Suspect and Non-Target Screening for Contaminants of Emerging Concern in Puget Sound

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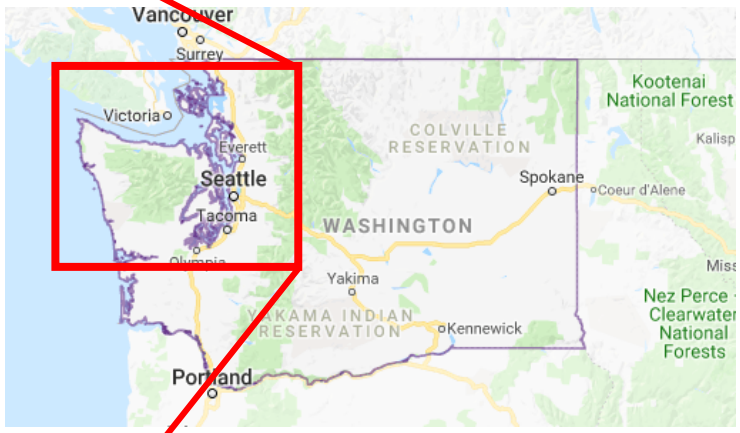
Outline

- Background
- Non-target and suspect screening method
- CECs identified in Puget Sound marine water
- Acknowledgements

Puget Sound & the Greater Seattle Area



- Second largest estuary in the US
- Puget Sound: a “dilutor” for the Greater Seattle Area
- Rapid development and population growth expected

Important habitat and fishery resources

- Salmon, Orca, and other marine animal species
- Can see seals, sea lions, and dolphins from our building

- Salmon in WA: economical, cultural, and political significance

Ecological concerns and water pollution

ANIMALS

Orca Mother Drops Calf, After Unprecedented 17 Days of Mourning

A Pacific Northwest orca likely bonded closely with her calf before it died, which could help explain her record-breaking emotional sojourn.

2 MINUTE READ

Environment | Local News

Toxic road runoff kills adult coho salmon in hours, study finds

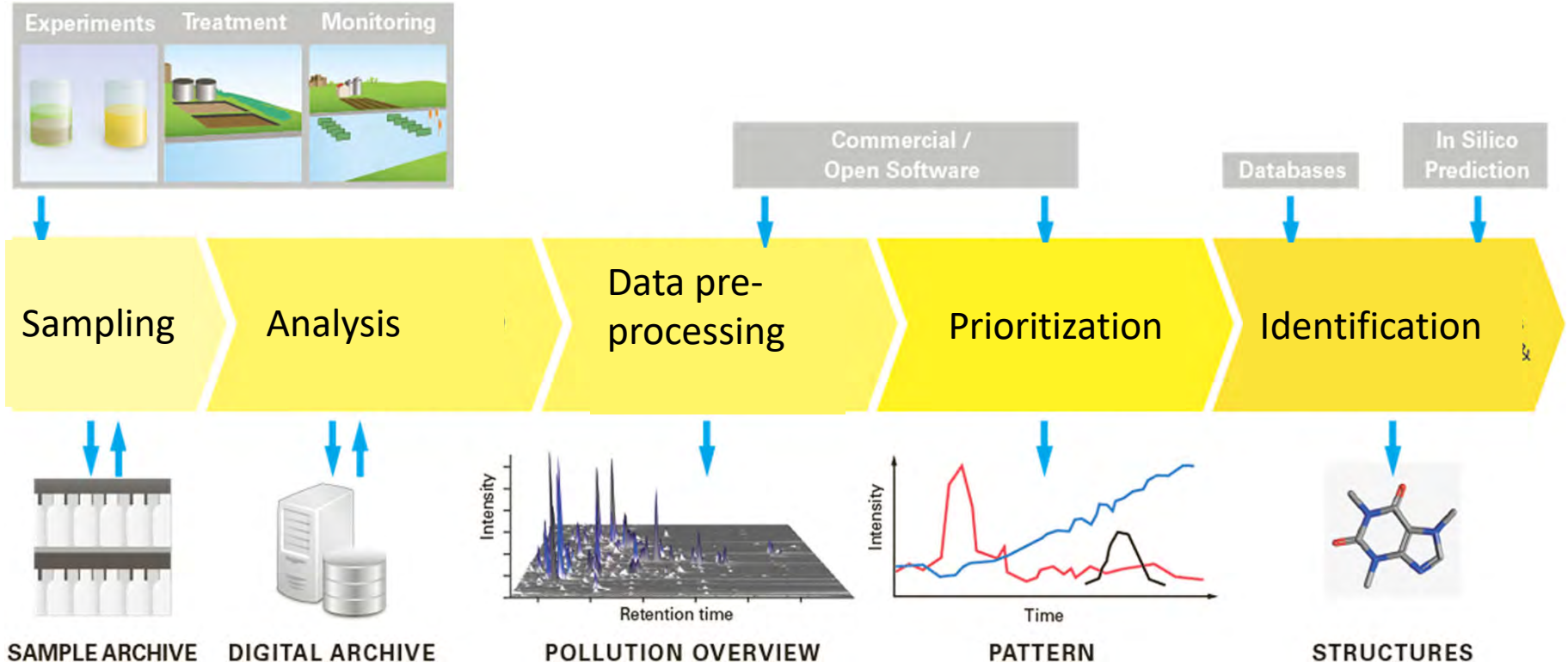
Originally published October 8, 2015 at 11:07 am | *Updated February 12, 2016 at 11:02 am*

- Declining Salmon and Orca population
- Water pollution is one of the major reason, but

We don't know what contaminants are causing these problems

https://www.nationalgeographic.com/animals/2018/08/orca-mourning-calf-killer-whale-northwest-news/
https://www.seattletimes.com/seattle-news/environment/whats-killing-coho-study-points-to-urban-road-runoff/

To answer the questions: non-target screening based on high resolution mass spectrometry

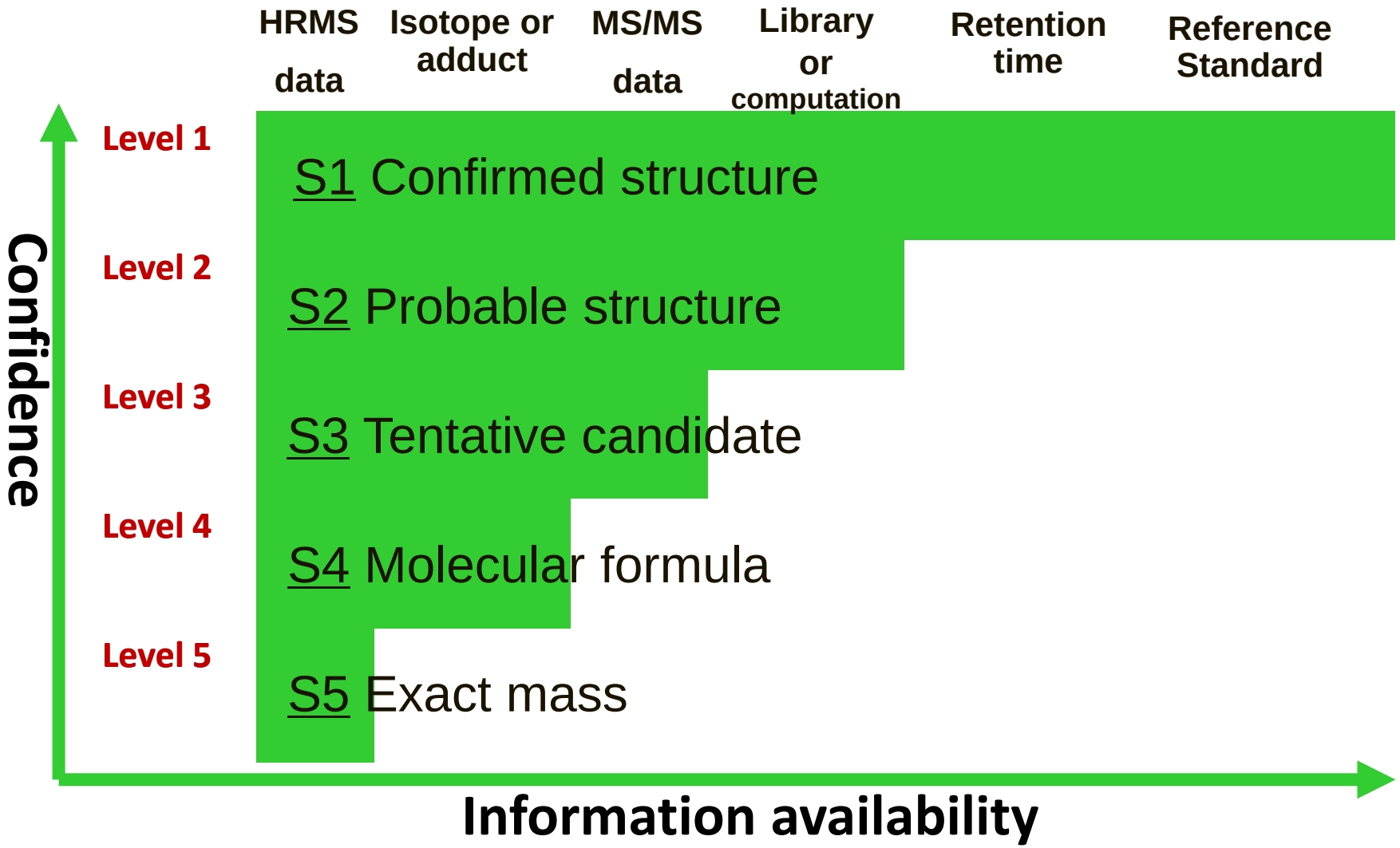


- Detect numerous pollutants **without** knowing IDs
- Prioritize pollutants for monitoring/regulation

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

Confidence level in HRMS detections

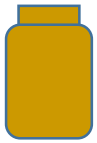
"We saw something" to "We know what it is"



Schymanski et al., 2014 ES&T

Sample processing and analytical methods

Sample Processing:



Water samples (1 L * 3)

Oasis HLB + micro glass beads

Zorbax Eclipse Plus RRHD 1.8 µm

Analyze on UPLC-qToF

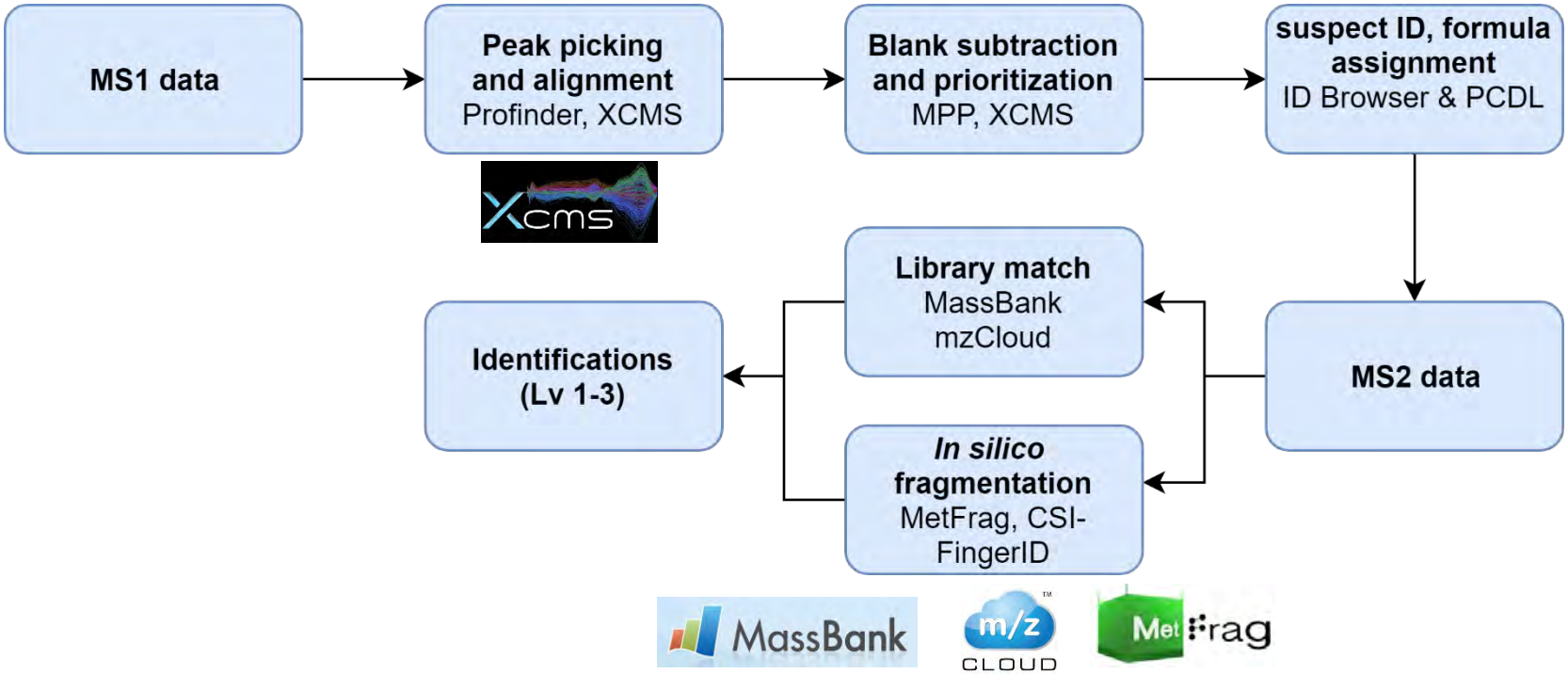
Agilent 6530

- ESI +: (A)Water (B)Methanol

  With 0.1% acetic acid & 5 mM NH_4Ac in both
- ESI -: (A)Water (B)Methanol

  With 1mM NH_4F in A
- Full scan MS1 and data-dependent acquisition MS2
- Isotope labeled internal standards spiked to monitor the performance

Suspect and non-target screening workflow

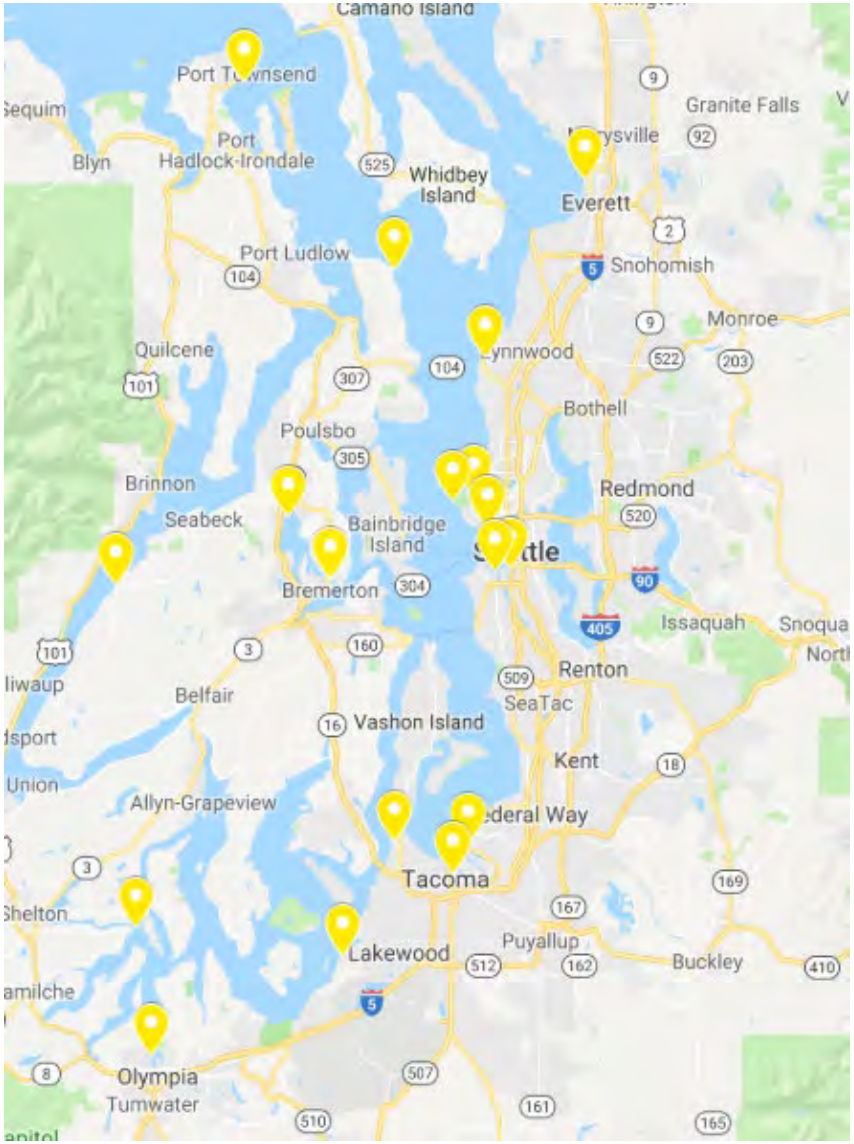


- In-house PCDL with exact mass and retention time (~1100)
- NORMAN PCDL for extensive suspect screening (~37,000, mass only)
- Batch mode *in silico* fragmentation

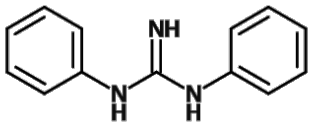
Marine water sampling sites

- 18 sampling sites
- 5 time points (April, May, June, August, October)
- Rainy days on April and Oct.

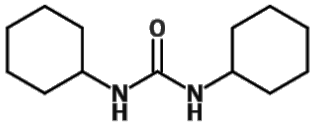
- 4L of subsurface marine water
- Pre-cleaned amber glass jar
- Field blks and method blks



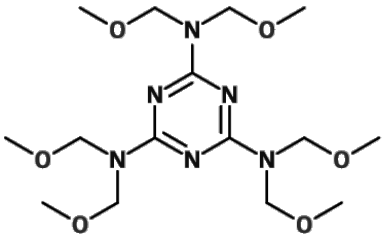
General trend: rainy days VS dry days



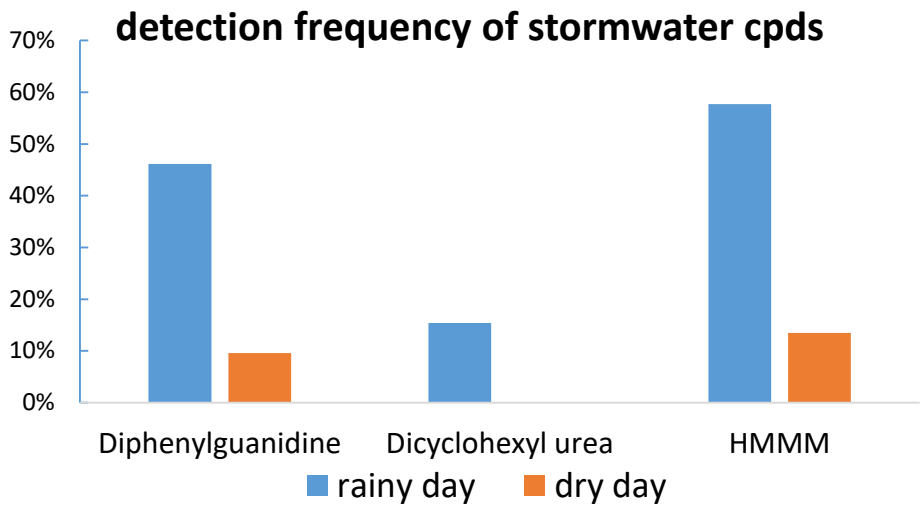
1,3-diphenyl guanidine
$C_{13}H_{13}N_3$



1,3-dicyclohexyl urea
$C_{13}H_{24}N_2O$



hexa(methoxymethyl)melamine (HMMM)
$C_{15}H_{30}N_6O_6$



- More contaminants detected in dry days (summer)
- But typical stormwater chemicals appear more in rainy days

General trend: hot spots

- All urban sites
- Impacted by wastewater effluent and non-point sources

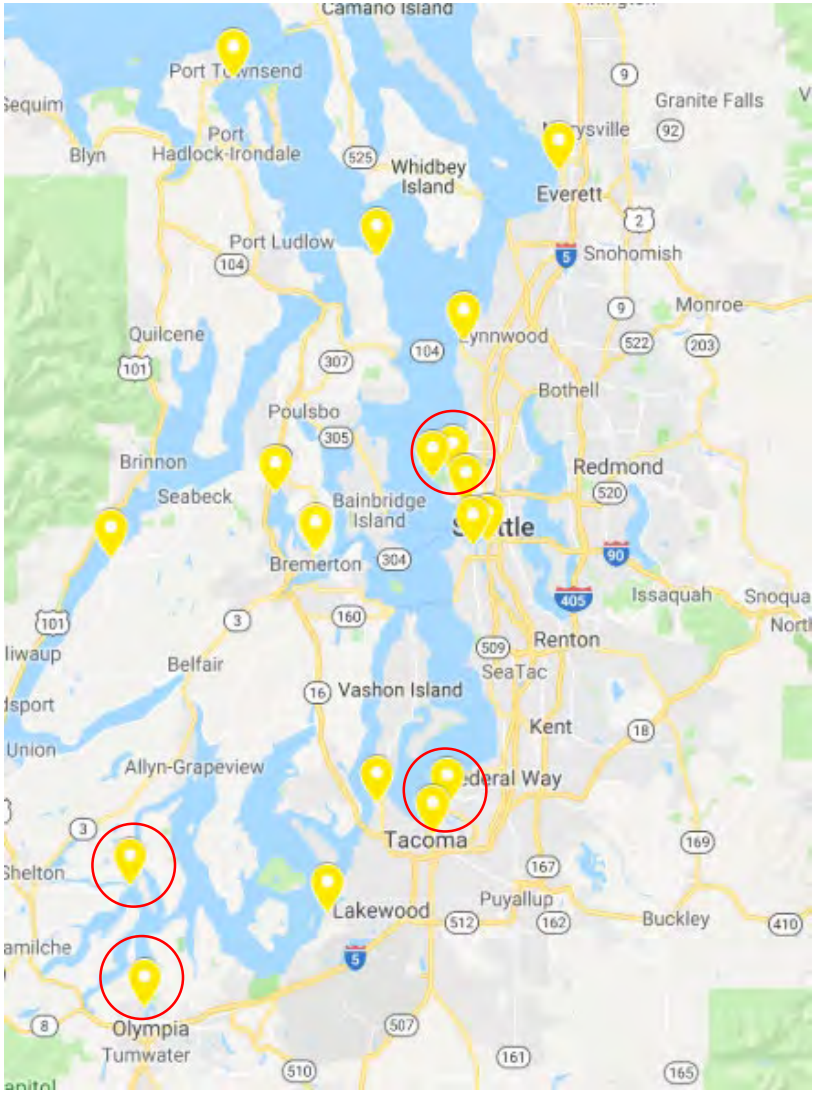
Northwest Seattle

(Salmon Bay and Smith Cove)

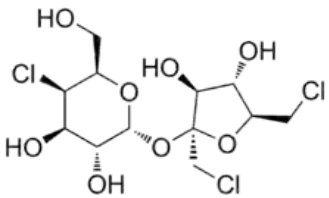
Commencement Bay at Tacoma

(Thea Foss waterway, Skookum)

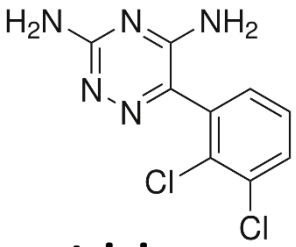
Budd Inlet, Hammersley Inlet



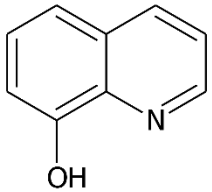
Most prevalent contaminants in Puget Sound



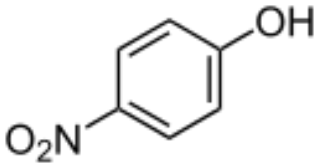
Sucralose
$C_{12}H_{19}Cl_3O_8$
Frequency: 96%
Up to ~250 ng/L



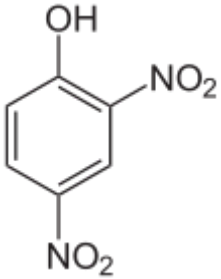
Lamotrigine
$C_9H_7N_5Cl_2$
Frequency: 91%
Estimated 3 – 20 ng/L



8-hydroxy quinoline
C_9H_7NO
Frequency: 97%



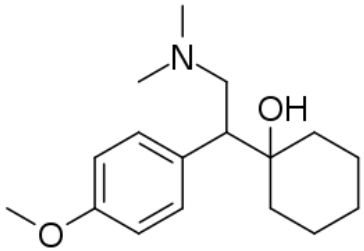
4-Nitrophenol
$C_6H_5NO_3$
Frequency: 87%



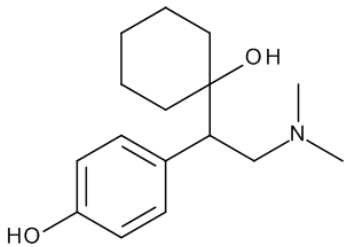
2,4-dinitropenol
$C_6H_4N_2O_5$
Frequency: 69%

Where do they come from?

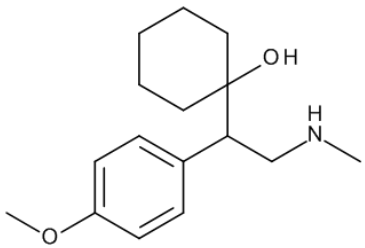
Pharmaceuticals



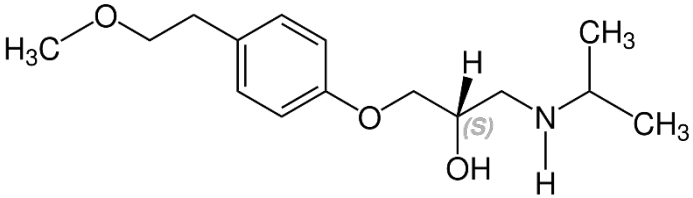
Venlafaxine
$C_{17}H_{27}NO_2$



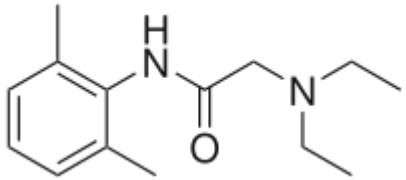
O-desmethyl venlafaxine
$C_{16}H_{25}NO_2$



N-desmethyl venlafaxine
$C_{16}H_{25}NO_2$



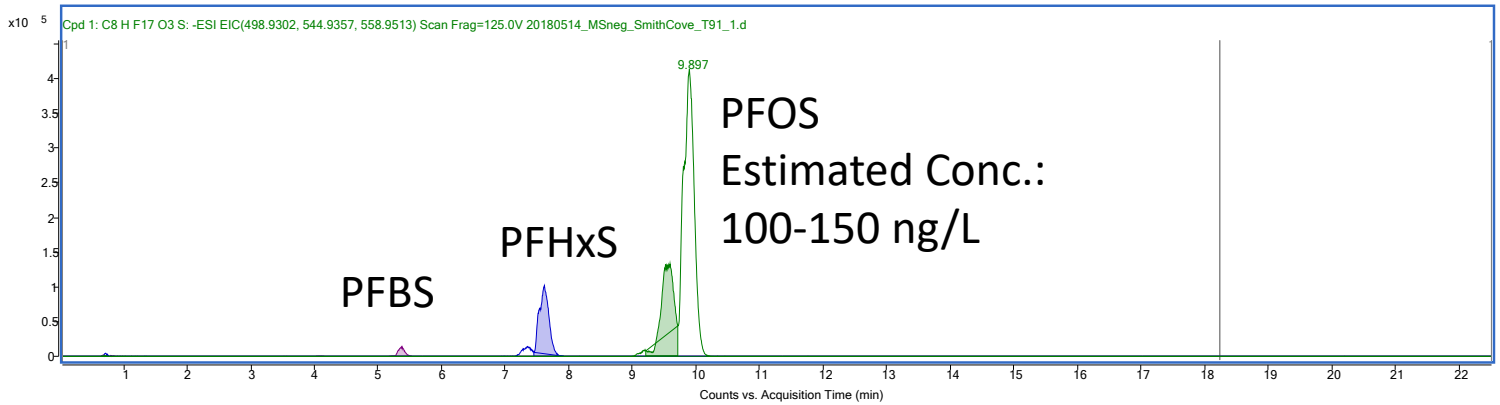
Metoprolol
$C_{15}H_{25}NO_3$

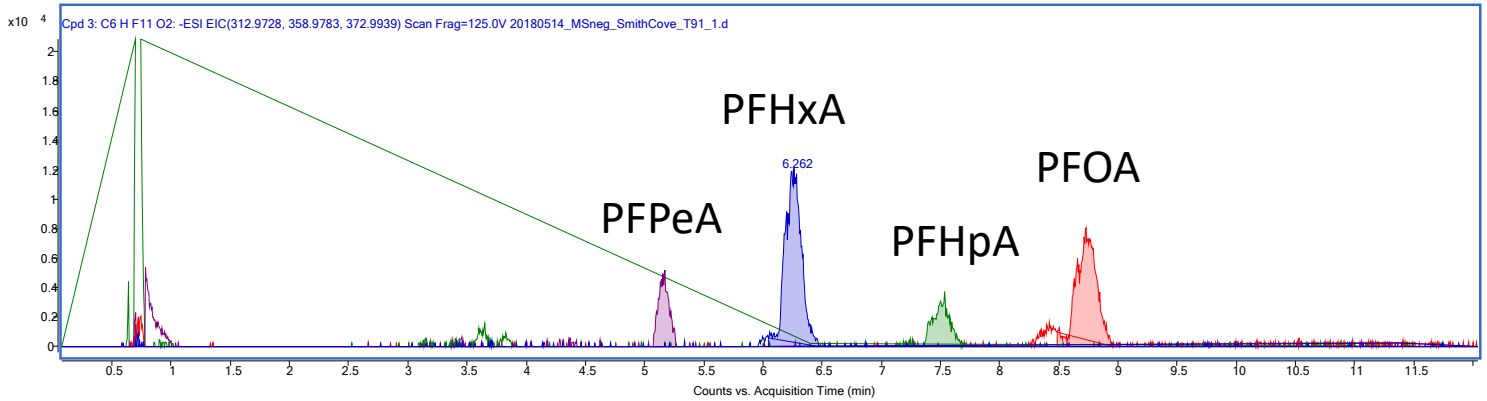


Lidocaine
$C_{14}H_{22}N_2O$

PFASs

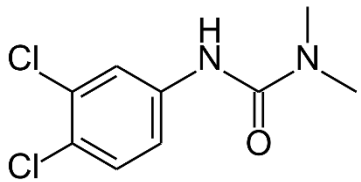
- Presented in multiple sites, all dry days
- one specific site is the “hot spot” for PFASs (Smith Cove Terminal 91 at NW Seattle)



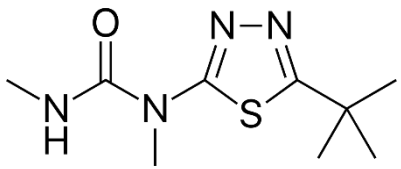


Herbicides and fungicides

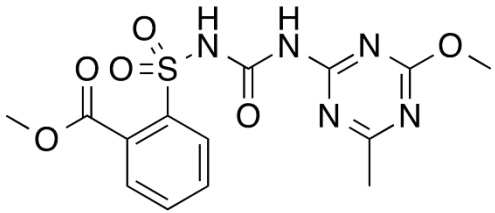
- Urban-use herbicides and fungicides
- Urea and carbamate used more often: “Uron” and “Carb”



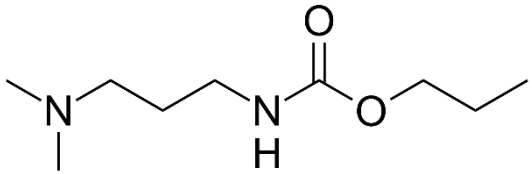
Diuron
$C_9H_{10}Cl_2N_2O$



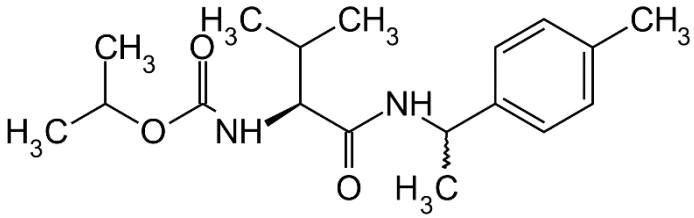
Tebuthiuron
$C_9H_{16}N_4OS$



mesulfuron-methyl
$C_{14}H_{15}N_5O_6S$

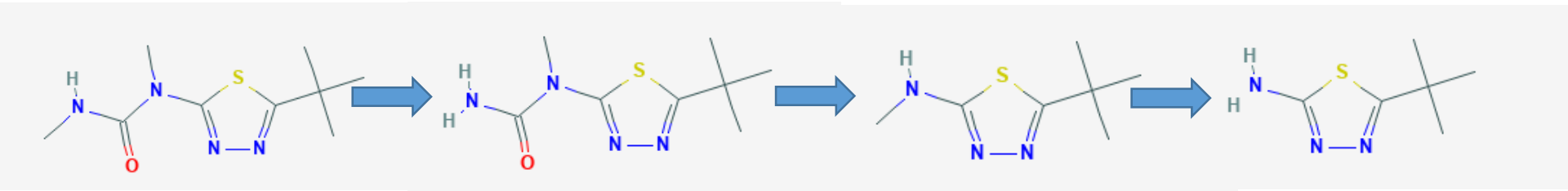


Propamocarb
$C_{19}H_{20}N_2O_2$



Iprovalicarb
$C_{18}H_{28}N_2O_3$

Unexpected discovery: transformation of tebuthiuron (herbicide)



Tebuthiuron
C9H16N4OS

Tebuthiuron TP1
C8H14N4OS
Known as *in vivo* metabolite

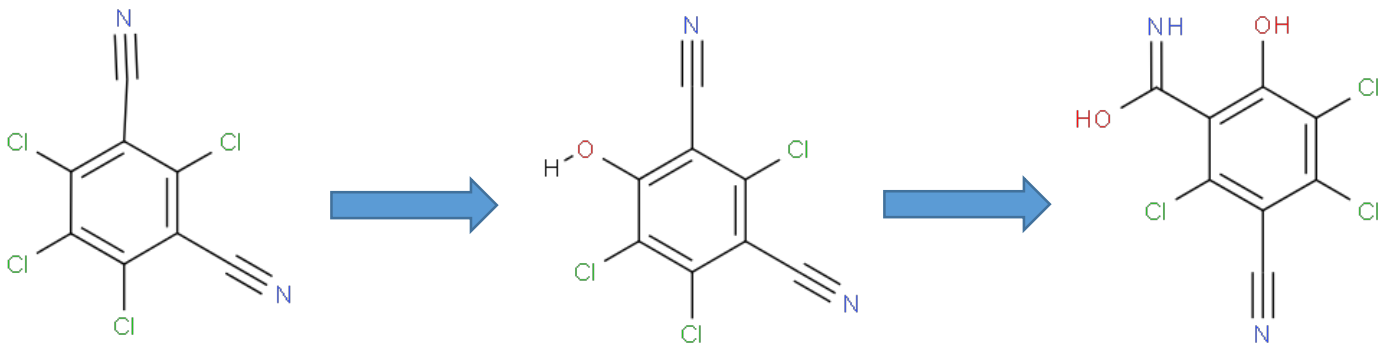
Tebuthiuron TP2
C7H13N3S

Tebuthiuron TP3
C6H11N3S

"Real unknowns"

in silico fragmentation (CSI: FingerID) helps identification

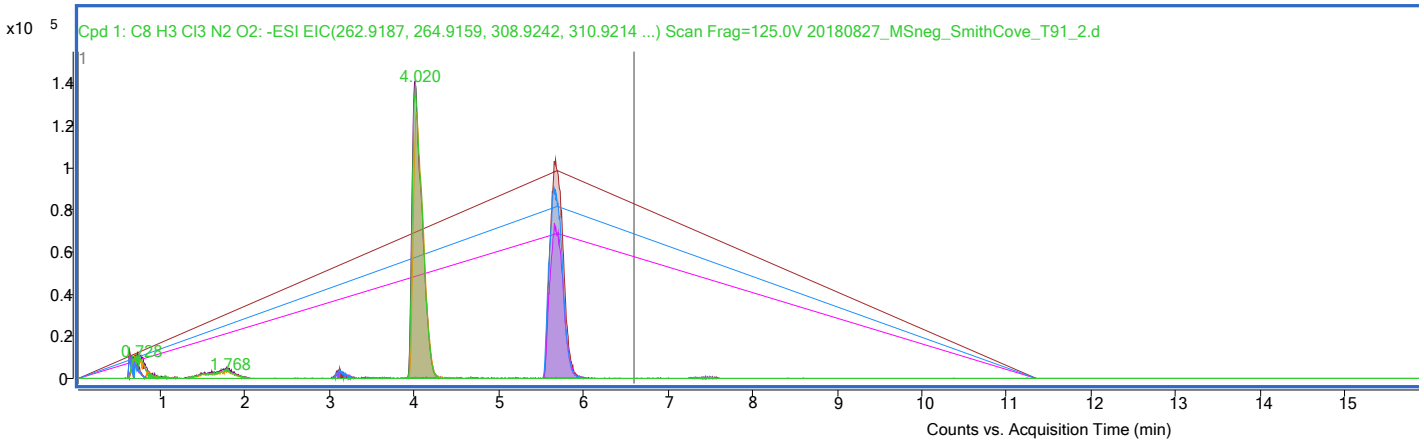
TPs of chlorothalonil (fungicide): more toxic and persistent?



Chlorothalonil
Highly toxic to fish, probable carcinogen

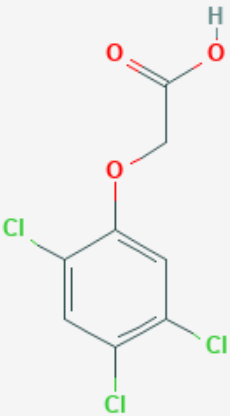
4-Hydroxy-chlorothalonil
C8HCl3N2O
More toxic to some species
More persistent

1-amide-4-Hydroxy-chlorothalonil
C8H3Cl3N2O2 (Lv 3)

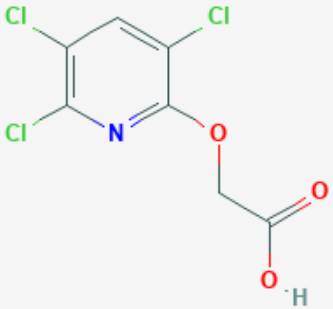


Triclopyr: the chemical “whack-a-mole”

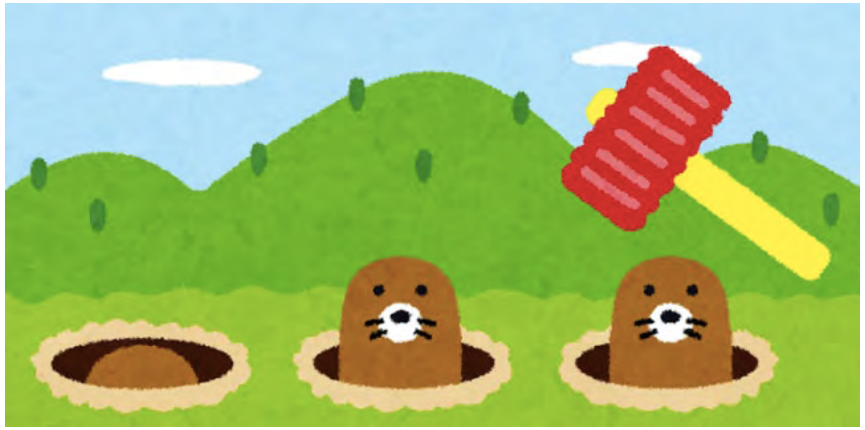
- Only detected in one site, but all summer months (May, June, August)
- Substitute for 2,4,5-T which is banned in 1985



2,4,5-T



Triclopyr
C7H4Cl3NO3



Preliminary results

- More than 70 contaminants identified (except for polymers)
- There is a wastewater contaminants “baseline” in Puget Sound
- Stormwater pollutants impact the sea in rainy days
- Alarming occurrence of herbicides/fungicides and PFASs

- **Future work:**
  - Risk evaluation by toxicity prediction models
  - Source tracking for prioritized CECs

Acknowledgements

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  Jennifer Lanksbury, Mariko Langness

Thanks for your attention!

Any question?