QACs: Detection in the Environment and Degradation Processes

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Acknowledgements

- Dr. Sarah Pati + Swiss NSF
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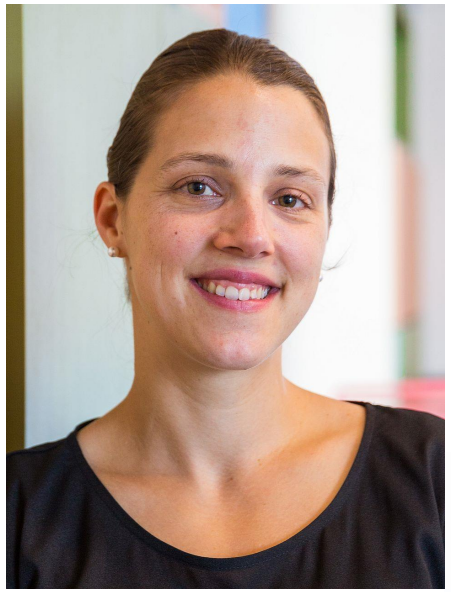
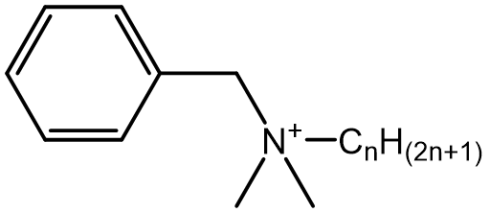
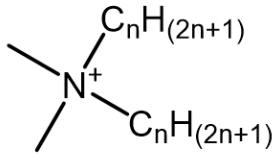


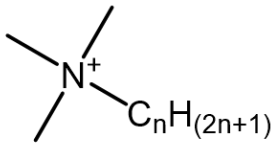
ENVIRONMENT
AND NATURAL RESOURCES
TRUST FUND

Quaternary ammonium compounds (QACs)

BACs / DADMACs / ATMACs

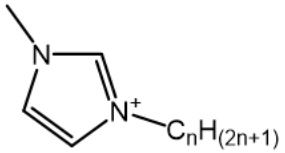


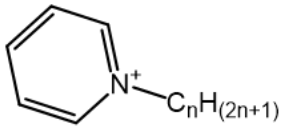


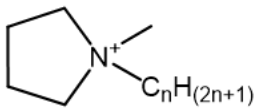


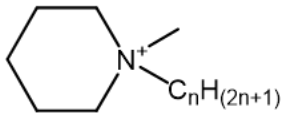
n = 12, 14, 16, 18, 20

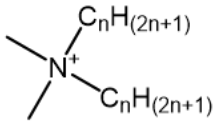
Ionic liquids



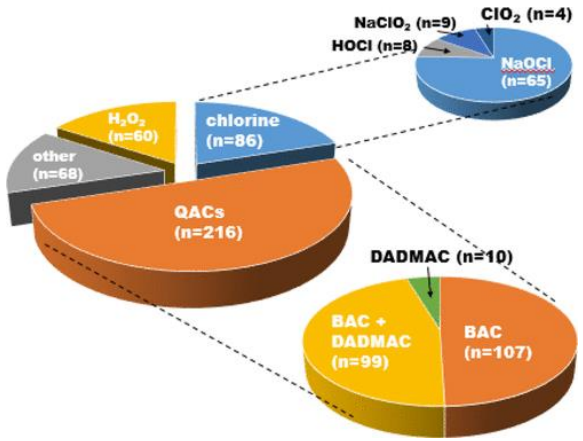




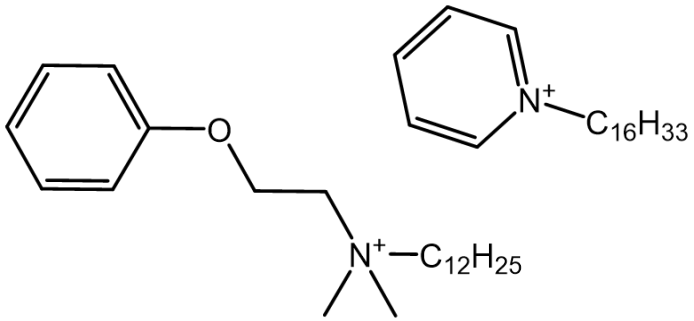


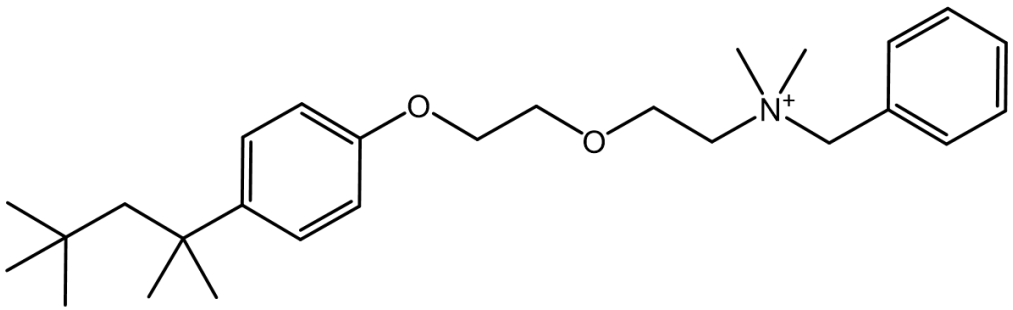


n = 2, 4, 6, 8, 10



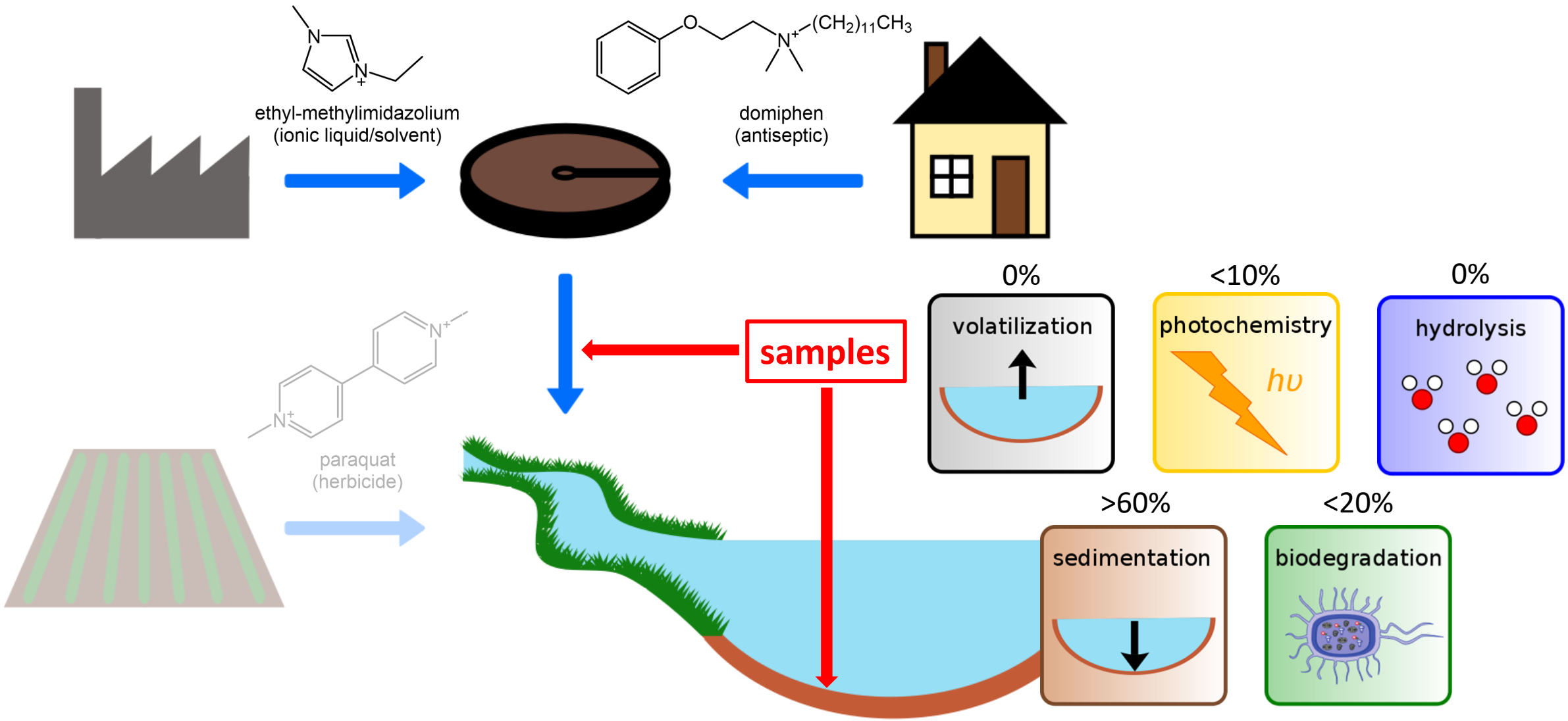
additional QACs





Hora et al., 2020, *ES&T Letters,* 7, 622.
https://doi.org/10.1021/acs.estlett.0c00437

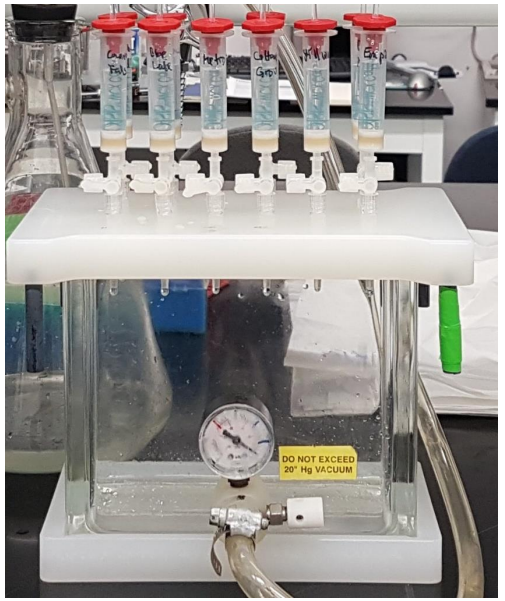
Input and fate of QACs in aquatic environments



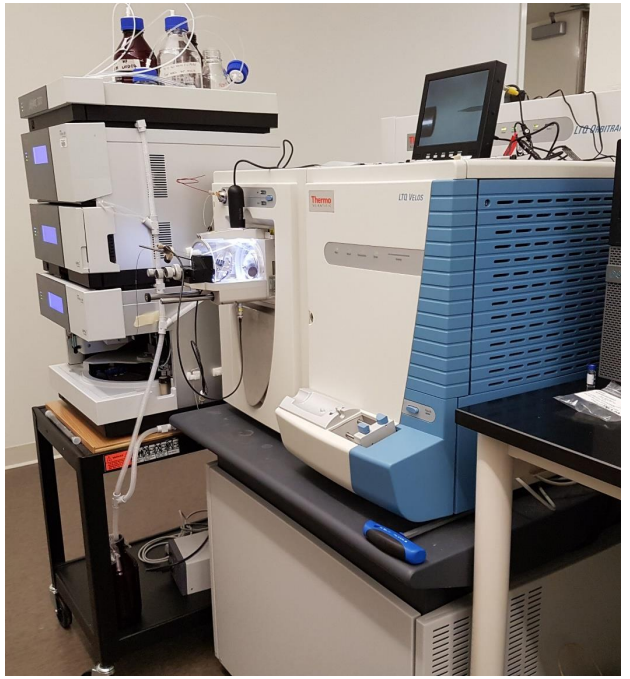
Tezel and Pavlostathis, In *Antimicrobial Resistance in the Environment.* **2012** 349

Analytical workflow

wastewater and
sediment samples

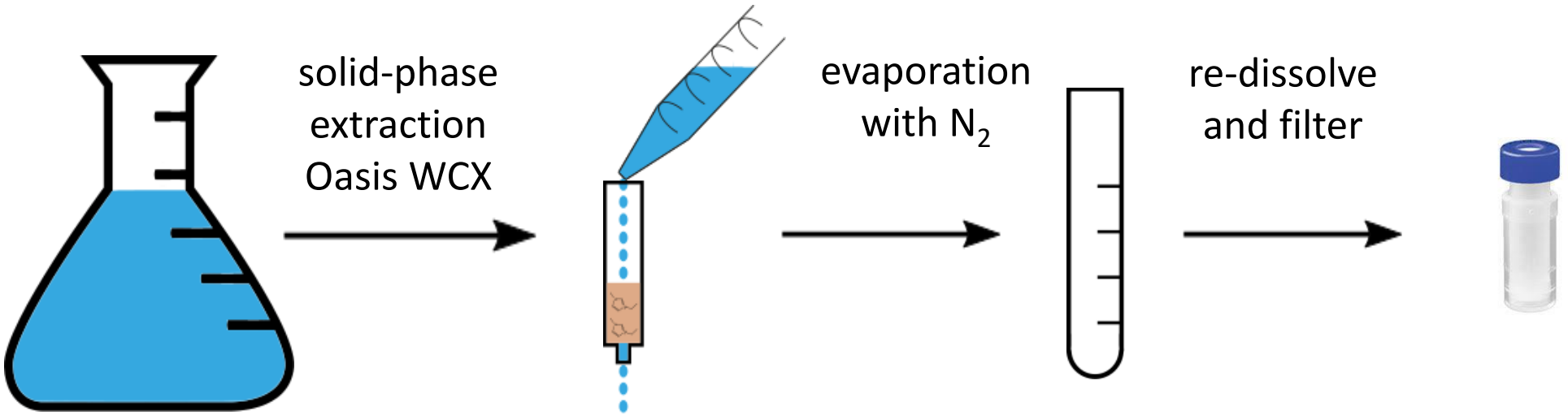


sample preparation
extraction/clean-up



liquid-chromatography
high-resolution
mass spectrometry

Solid-phase extraction procedure for effluent samples



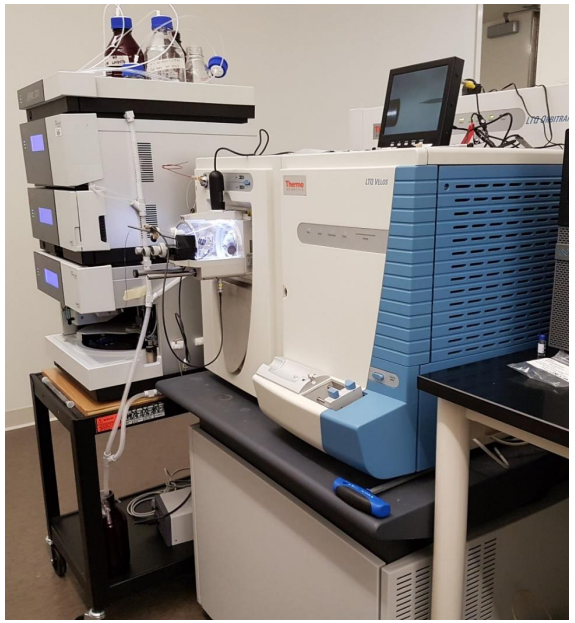
250 mL sample
+ surrogate-mix

6 mL extract
(2% formic acid (FA)
in acetonitrile (ACN))

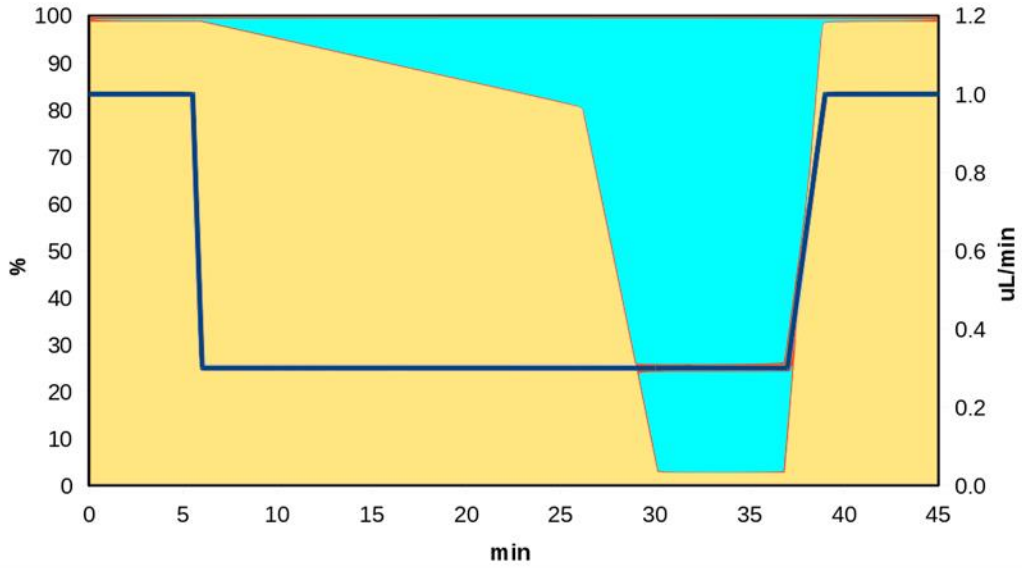
dry extract

1 mL ACN
+ISTD-Mix

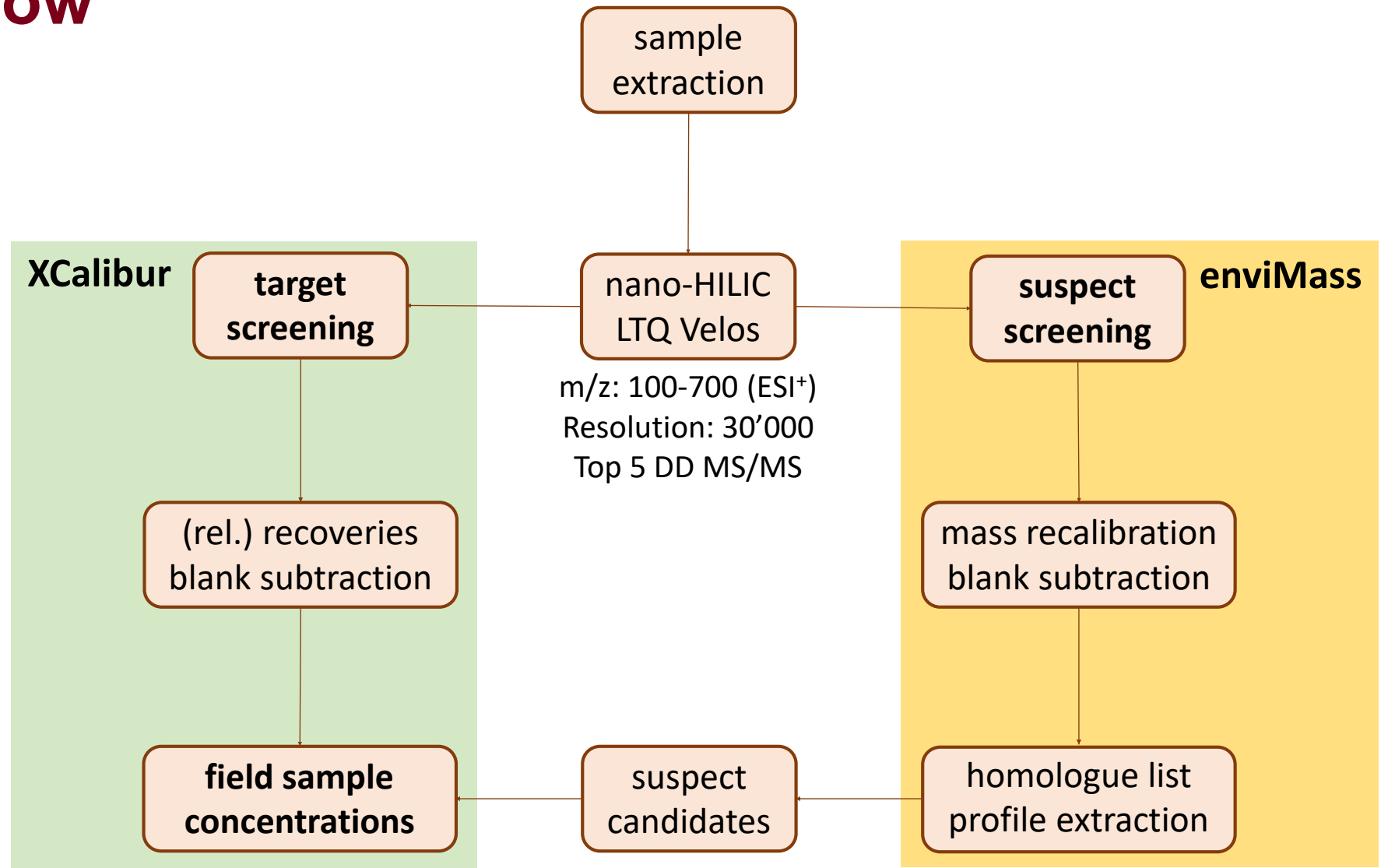
LC/HRMS method



- Cogent 4 Diamond Hydride column (nanoflow HILIC column)
- Injection volume: 2 µL
- 0.1% FA in ACN (A) and 0.1% FA in 5mM ammonium acetate (B)
- Electrospray ionization positive mode
- Full scan: m/z = 100-700, resolution = 30,000
- Data-dependent MS/MS scans: top-5 from suspect/target mass list

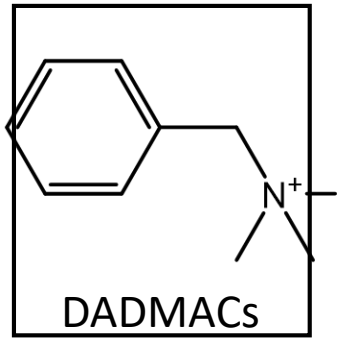


Workflow



Loos, M. *enviMass* v3.5 **2018** Zenodo; Chiaia-Hernández et al., *Environ. Sci. Technol.* **2017** 12547-12556

Wastewater effluents: Target screening



DADMACs

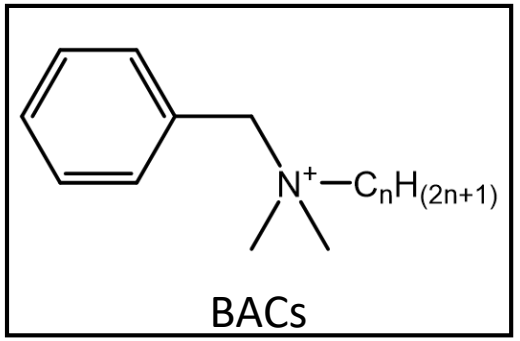
LOQ: 44–131 ng/L

Rel. Recovery: 9–16%

Mean: 204–1419 ng/L

Max.: 2745 ± 393 ng/L (C_{18})

>LOQ: 77–85% of samples



BACs

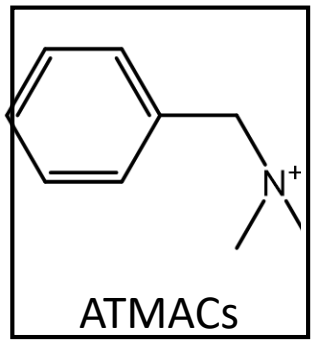
LOQ: 2–14 ng/L

Rel. Recovery: 21–143%

Mean: 1–195 ng/L

Max.: 1073 ± 145 ng/L (C_{14})

>LOQ: 77–92% of samples



ATMACs

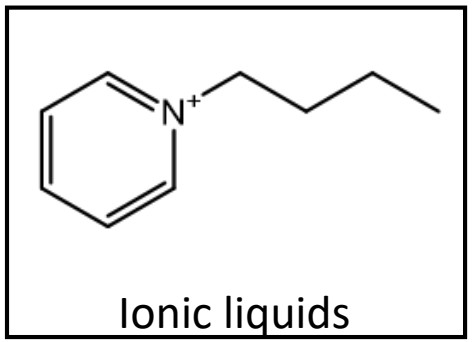
LOQ: 1–25 ng/L

Rel. Recovery: 25–109%

Mean: 0–19 ng/L

Max.: 69 ± 15 ng/L (C_{18})

>LOQ: 0–85% of samples



Ionic liquids

LOQ: 42 ng/L

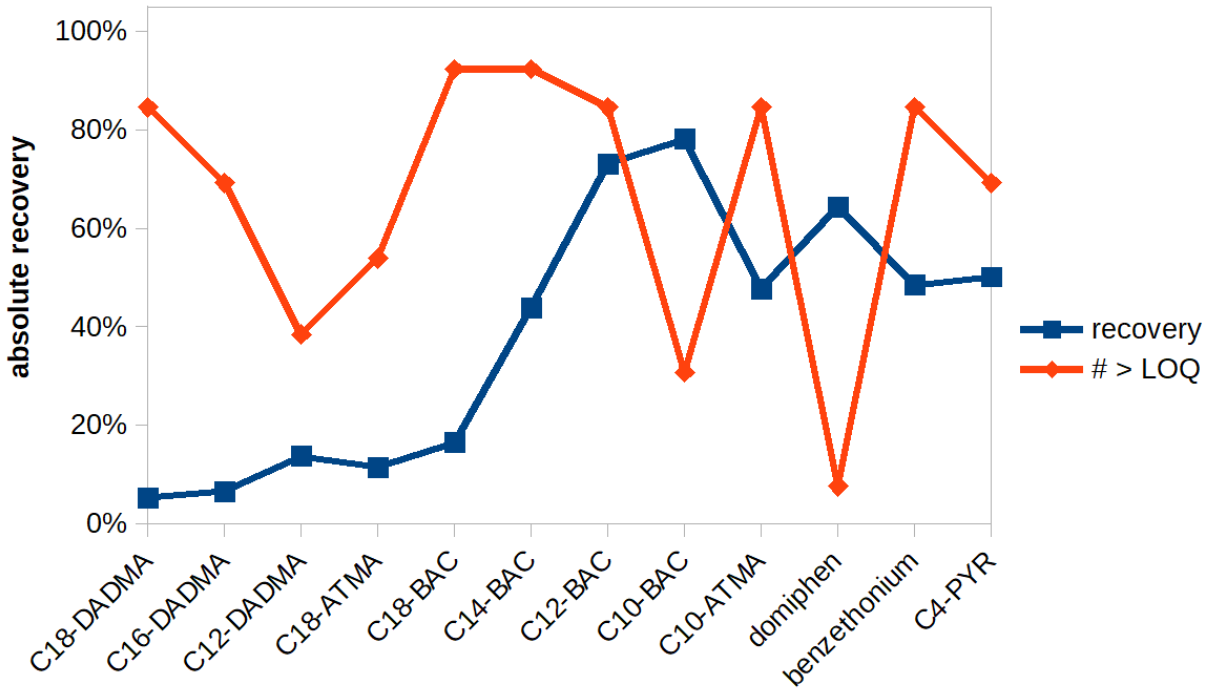
Abs. Recovery: 49%

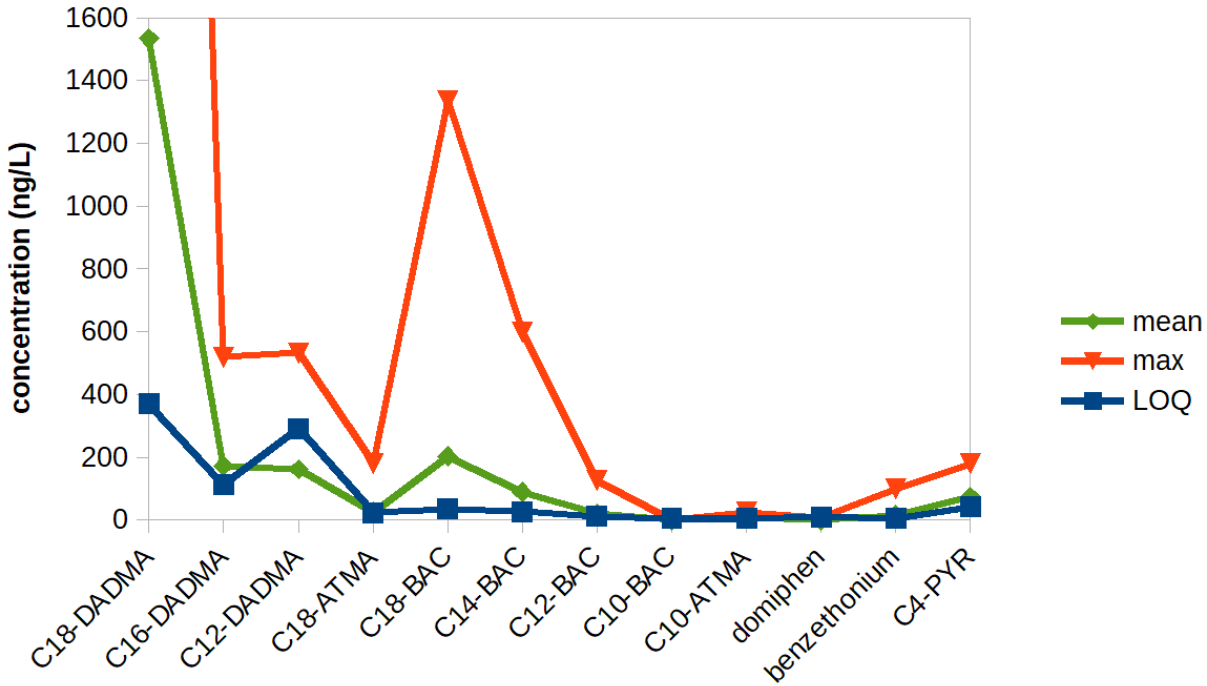
Mean: 87 ± 35 ng/L

Max.: 179 ± 85 ng/L (C_4)

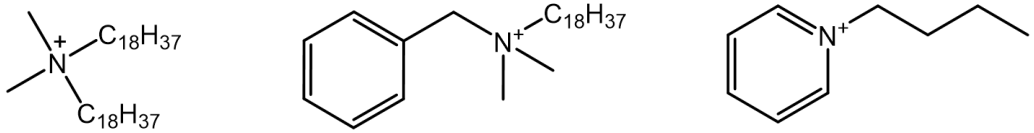
>LOQ: 69% of samples

Wastewater effluent samples



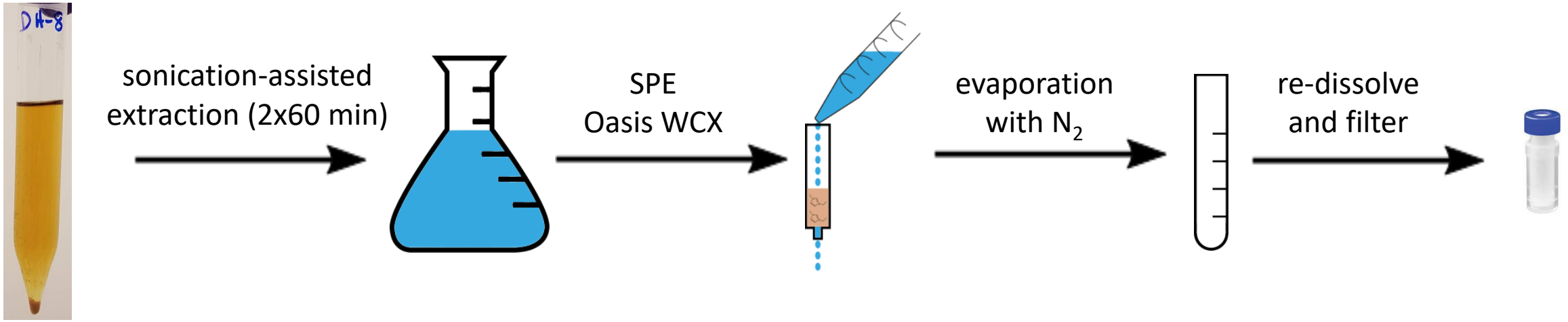


12 out of 22 QACs detected at least once



Pati and Arnold, 2020, *ESPI,* 22, 430.
http://dx.doi.org/10.1039/C9EM00554D

Sediment sample preparation procedure



250 mg sediment
2x5 mL 1 M HCl in MeOH
+ surrogate-mix

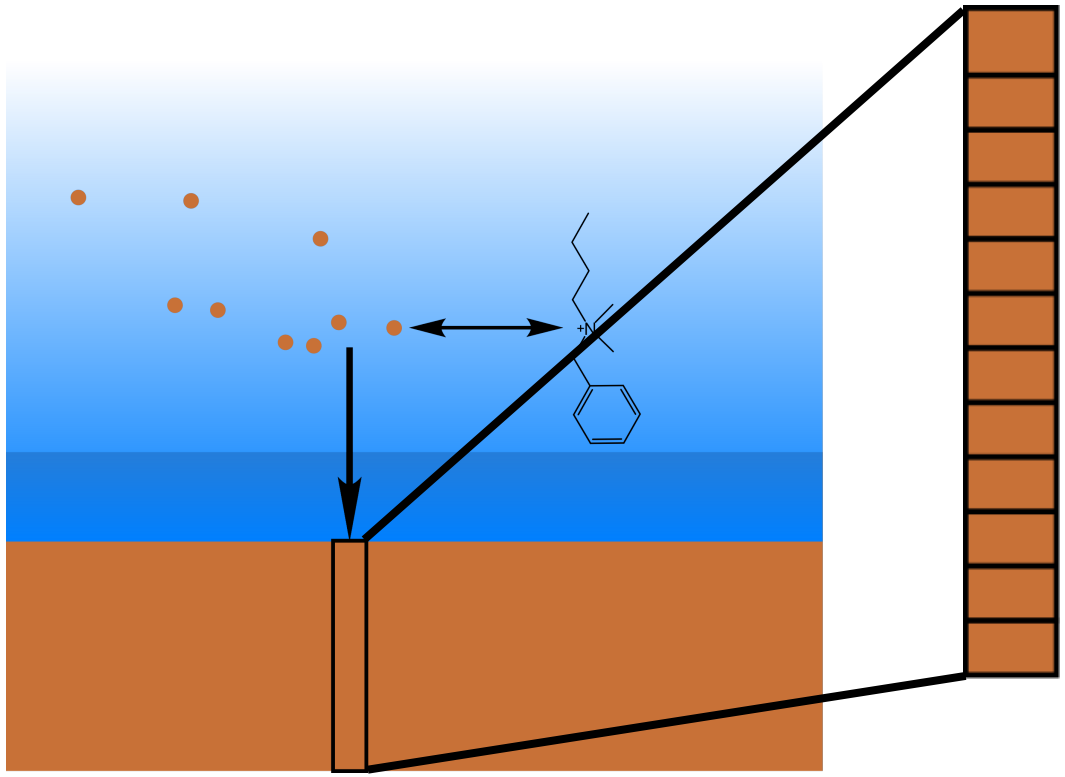
10 mL extract
+ 100 mL buffer
(citrate, pH≈5.5)

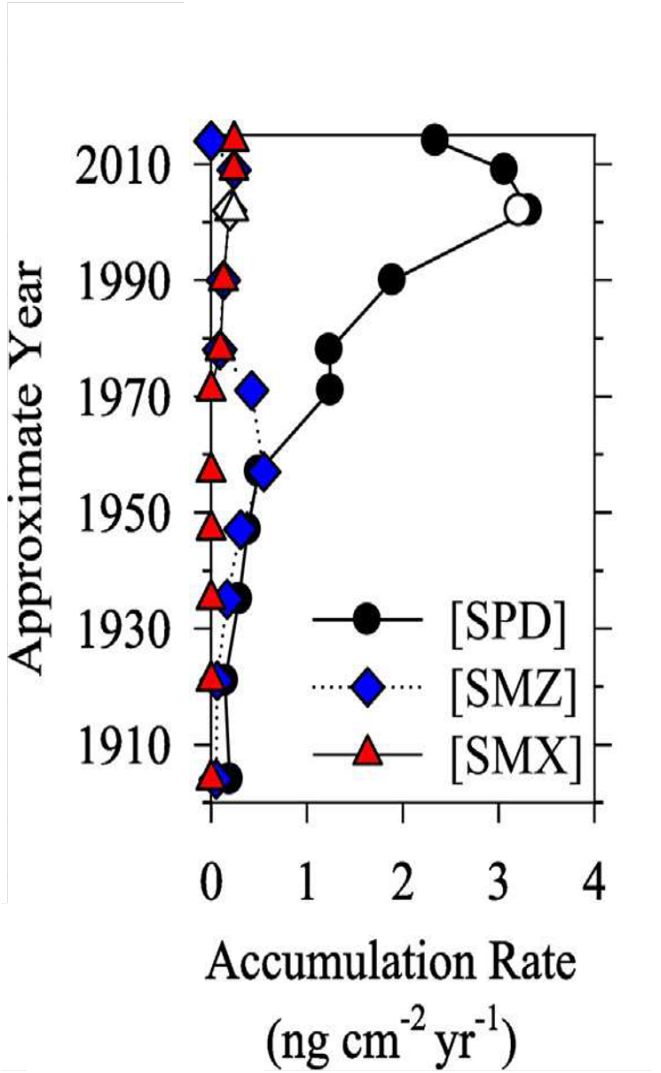
6 mL extract
(2% FA in ACN)

dry extract

1 mL ACN
+ ISTD-Mix

Sediments as archives of chemical pollution



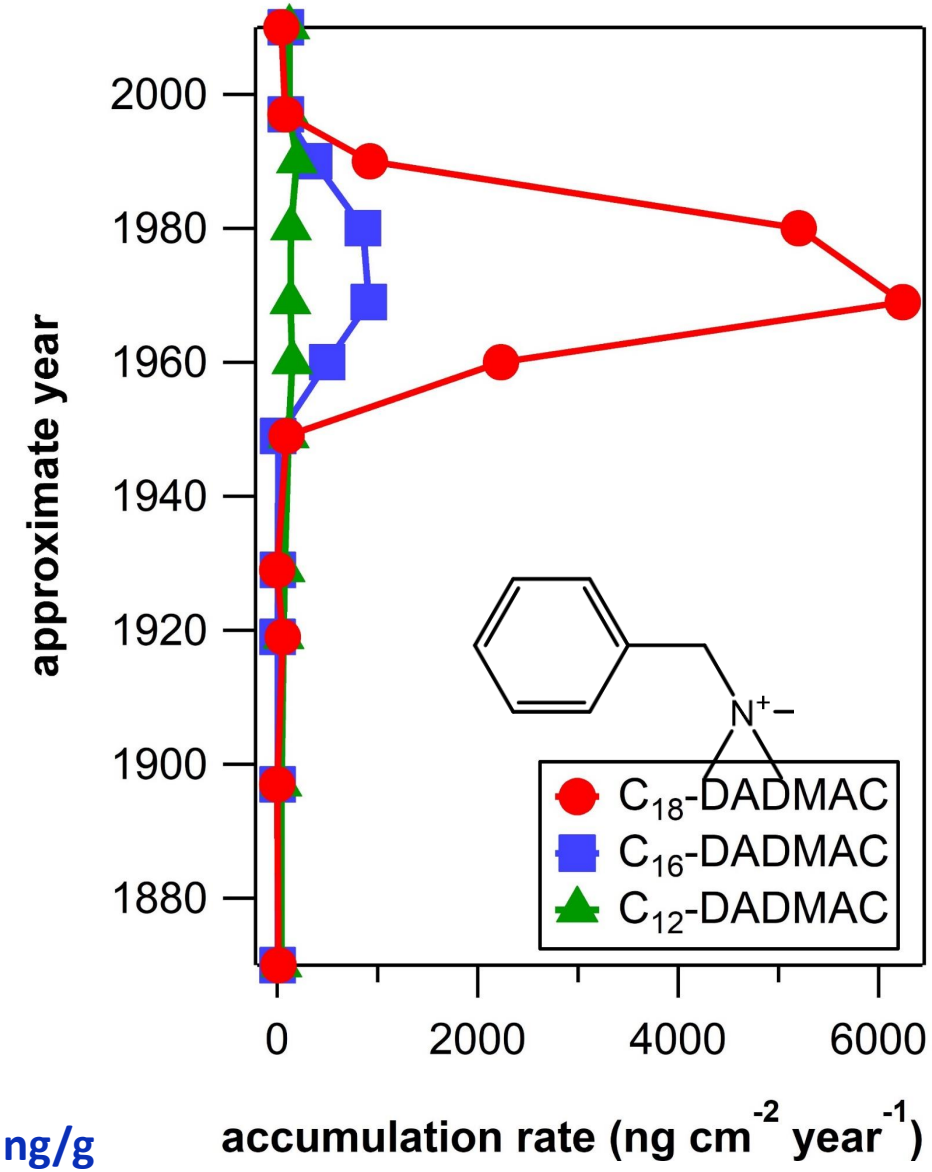


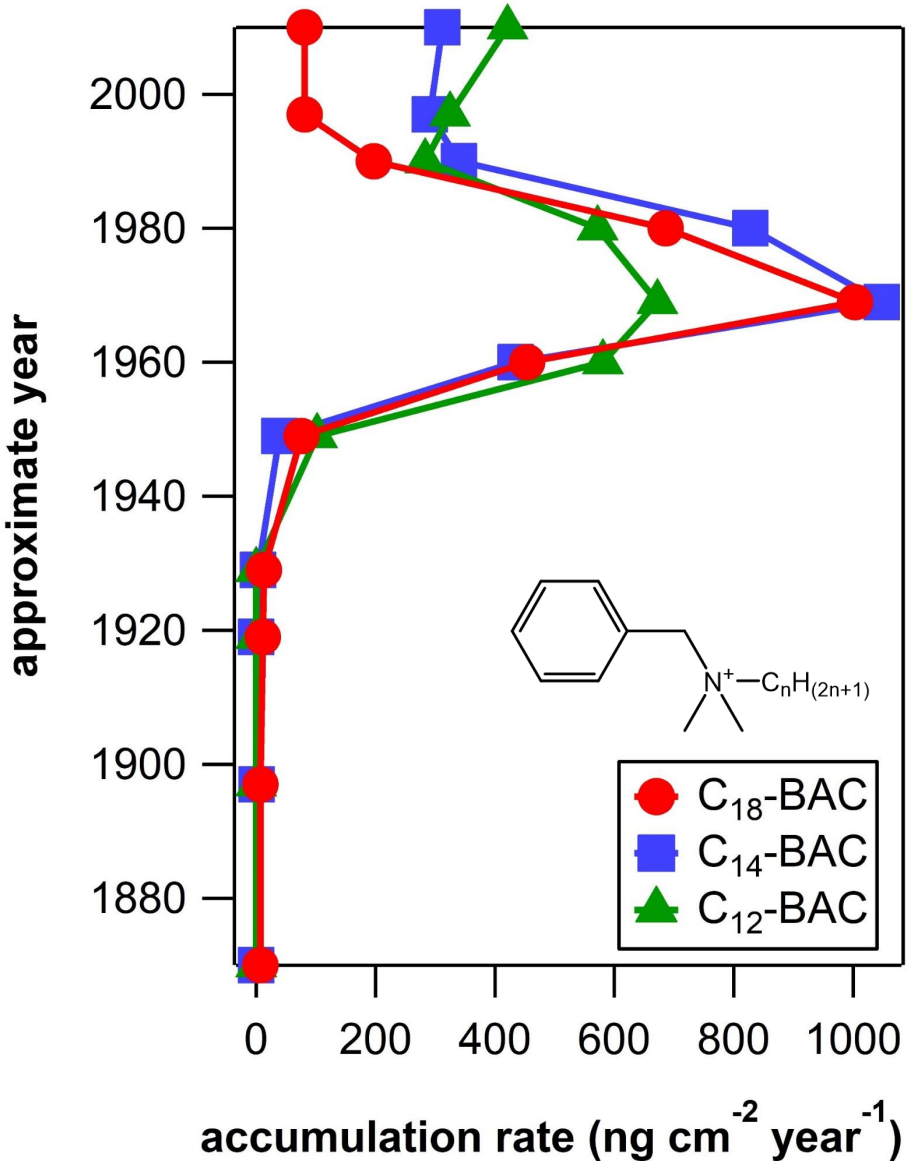
SPD = sulfapyridine
SMZ = sulfamethazine
SMX = sulfamethoxazole

Kerrigan et al., *Sci. Total Environ.* **2018** 970-979

Lake Pepin

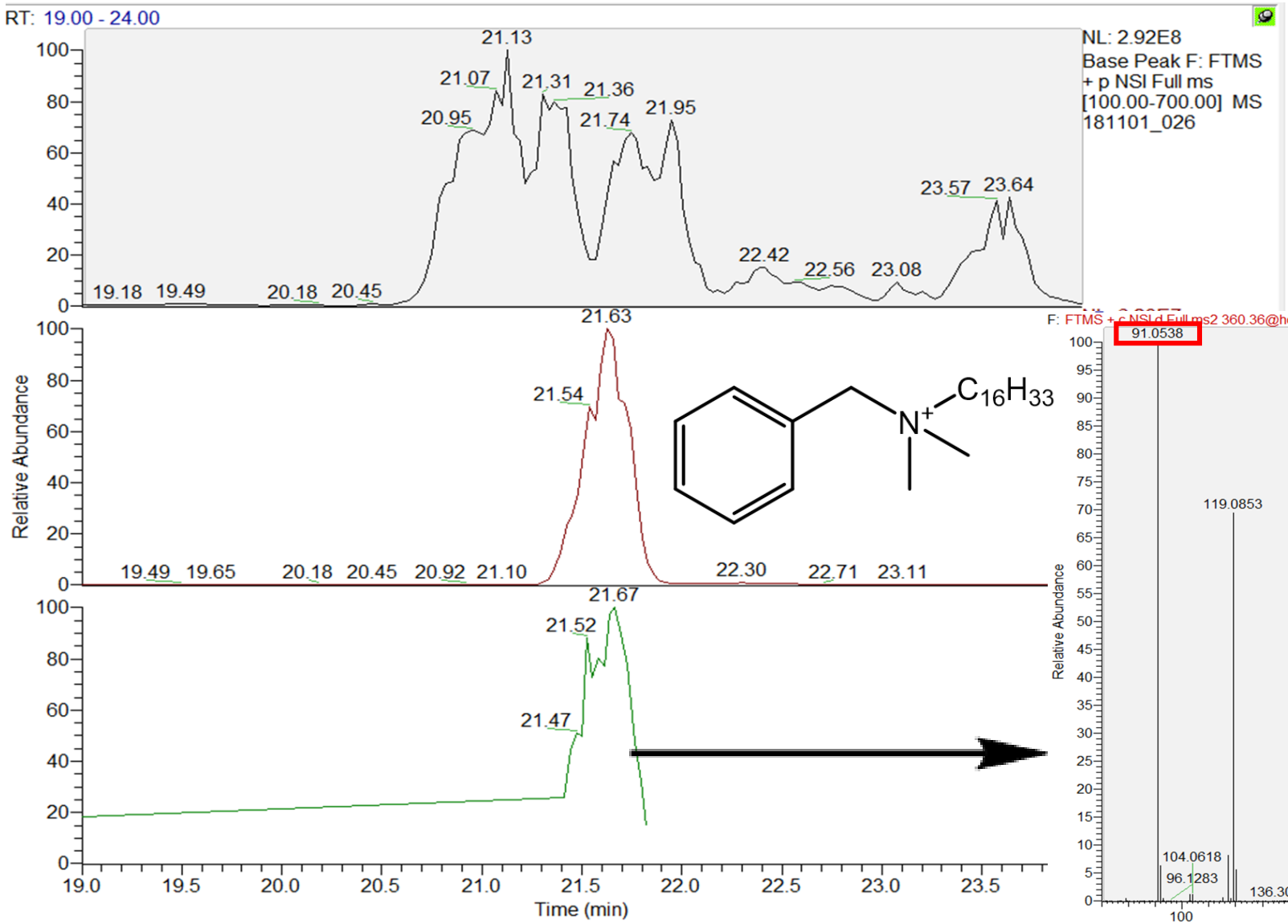
Pati and Arnold, 2020, *ESPI,* 22, 430.
http://dx.doi.org/10.1039/C9EM00554D

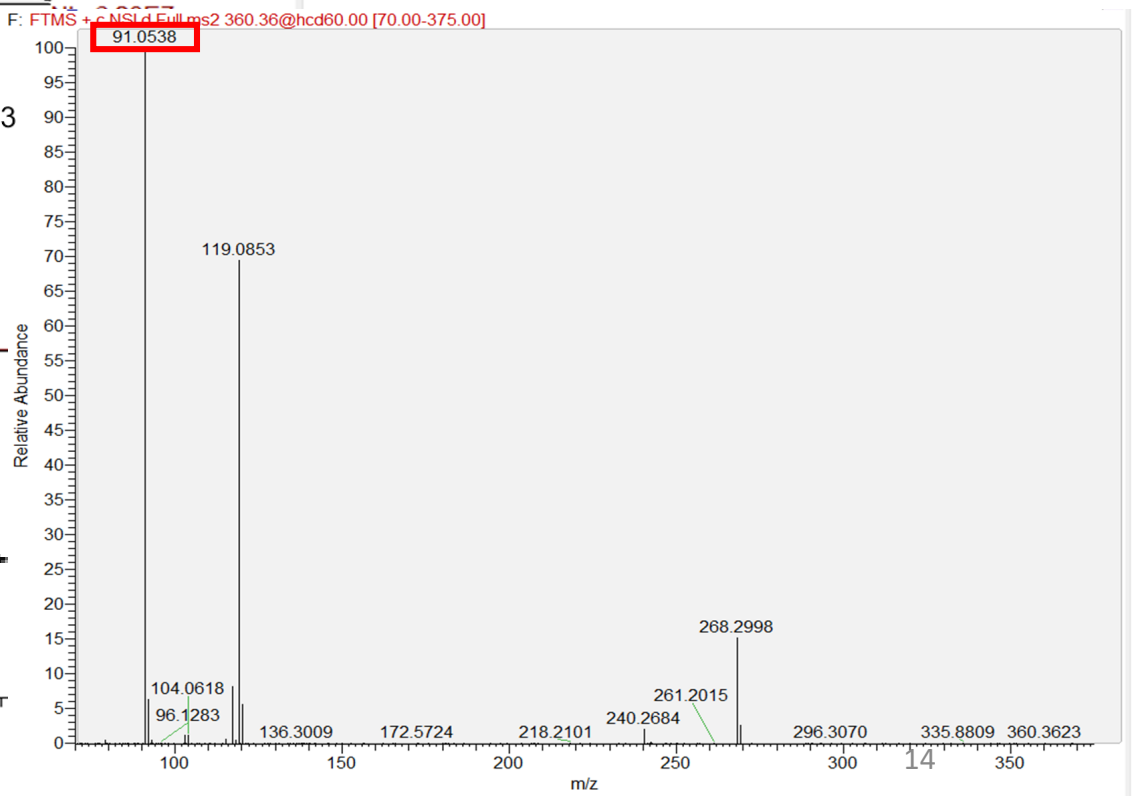




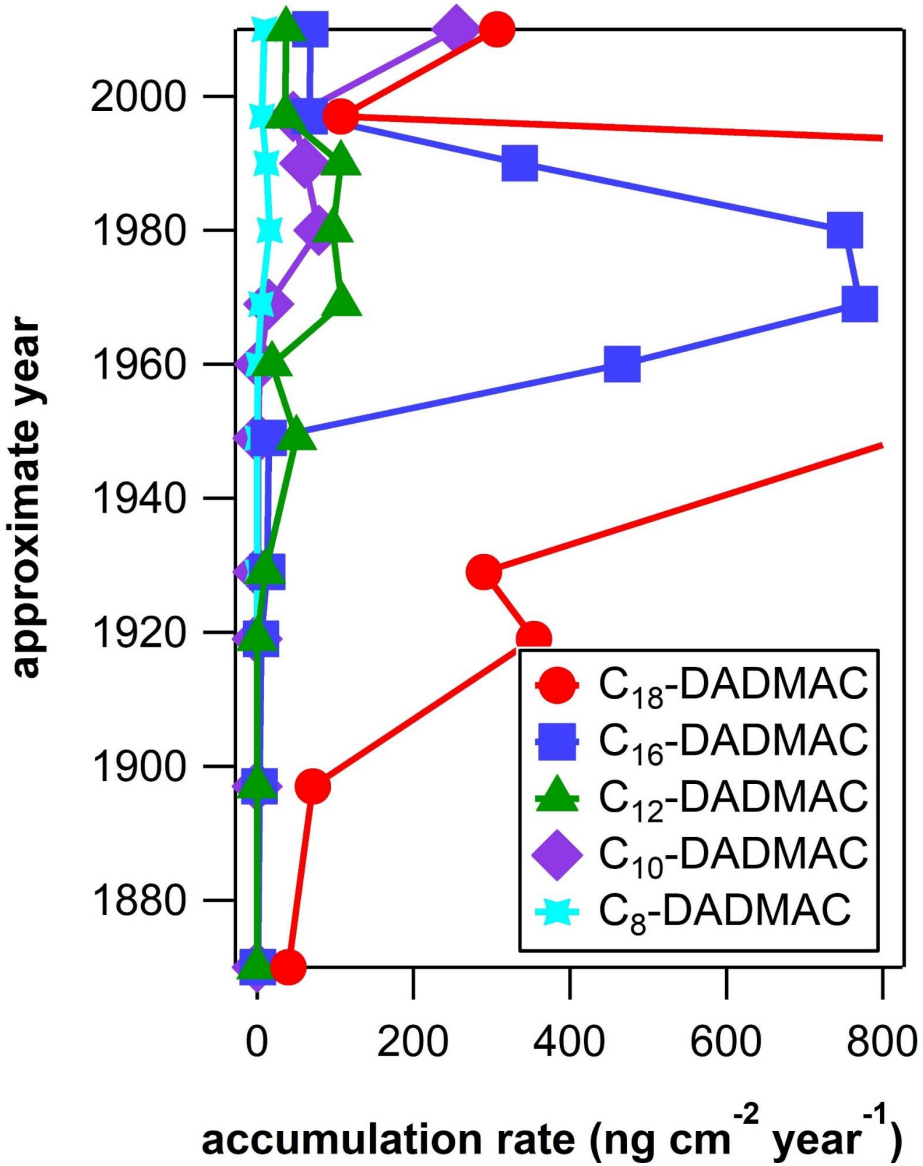
10s-1000s ng/g

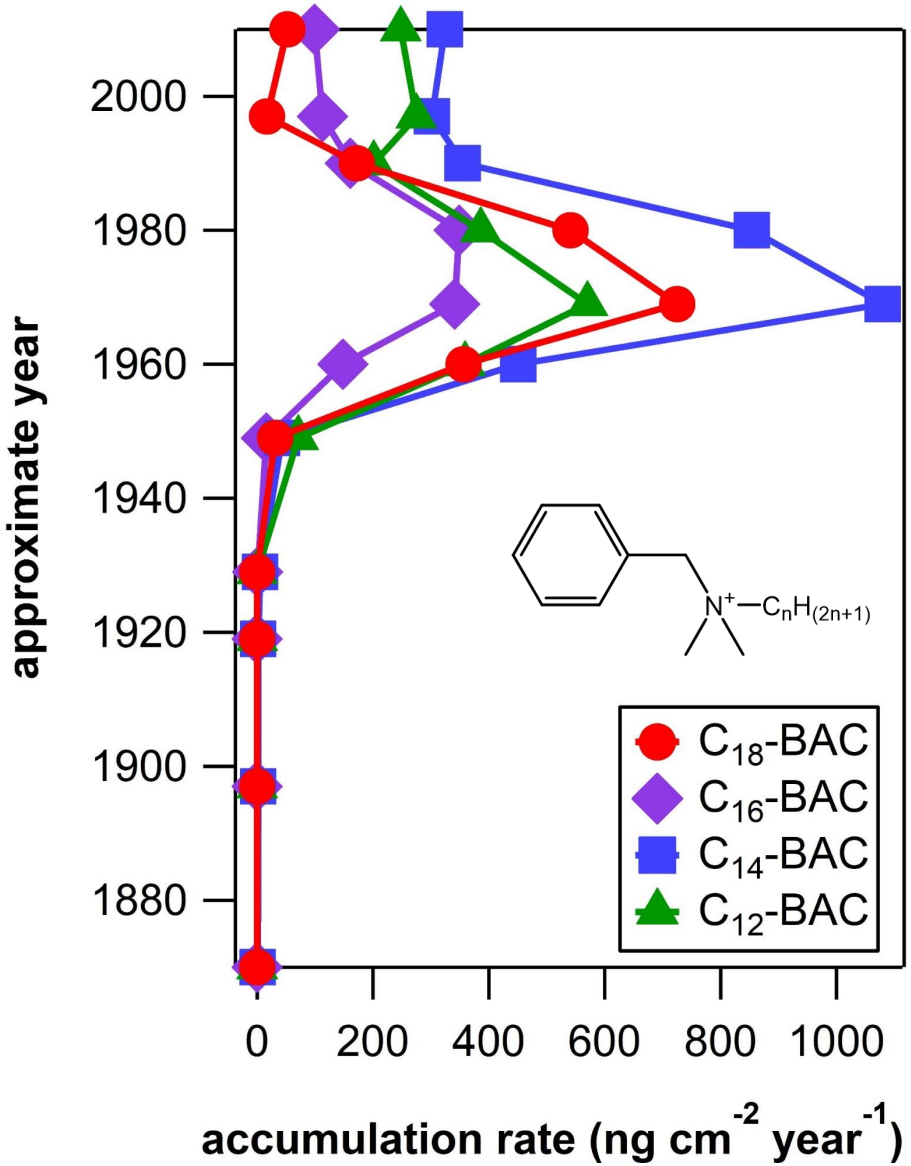
Suspect screening: Lake Pepin





Lake Pepin: Target & suspect screening

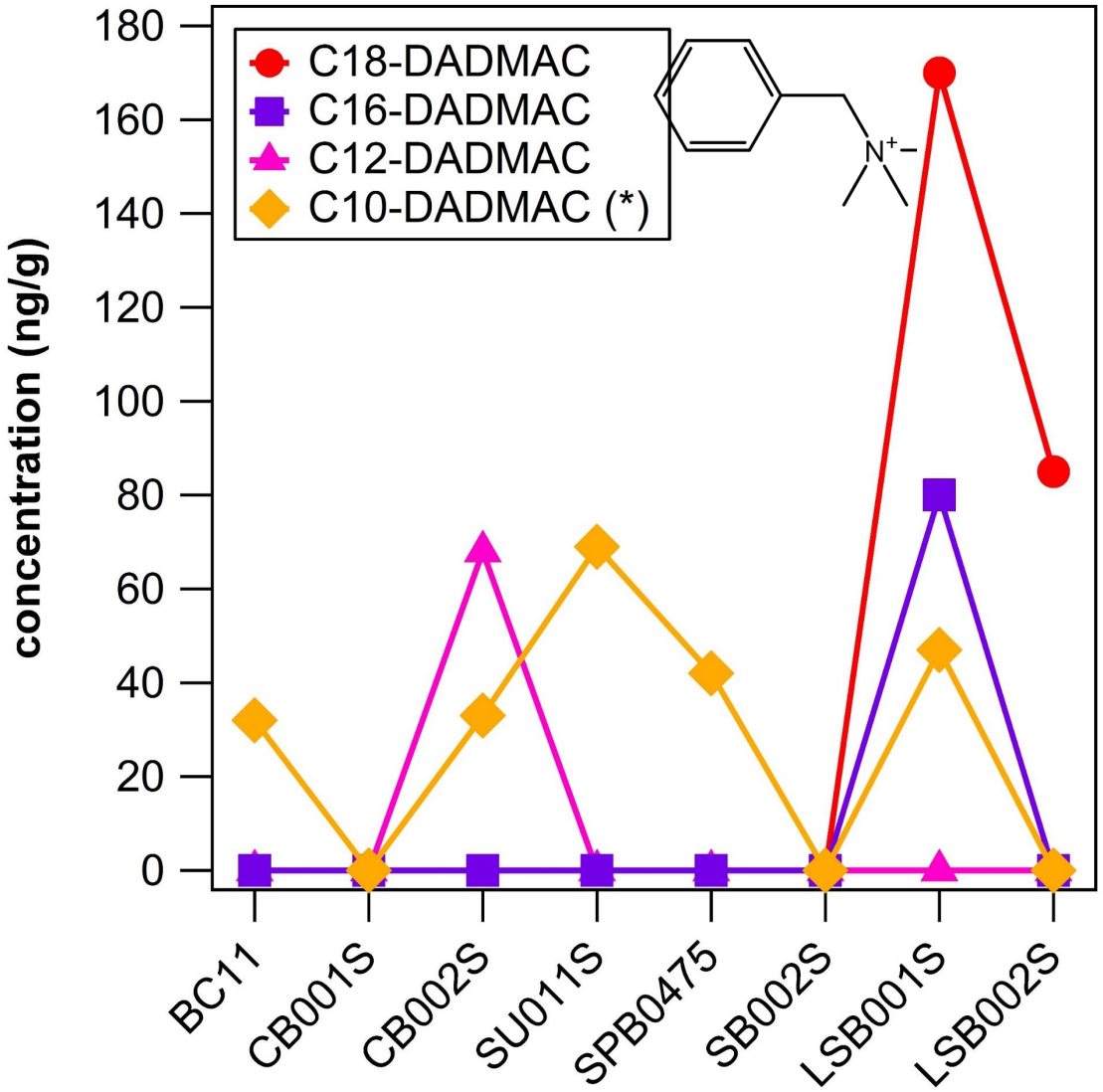


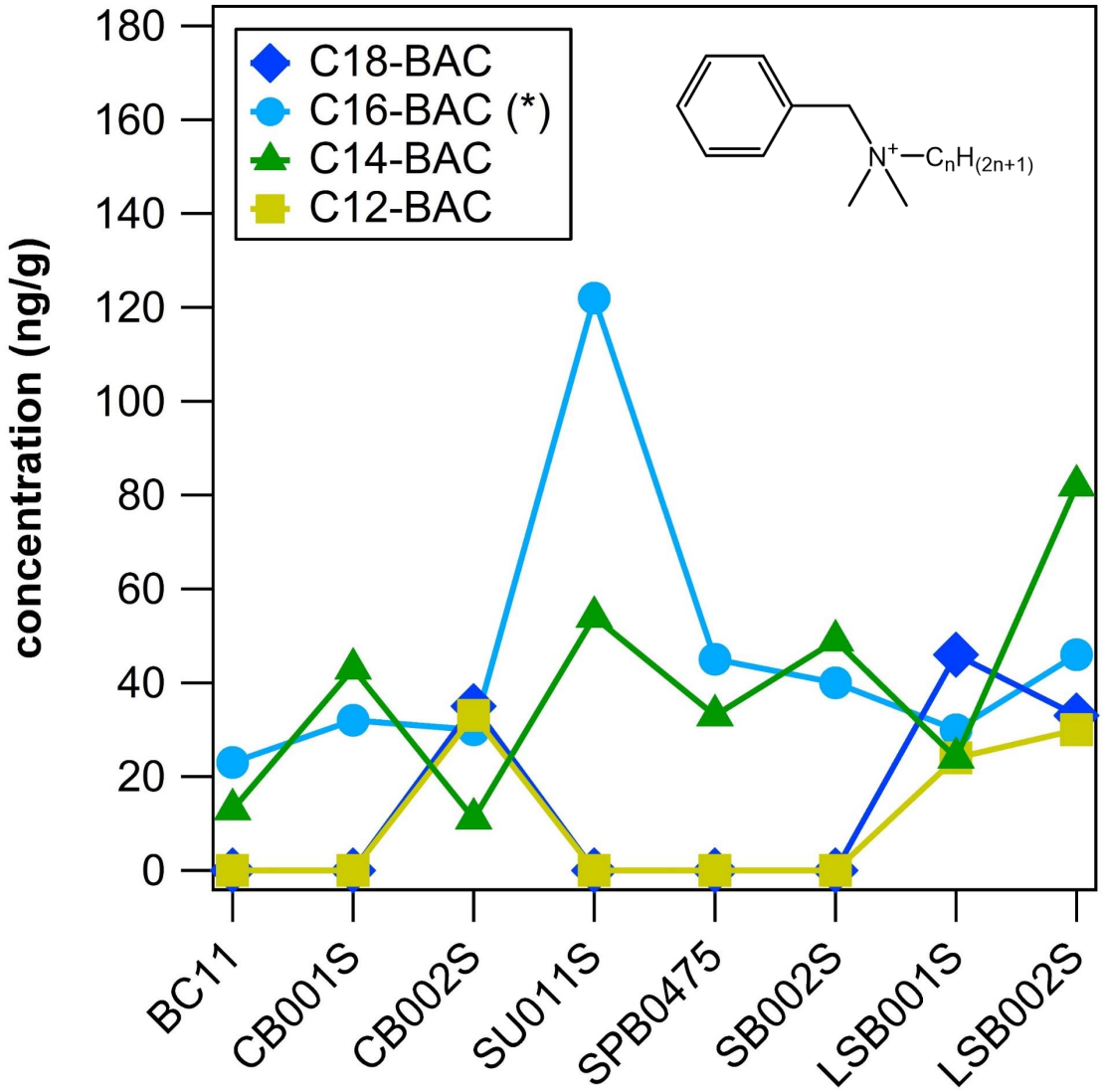


Sampling Sites

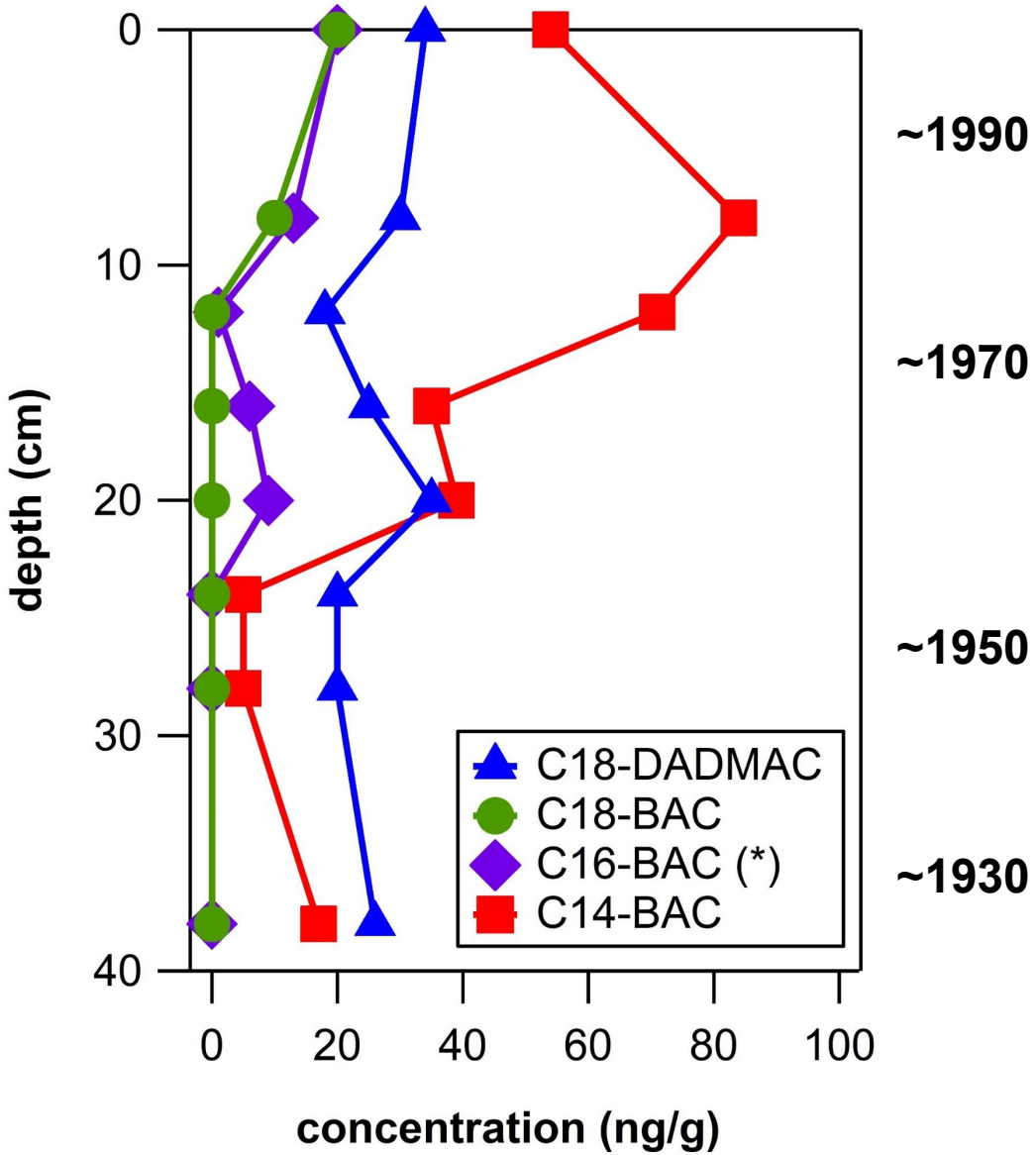
(*) indicates suspect screening results
Lines are only to guide the eye

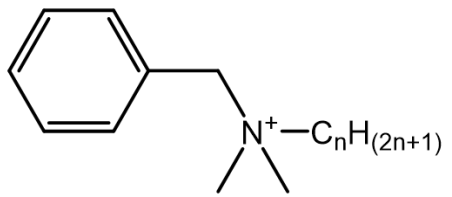
San Francisco surface sediments

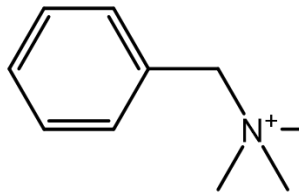




San Francisco sediment core (CB001S)



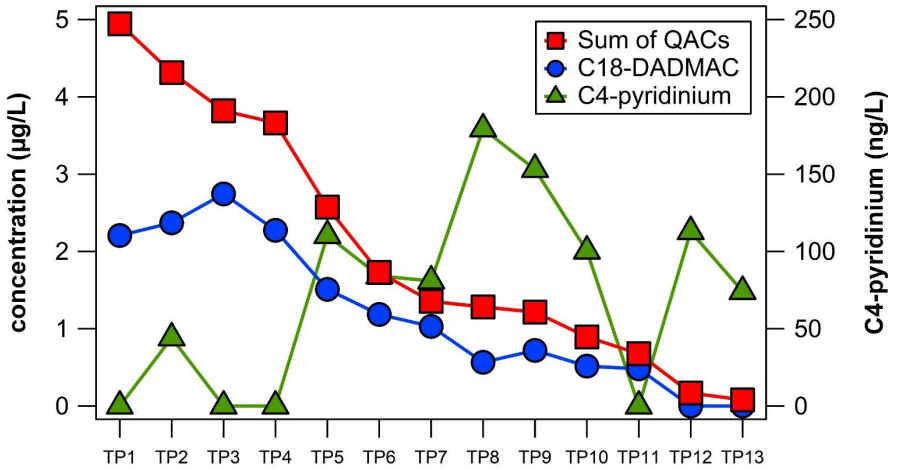


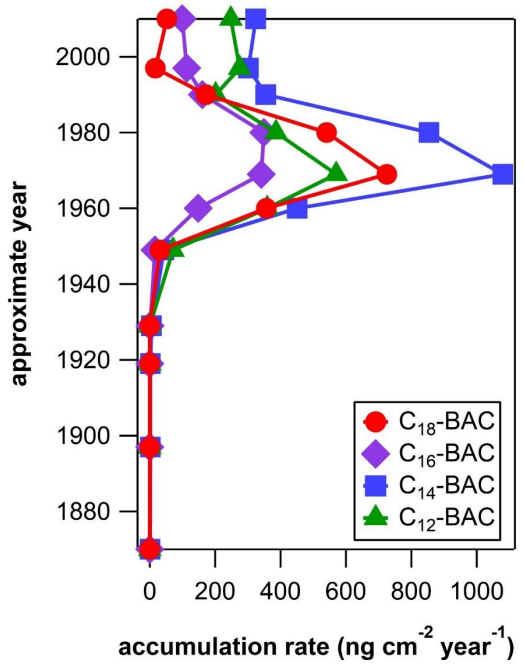


(*) indicates suspect screening results

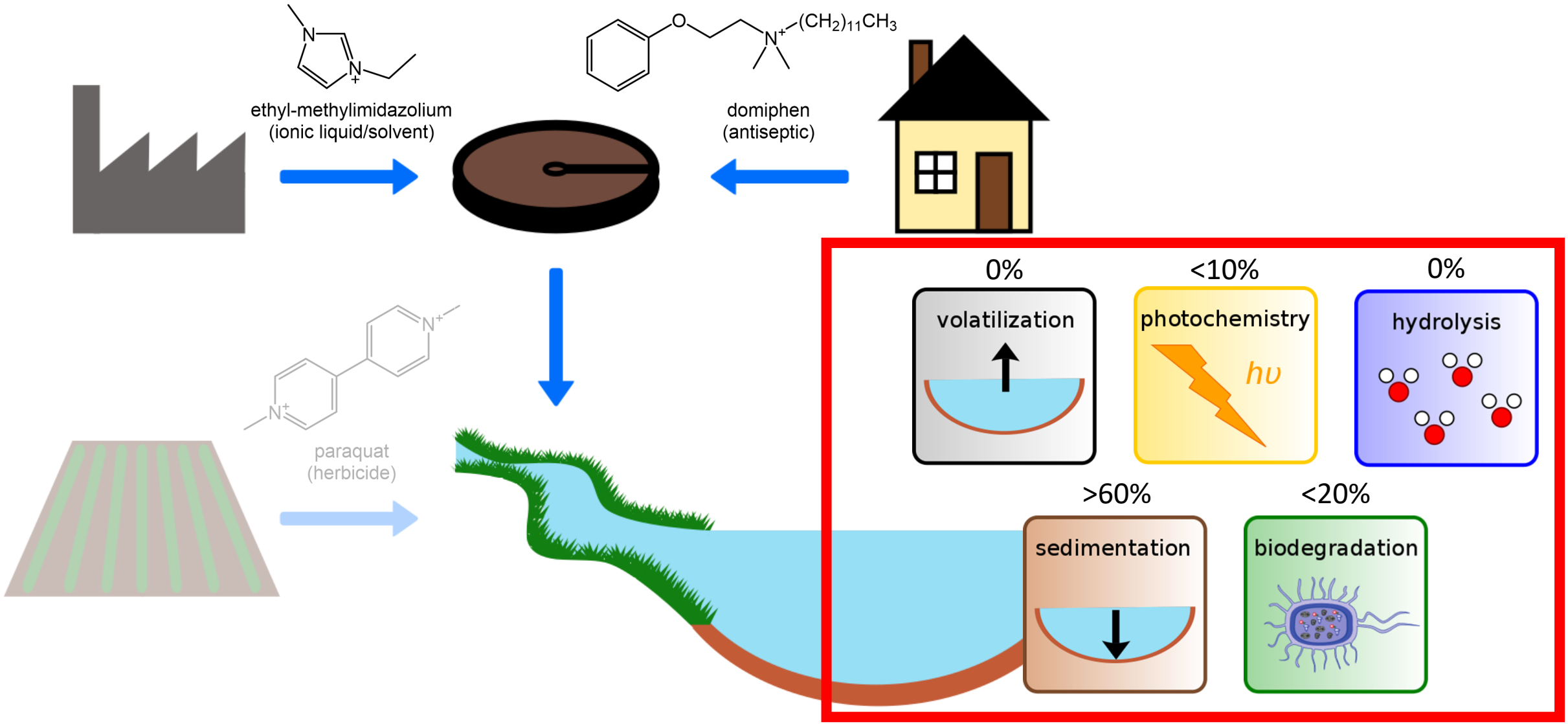
Field Work Summary

- QACs are detected in wastewater effluents and sediments in µg-range
- DADMAC and BAC are most frequent and highest levels
- What happens in-between?



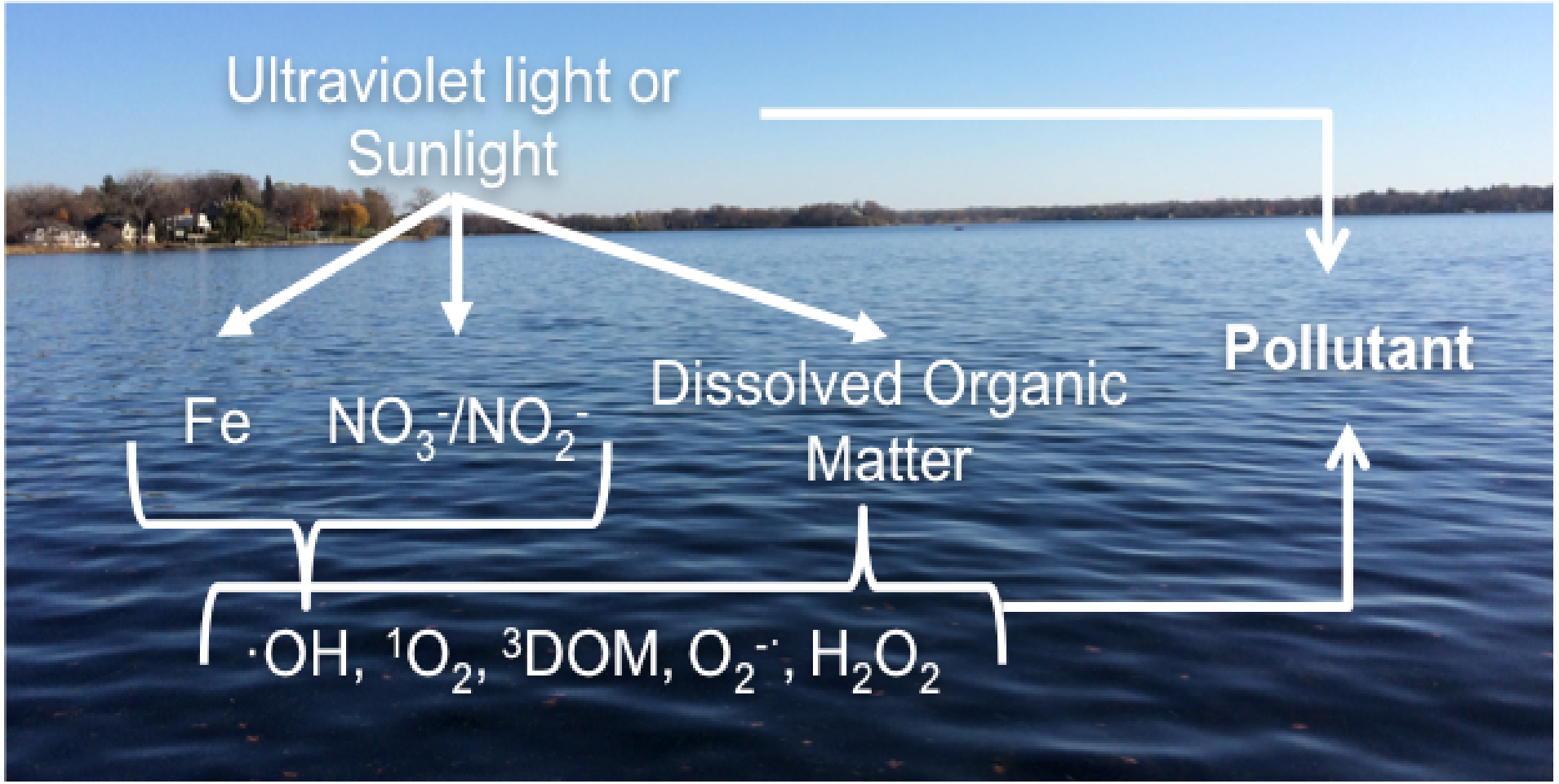


Input and fate of QACs in aquatic environments

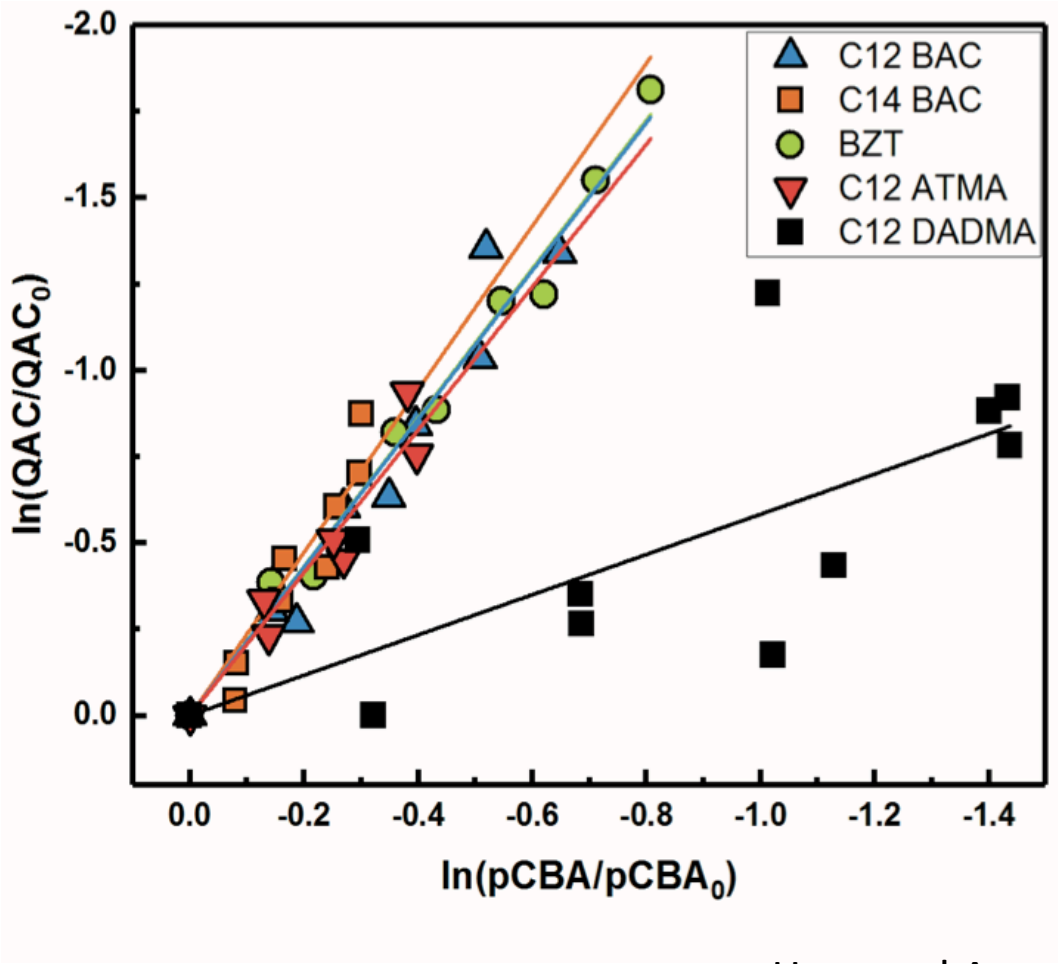


Tezel and Pavlostathis, In *Antimicrobial Resistance in the Environment.* **2012** 349

Photolysis


Ultraviolet light or
Sunlight
Fe
NO_3^-/NO_2^-
Dissolved Organic
Matter
Pollutant
$\cdot OH$, $^1O_2$, ^3DOM, $O_2^{-\cdot}$, H_2O_2

Competition kinetics



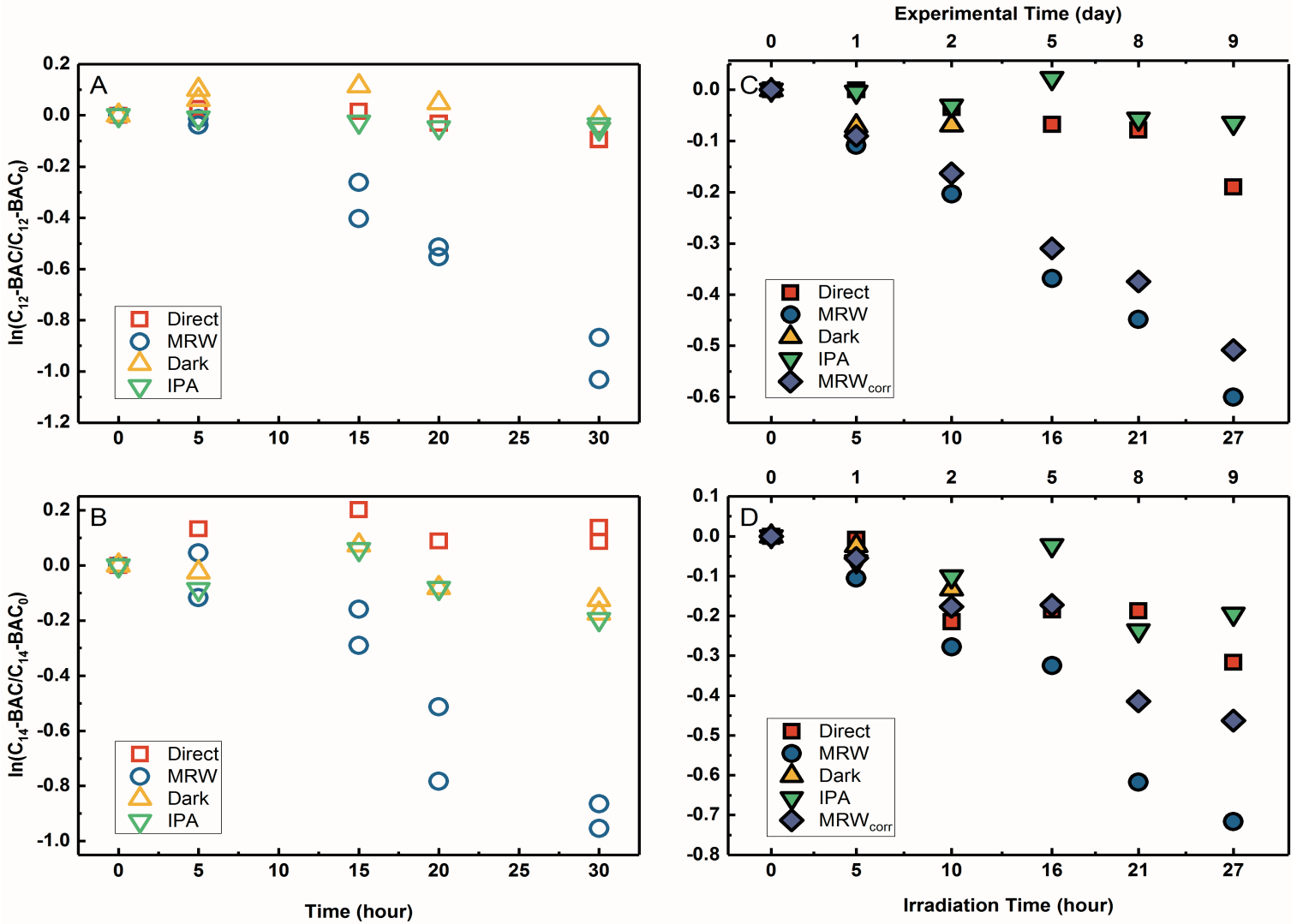
- UV/H_2O_2 to generate •OH
- p-chlorobenzoic acid (pCBA) as reference
- $k_{•OH} \sim 10^{10}\ M^{-1}\ s^{-1}$
- Limited reaction via
  - Direct photolysis
  - $^1O_2$
  - $^3DOM^*$

Hora and Arnold, 2020, *ESPI,* 22, 1368.
http://dx.doi.org/10.1039/D0EM00086H

- Results demonstrate •**OH** drives photochemical loss

- Near surface $t_{½}$ ~3 weeks

Simulated sunlight Sunlight



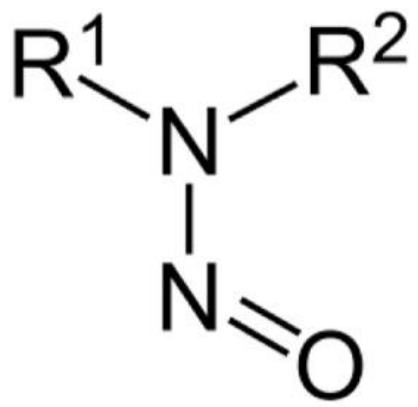
Biodegradation in river water

- Filtered river water, quadruplicate
- Environmentally relevant concentrations
- Monitor QACs (LC-MS/MS), microbial community
  - Degradation occurs over 3-7 days
  - Faster with repeated dosing
  - Taxonomic shifts, decreased richness/evenness
  - No increase in antibiotic resistance genes

Priya Hora, Ph.D. Thesis.

Formation of Nitrosamines

- QACs + chloramines under uniform formation conditions
  - Standards
  - Purified standards (SPE)
  - Commercial products
  - Purified commercial products (SPE)
- Total nitrosamine analysis by William Mitch Lab (Stanford)

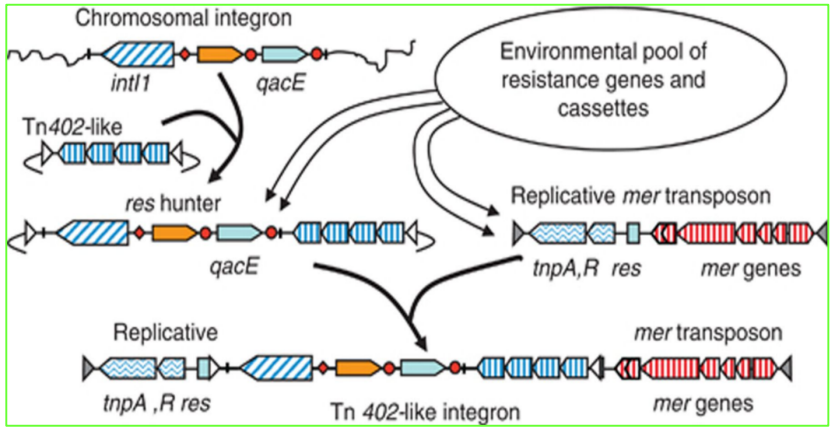


Total Nitrosamine Yield: 0.003 to 0.03% (BACs highest)

Future Work

- QACs in WW during COVID-19 (MN and SF area)
- Storm water QACs – SF
- Spatial sampling + modeling

- Potential issues
  - WWTP operation disruption
    - Activated sludge
    - Anaerobic digestion
  - Aquatic tox?
  - Resistance?
  - Nitrosamines?
  - Improved treatment?



FEMS Microbiology Reviews, Volume 35, Issue 5, 01 September 2011, Pages 790–819, https://doi.org/10.1111/j.1574-6976.2011.00273.x