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Climate Change Canada

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Air Monitoring in the Canadian Arctic and Great Lakes Regions

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Environment and Climate Change Canada

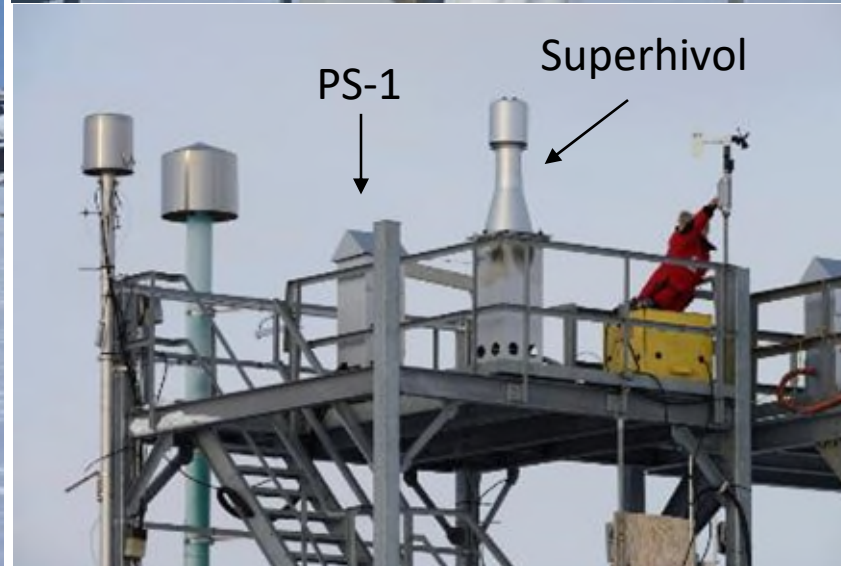
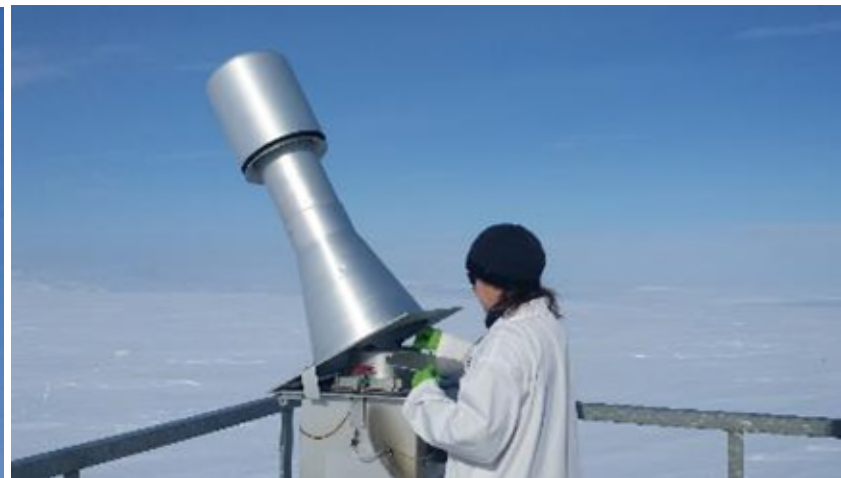


Canada

OUTLINE

- Introduction of the Canadian Arctic and Great Lakes Air Monitoring Programs
 - Experience and challenges for CECs measurements
 - PFAS
 - Novel FRs
 - Breakthrough of volatile chemicals
 - Brake and tire wear chemicals
 - Atmospheric transformation products
 - Non-target analysis
-

NCP/AMAP Canadian Master Station Alert, Nunavut, Canada (82.4 °N, 62.3 °W)



Great Lakes Basin (GLB) Monitoring & Surveillance Program

- Canada/US Great Lakes Water Quality Agreement (GLWQA) ➤ Air and precipitation monitoring for POPs started in late 80s.



- Collab. with the US Integrated Atmospheric Deposition Network (IADN)

- Chemicals of Mutual Concern (CMC) – GLWQA Annex 3

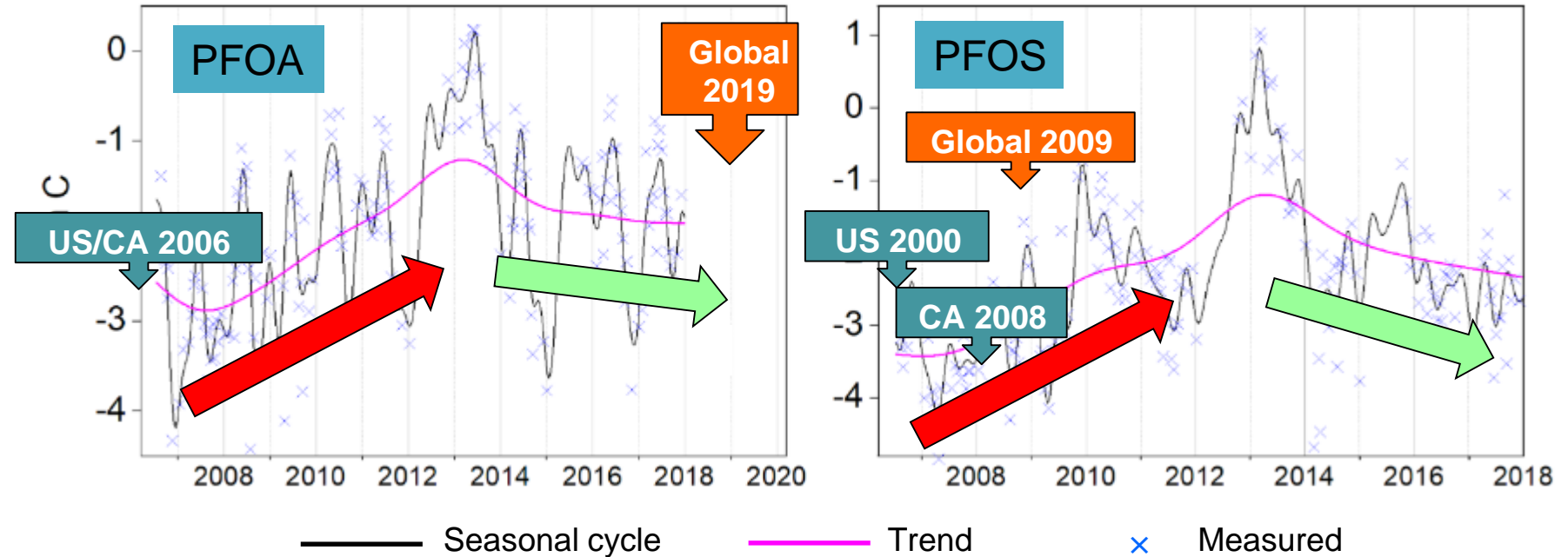
- PCB ✓
 - PBDE ✓
 - PFOS ✓
 - PFOA ✓
 - LC-PFCAs ✓
 - Mercury ✓
 - HBCDD ✓
 - SCCP (screening) ✓
- Oct 2018 (Point Petre)
May 2019 (Evansville)

- Additional CECs:
Other PFAS and precursors; OPEs;
OCPs

PFAS in Arctic Air



Alert, Nunavut



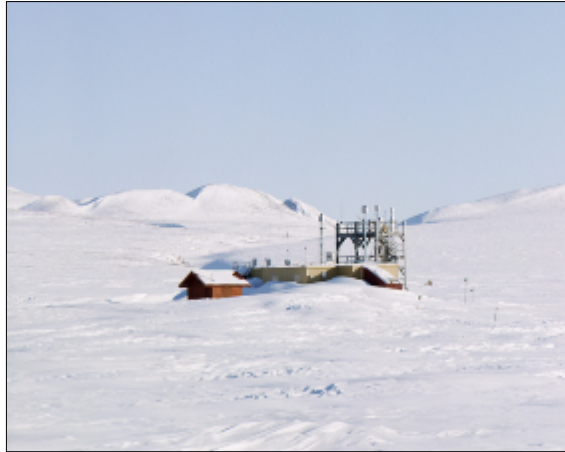
Presence in landfills and in existing products result in lag time for decline.

Wong et al. (2021) Science of the Total Environment 775: 145109



Canada's Proposal to Stockholm Convention

Long-chain (C9-14) PFCAs

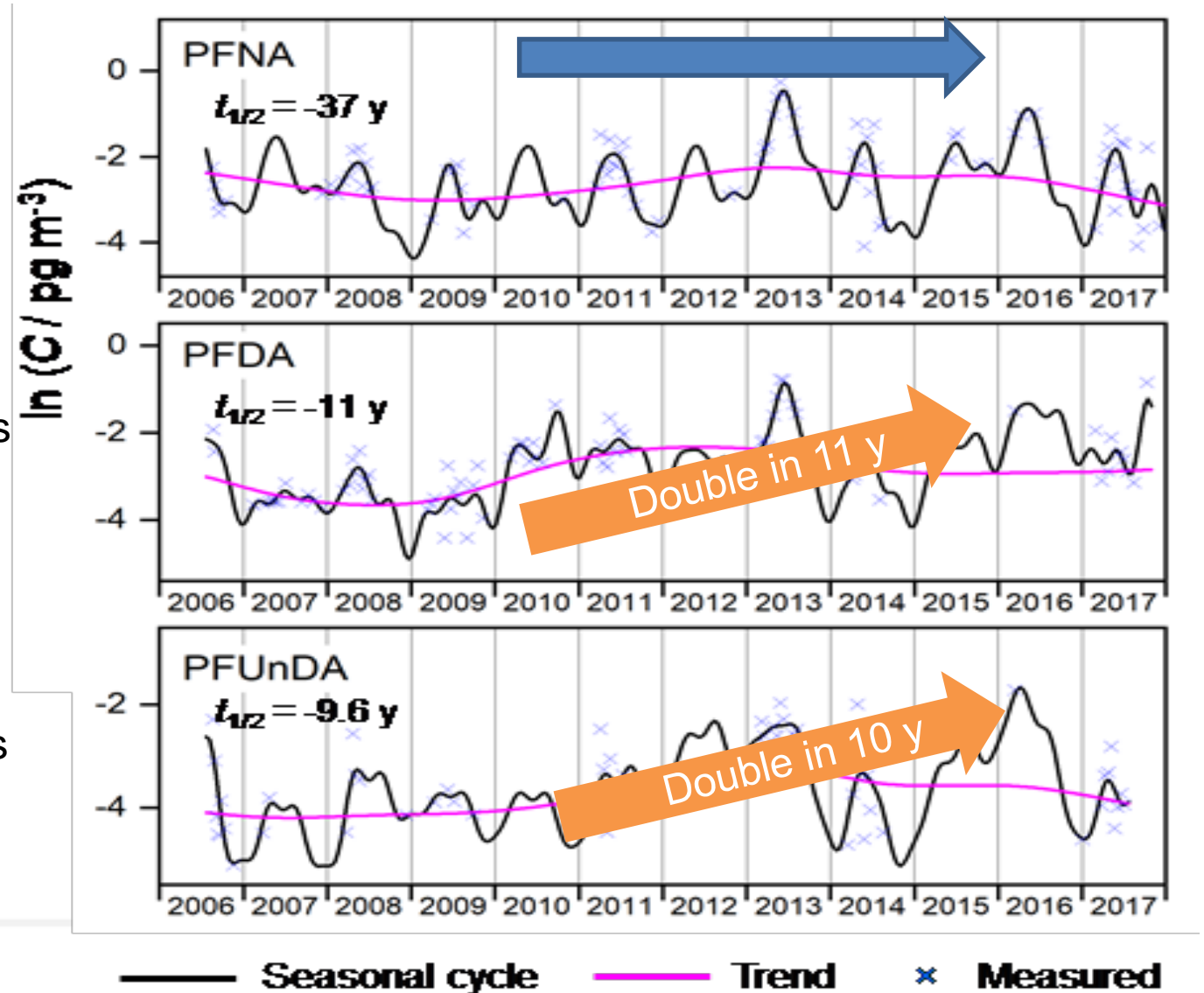


Alert, Nunavut

9 carbons

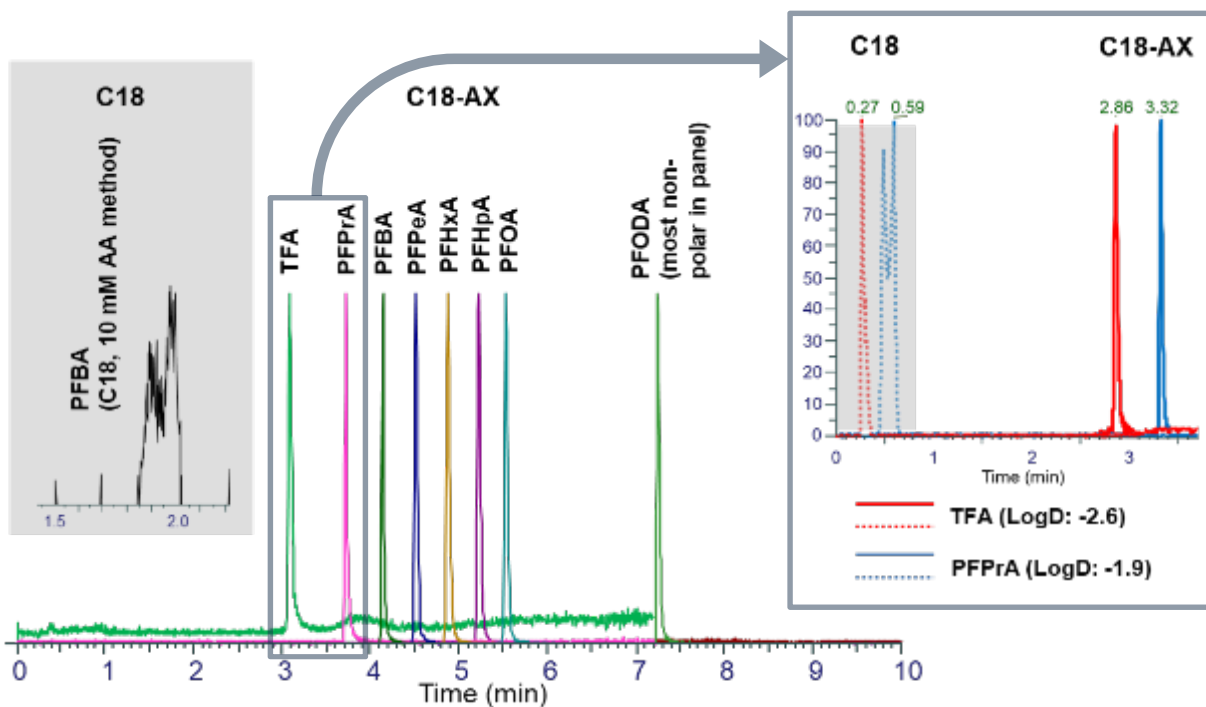
10 carbons

11 carbons



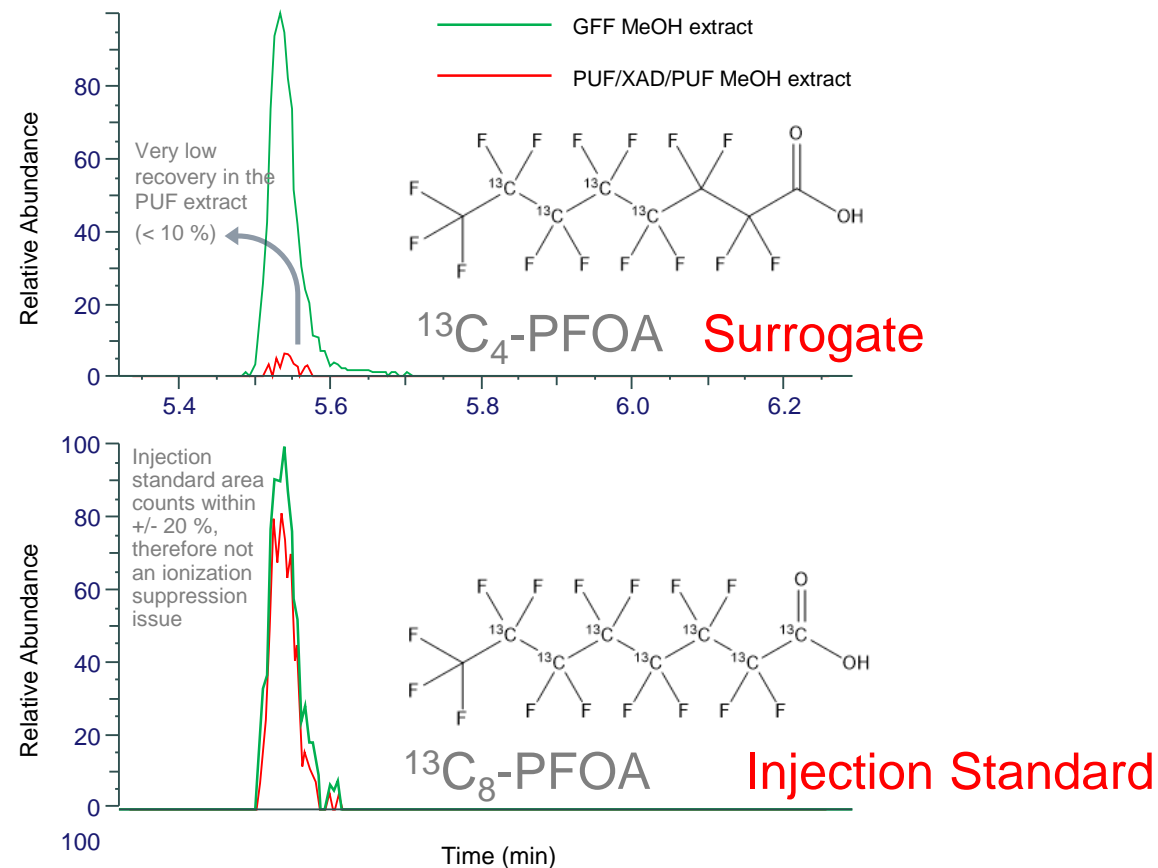
PFAS ANALYSIS DIFFICULTIES

INCORPORATION OF POLAR ANALYTES INTO LCMS METHOD



Improvement of retention of short-chain ionic PFAS (TFA, PFPrA, TFMS, PFPrS, PFBA, PFBS) with a switch of LC column and separation conditions

MATRIX EFFECTS AND RECOVERY



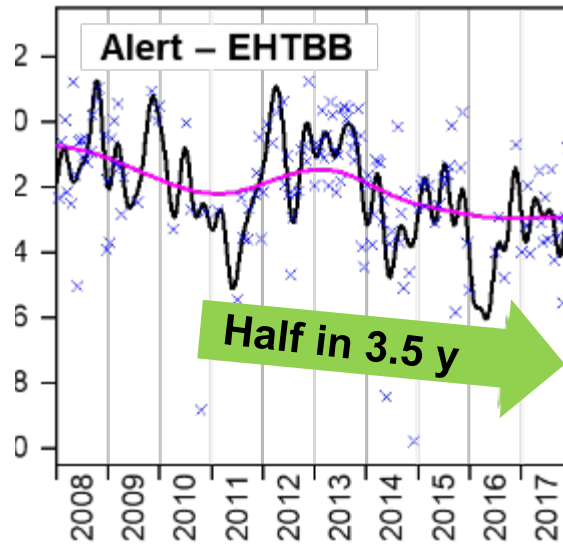
Recovery issues found in select PUF samples, by examining the injection and surrogate standards one can get a hint to if the issue was inappropriate spiking, ionization suppression, or both

Emerging Flame Retardants in Alert Air

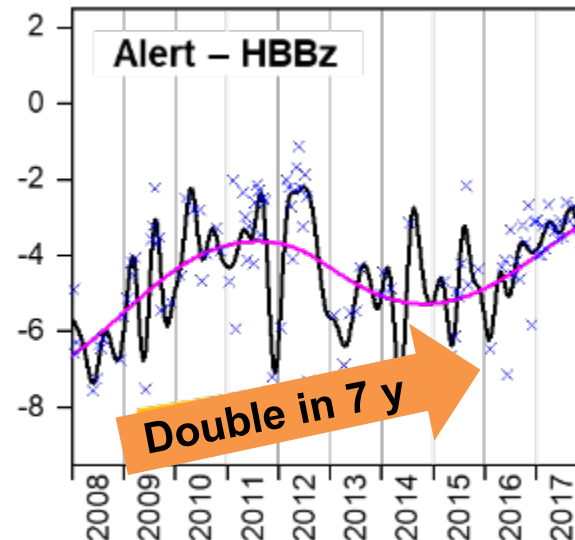


BDE-47

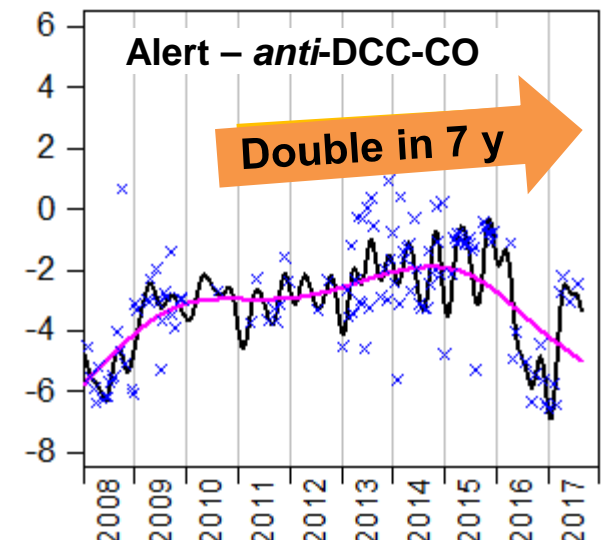
Regulated



EHTBB



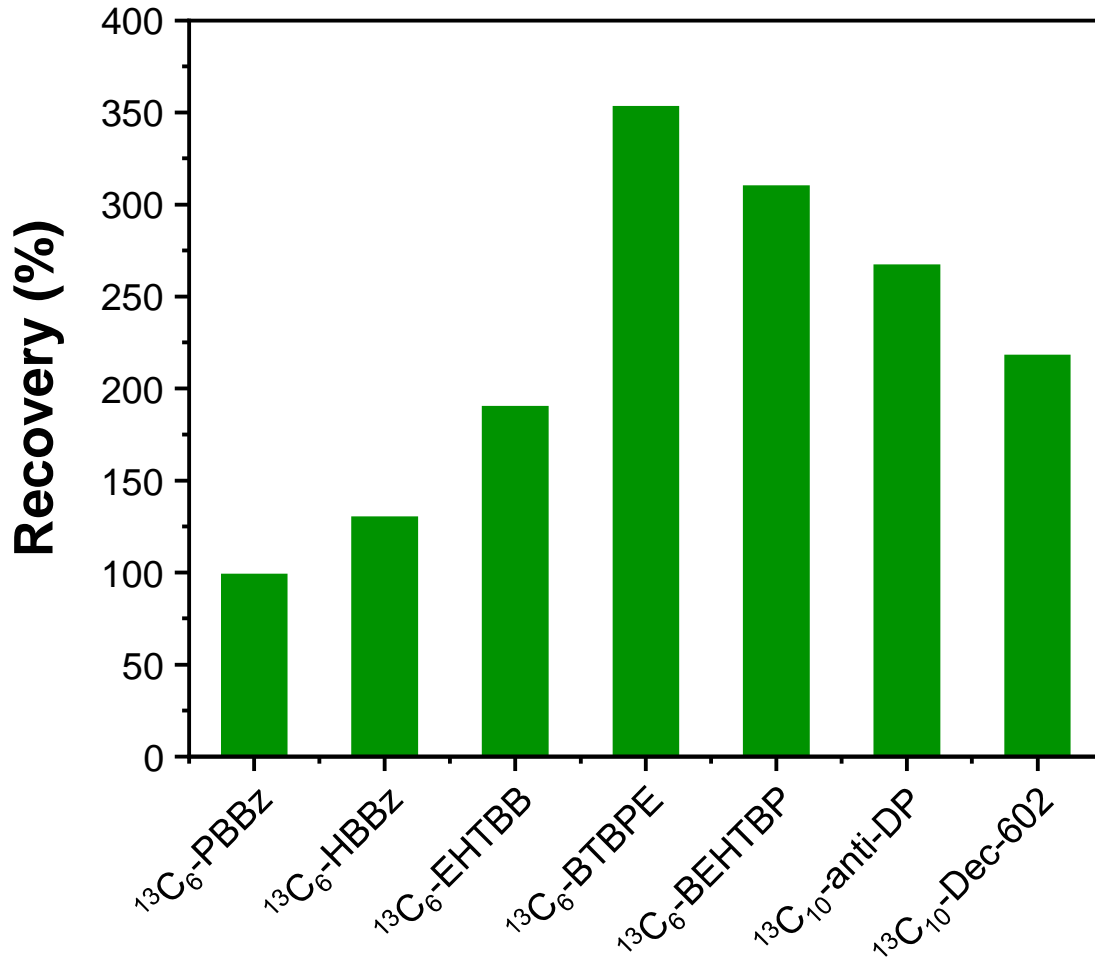
HBBz



Dechlorane Plus

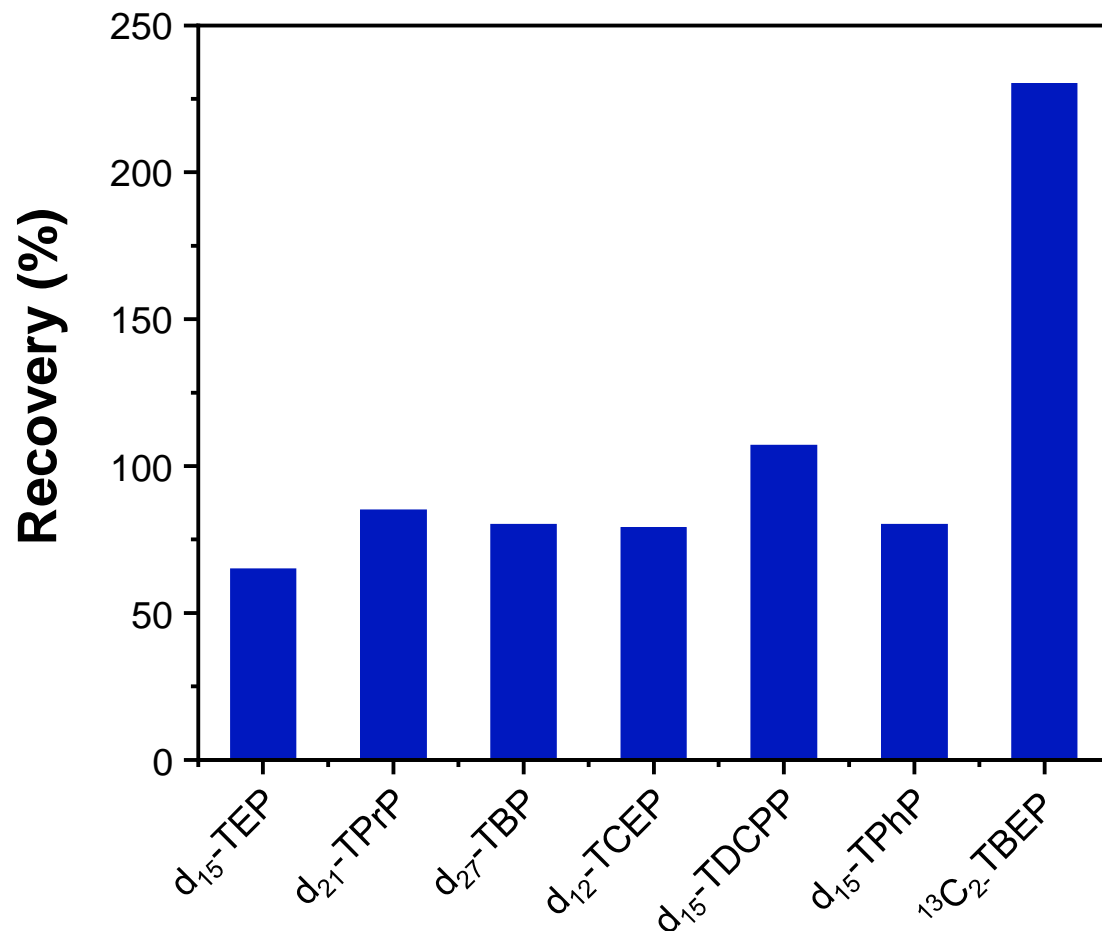
Emerging Flame Retardants

Matrix Effects – Halogenated Flame Retardants in PUF/XAD



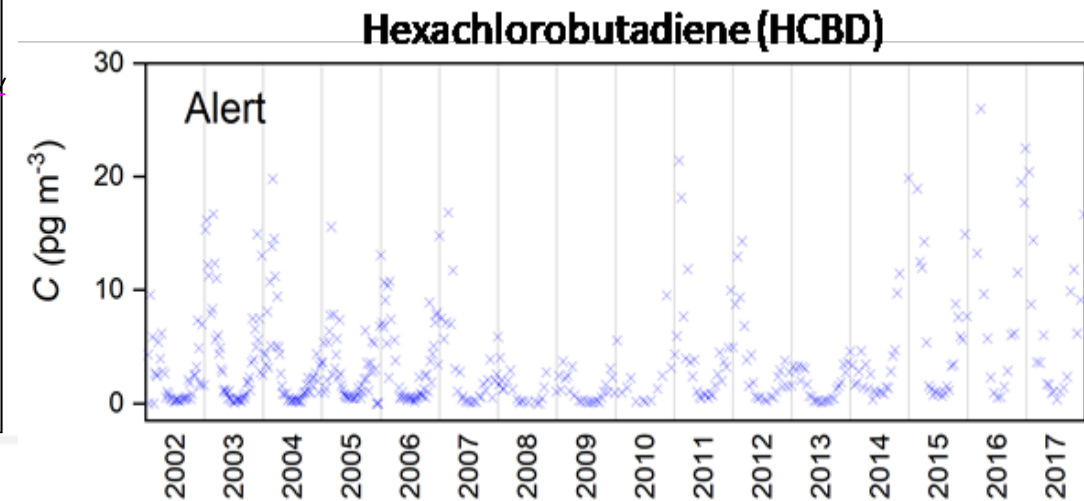
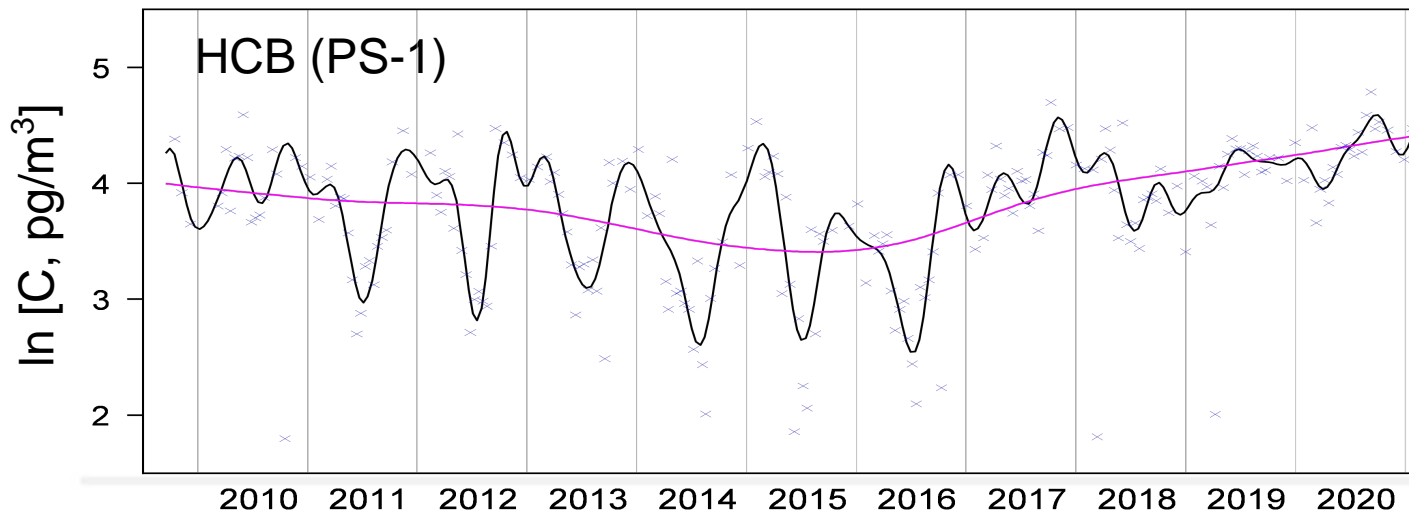
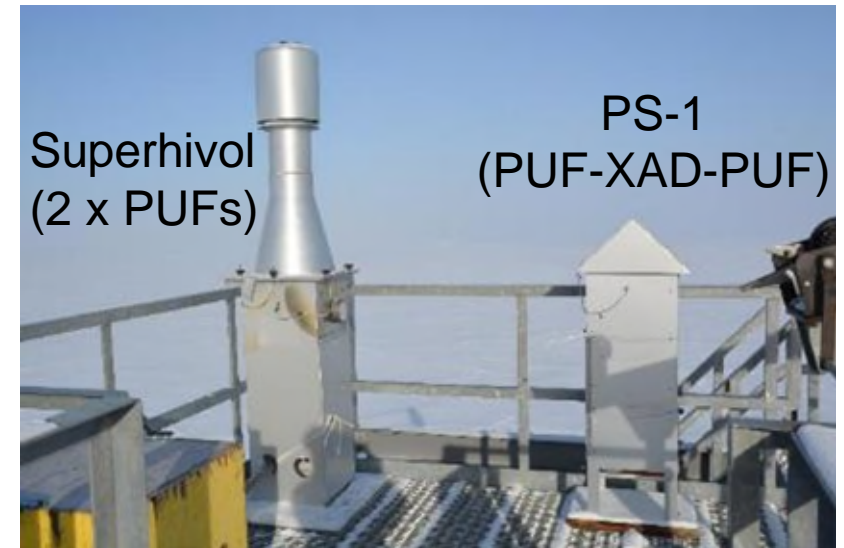
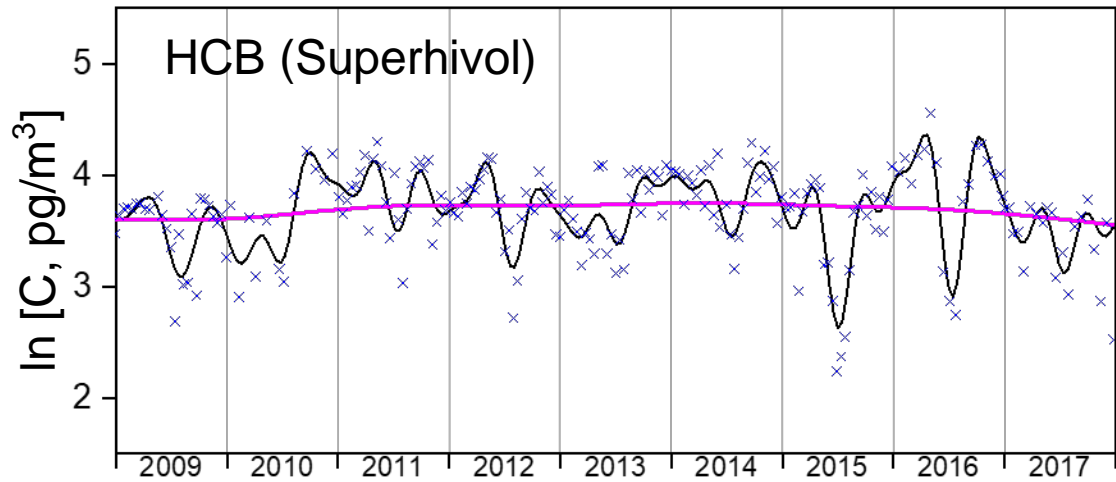
- Recovery results for PBBz and HBBz are 99% and 130%, respectively, indicating reasonable accuracy and precision
- Exceptions were EHTBB, BTBPE, BEHTBP, anti-DP and Dec-602, which showed higher recoveries

Matrix Effects – Organophosphate Esters in PUF/XAD



- Recovery results for TEP, TprP, TBP, TCEP, TDCPP and TphP ranged from 65% and 107%, indicating reasonable accuracy and precision
- Exception was, TBEP, which showed higher recoveries
- During ionization, target compounds and their labeled analogs can be affected by suppression or enhancement effects, which depend on the matrix

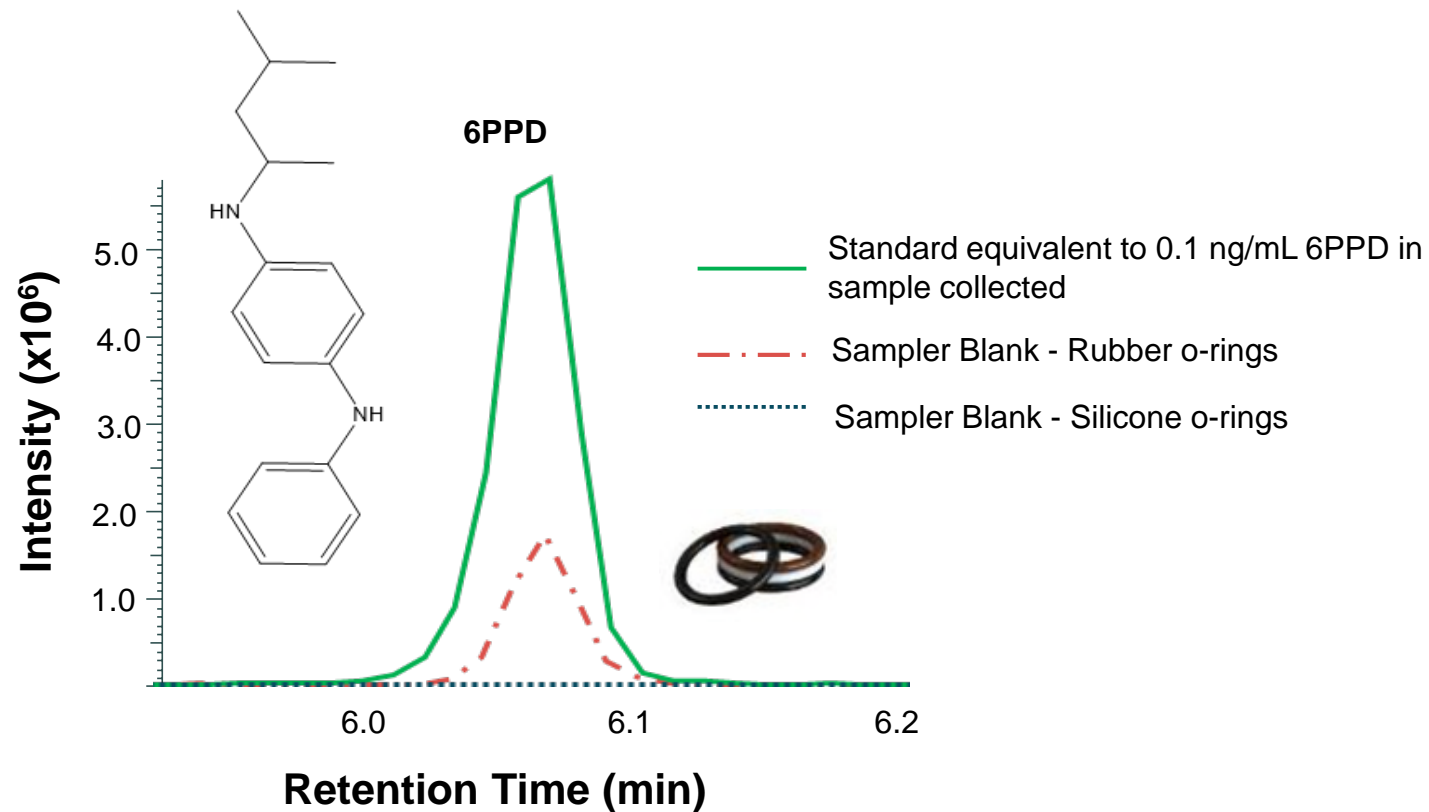
BREAKTHROUGH OF VOLATILE CHEMICALS



Challenges and Concerns Surrounding 6PPD and 6PPDQ

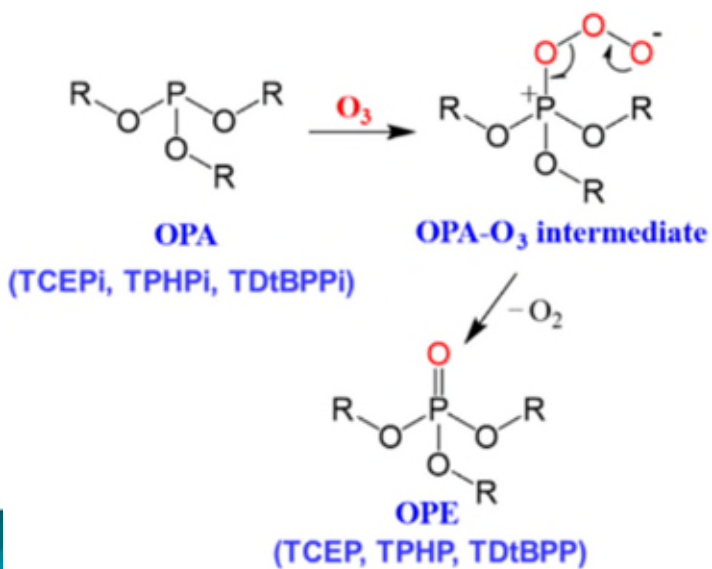
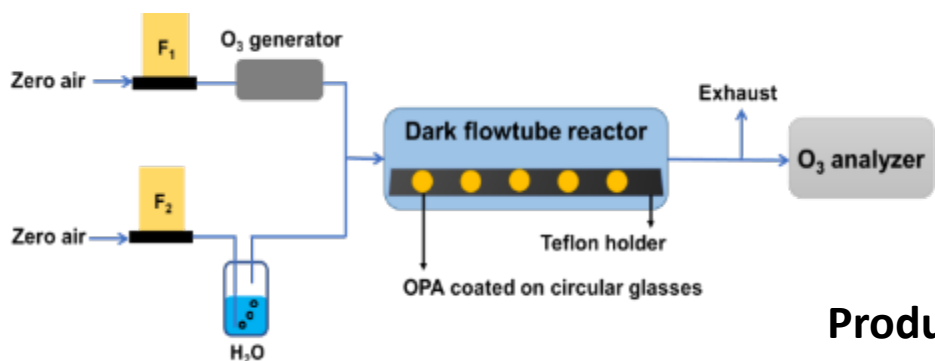
6PPD and 6PPDQ: Not detected in blanks for air samples

6PPD: Detected in the rubber o-rings of the total deposition sampler

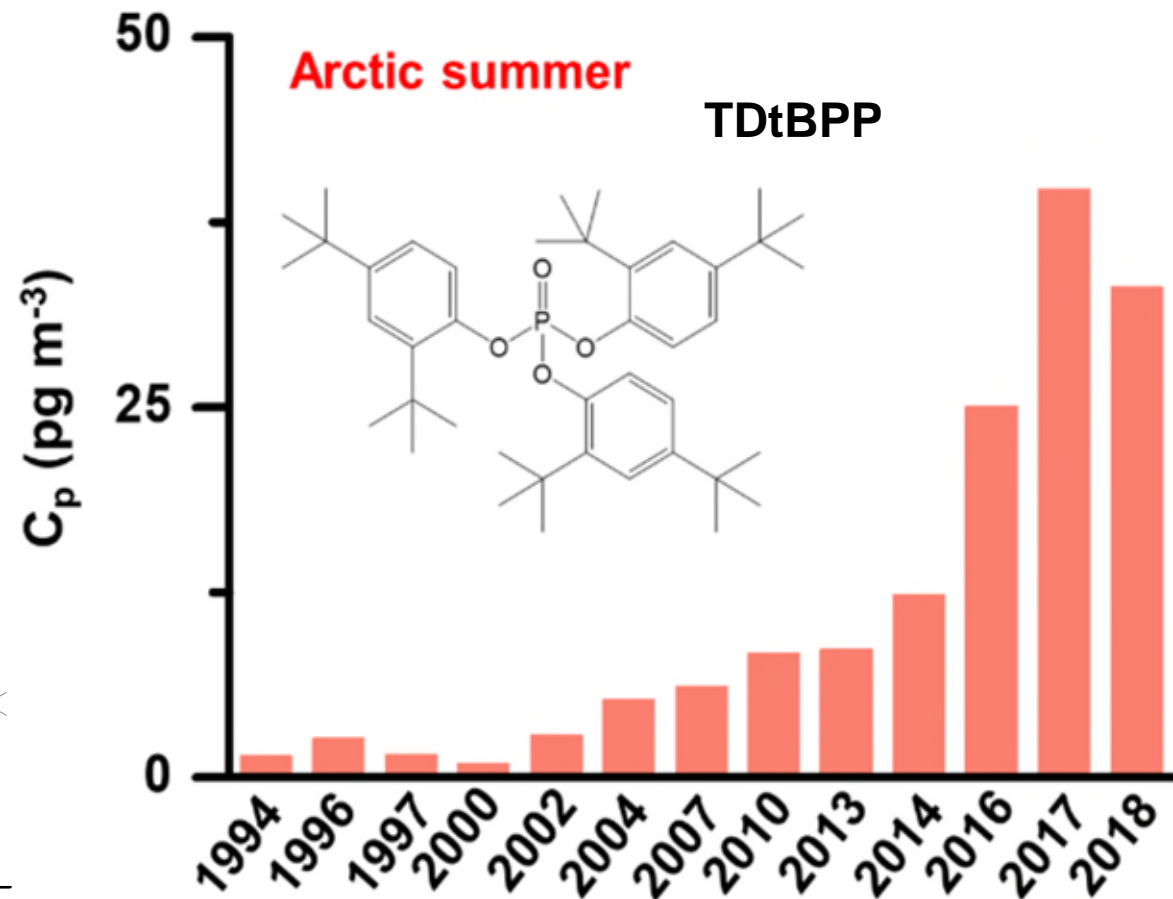
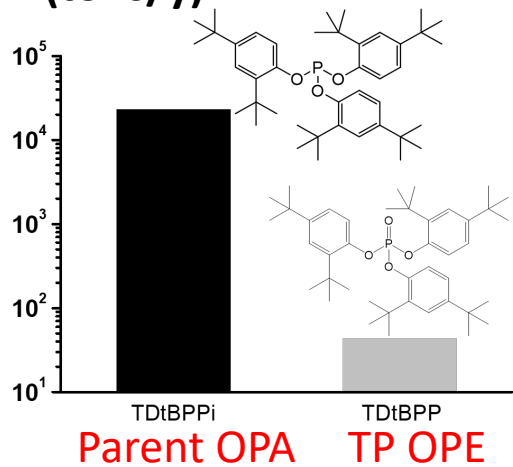


Retrospective Analysis of Alert Air Samples for Transformation Products of Organophosphite Antioxidant (OPA)

Heterogenous O₃-OPA reaction study



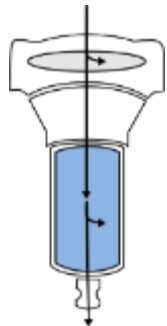
Production volume (tons/y)



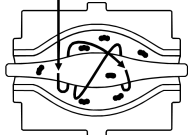
Liu et al. (2023) *Oxidation of commercial antioxidants is driving increasing atmospheric abundance of organophosphate esters: Implication for global regulation* One Earth 6, 1–11

THE VALUE OF HRMS

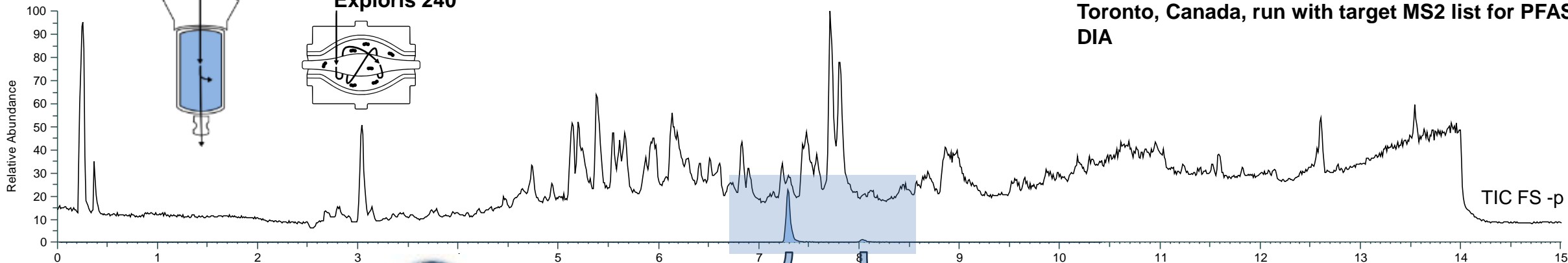
High Volume Sampling Cartridge with PUF/XAD/PUF



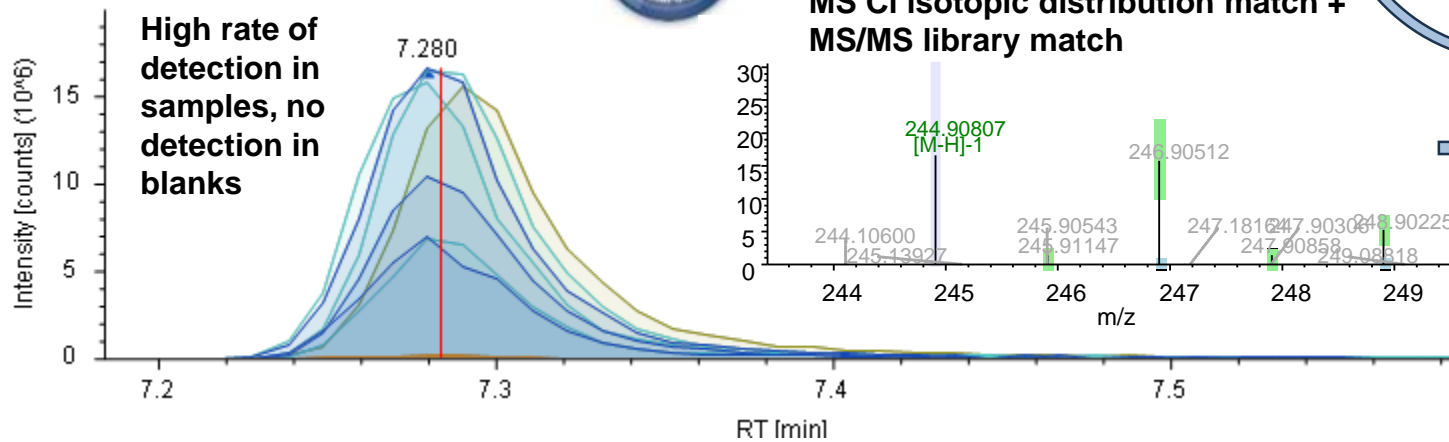
LC-HRMS Exploris 240



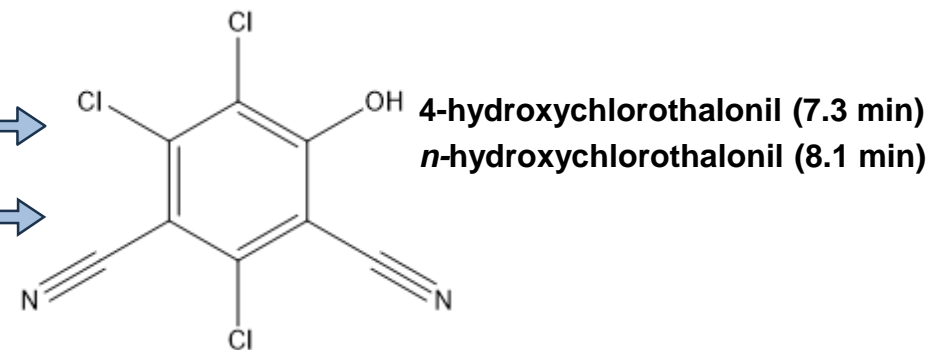
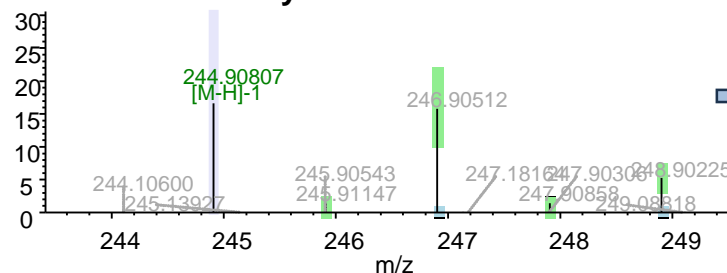
PUF/XAD/PUF methanol extract, sample collected at Toronto, Canada, run with target MS2 list for PFAS + DIA



Processed w/ Compound Discoverer



MS Cl isotopic distribution match + MS/MS library match



Level 4 detection of environmental degradation products of chlorothalonil

Acknowledgements

Funding from Environment and Climate Change Canada's Chemicals Management Plan (CMP) and Northern Contaminants Program (NCP)

OAL team members, all sites and laboratory operators and students

