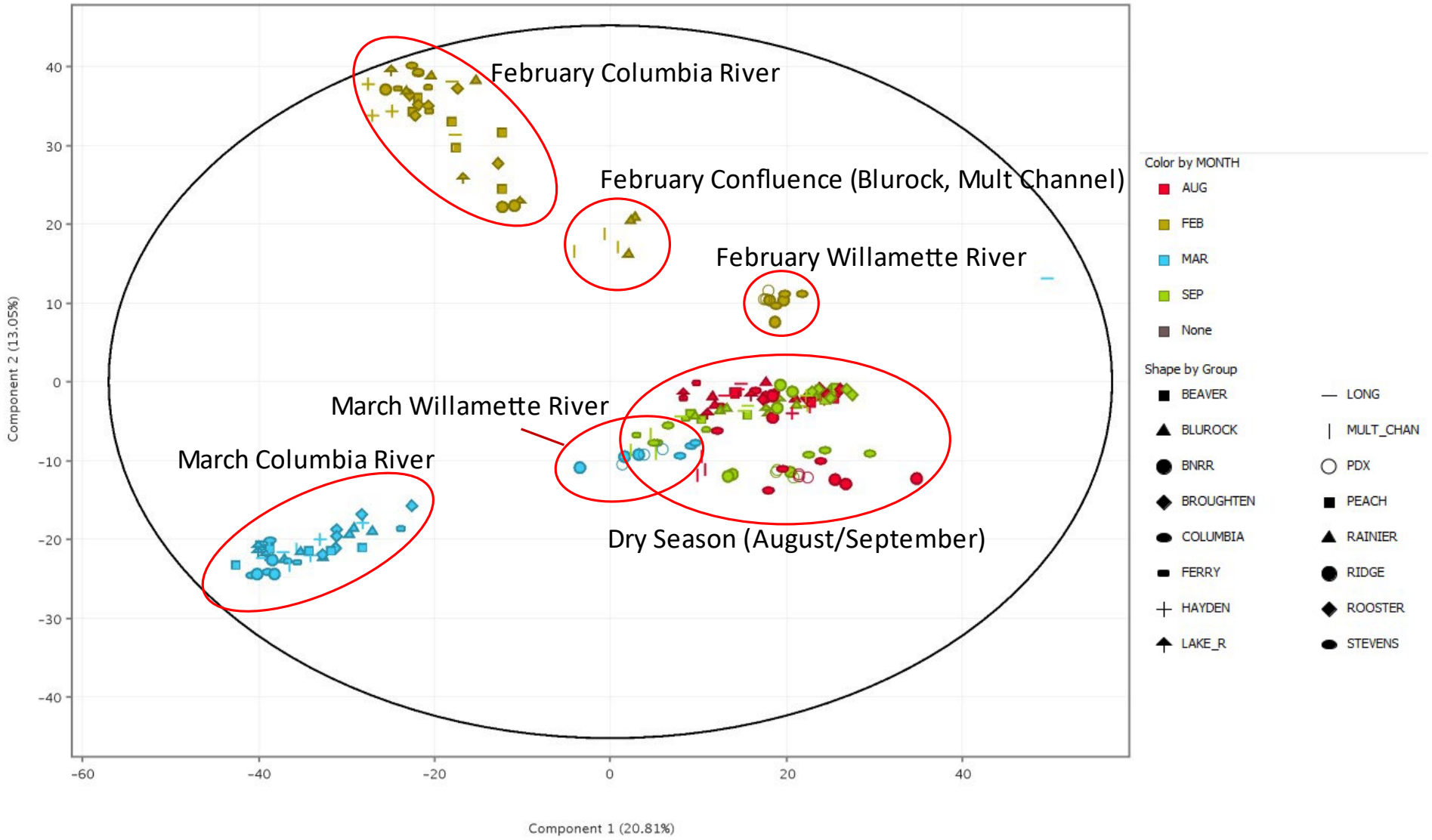
- Compound focus
  - Identify based on in house database of > 1000 compounds. Pharmaceuticals, automobile related compounds, common use chemicals, agricultural antibiotics, etc.
  - Identify compounds based on existing libraries and fragmentation patterns
  - Identify potential source contributions based on existing source signature patterns

Prioritization

Effects data and threshold

Two different data sets to identify ecological thresholds that are indicative of a biological response. Lower threshold → potentially more important compound

- Predicted No Effects Concentration (PNEC) from EU NORMAN program results
- CompTox – results of laboratory testing from Tox21 and ToxCast programs includes information on interactions with or effects on cells, proteins, DNA, RNA, receptors



All Samples ESI-
(supplemental slide)

(1) Baker, B. B.; Haimbaugh, A. S.; Sperone, F. G.; Johnson, D. M.; Baker, T. R. Persistent Contaminants of Emerging Concern in a Great Lakes Urban-Dominant Watershed. Journal of Great Lakes Research 2022, 48 (1), 171–182. https://doi.org/10.1016/j.jglr.2021.12.001.
(2) Gould, S. L.; Winter, M. J.; Norton, W. H. J.; Tyler, C. R. The Potential for Adverse Effects in Fish Exposed to Antidepressants in the Aquatic Environment. Environ. Sci. Technol. 2021, 55 (24), 16299–16312. https://doi.org/10.1021/acs.est.1c04724.
(3) James, C. A.; Sofield, R.; Faber, M.; Wark, D.; Simmons, A.; Harding, L.; O'Neill, S. The Screening and Prioritization of Contaminants of Emerging Concern in the Marine Environment Based on Multiple Biological Response Measures. Science of The Total Environment 2023, 886, 163712. https://doi.org/10.1016/j.scitotenv.2023.163712.
(4) Liu, Y.; Wu, D.; Xu, Q.; Yu, L.; Liu, C.; Wang, J. Acute Exposure to Tris (2-Butoxyethyl) Phosphate (TBOEP) Affects Growth and Development of Embryo-Larval Zebrafish. Aquatic Toxicology 2017, 191, 17–24. https://doi.org/10.1016/j.aquatox.2017.07.015.
(5) Nakamura, J.; Azuma, N.; Kameya, T.; Kobayashi, T.; Urano, K. Analysis of the Toxicity-Weighted Release Amount Ranking of PRTR Chemicals in Japan. Journal of Environmental Science and Health, Part A 2008, 43 (5), 452–459. https://doi.org/10.1080/10934520701796226.
(6) Rúa-Gómez, P. C.; Püttmann, W. Occurrence and Removal of Lidocaine, Tramadol, Venlafaxine, and Their Metabolites in German Wastewater Treatment Plants. Environ Sci Pollut Res 2012, 19 (3), 689–699. https://doi.org/10.1007/s11356-011-0614-1.
(7) Xu, Q.; Wu, D.; Dang, Y.; Yu, L.; Liu, C.; Wang, J. Reproduction Impairment and Endocrine Disruption in Adult Zebrafish (Danio Rerio) after Waterborne Exposure to TBOEP. Aquatic Toxicology 2017, 182, 163–171. https://doi.org/10.1016/j.aquatox.2016.11.019.