Biodegradation of Fluorotelomer-Based PFAS by Soil Cultures Enriched with Various Carbon Sources

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CHU LABORATORY

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Supported by SERDP DOD ▪ EPA ▪ DOE

Per- and Polyfluoroalkyl Substances (PFAS)

- PFAS are a group > 3,000 man-made fluorinated chemicals as of 2018

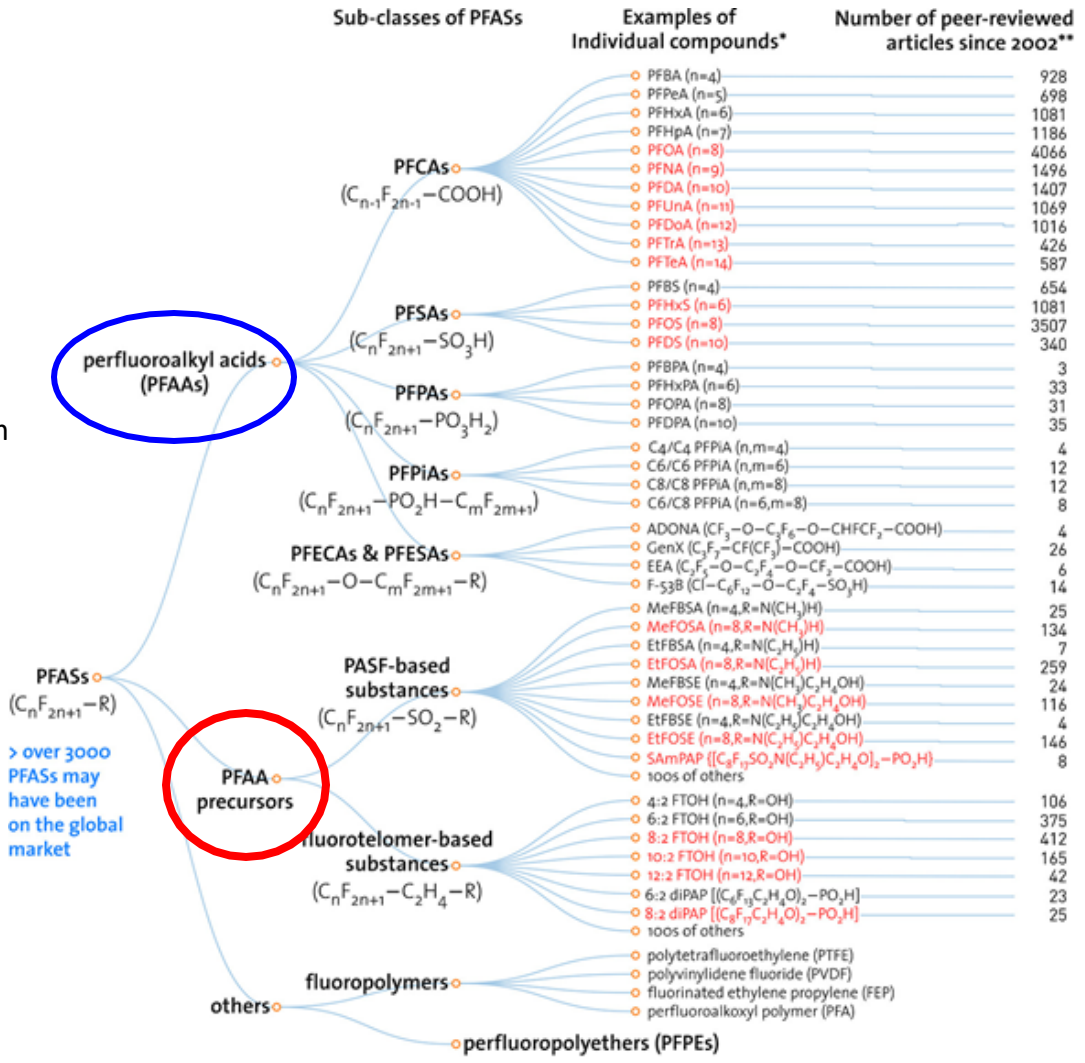
  (10.1021/acs.est.6b04806)

- > 9000 PFAS has been identified (source: CDC)

(https://www.cdc.gov/niosh/topics/pfas/default.htm

Precursors

Various chain-length PFAS



FTOH-based PFAS

- **Man-made fluorinated chemicals**
- **Unique property**
  - Thermally stable and chemically inert
  - High surface activity
  - Water- and oil-repellent

Per – fully fluorinated
Poly – partially fluorinated

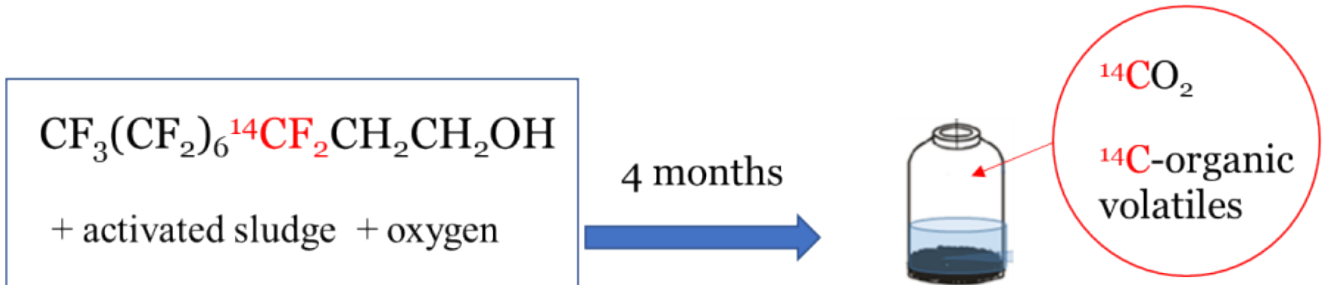
FTOHs are biodegradable

ENVIRONMENTAL Science & Technology

Environ. Sci. Technol. 2005, 39, 19, 7516-

Fluorotelomer Alcohol Biodegradation – Direct Evidence that Perfluorinated Carbon Chains Breakdown

Ning Wang, Bogdan Szostek, Robert C. Buck, Patrick W. Folsom, Lisa M. Sulecki, Vladimir Capka, William R. Berti, and John T. Gannon



^{14}C-8-2 FTOH

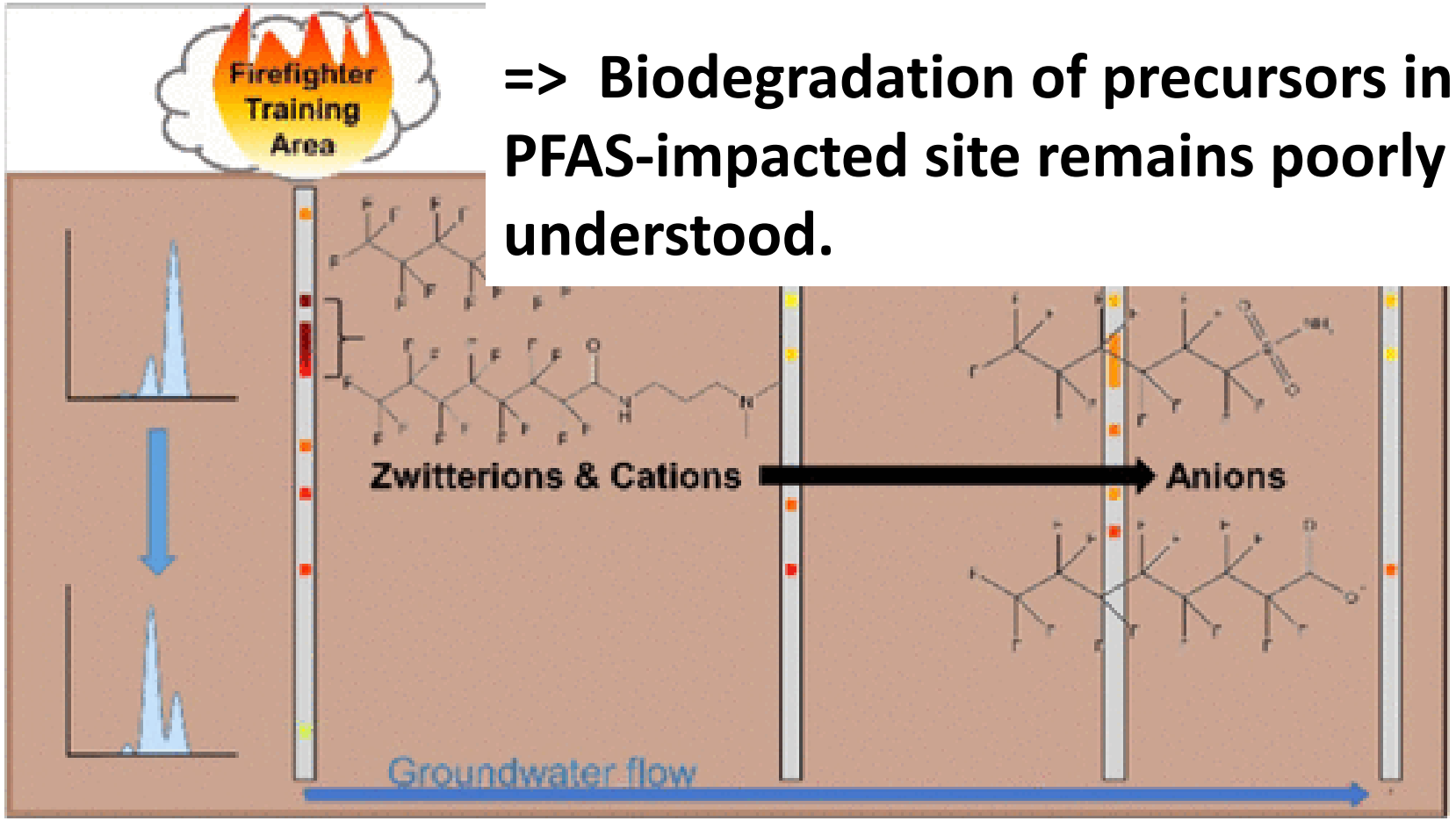
ENVIRONMENTAL Science & Technology
pubs.acs.org/est

Spatial Trends of Anionic, Zwitterioni AFFF-Impacted Site

Anastasia Nickerson, Alix E. Rodowa, David T. Adamson John J. Kornuc, and Christopher P. Higgins*

- **52%** of the PFAS transported downgradient was associated with **polyfluorinated precursors**

=> Biodegradation of precursors in PFAS-impacted site remains poorly understood.



Question

- **Will biostimulation or bioaugmentation promote rapid bioconversion of the precursors?**

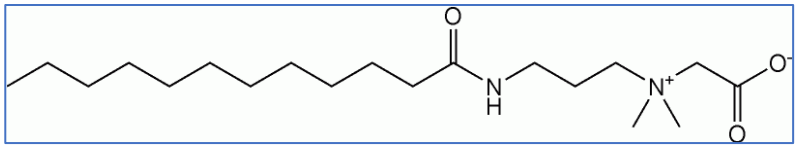
Soil Enrichment Cultures With Different Carbon Sources

- **C2 Background soil from a former air force base**

- **Carbon sources.**
  - ✓ ethanol (EtHO, 0.05%),
  - ✓ 1-propanol (1-PrOH, 5mM),
  - ✓ 1-butanol (1-BuOH, 5mM),
  - ✓ hexane (0.05%),
  - ✓ octane (0.05%)
  - ✓ phenol (0.05%)
  - ✓ cocamidopropyl betaine (CPB) (0.05%).

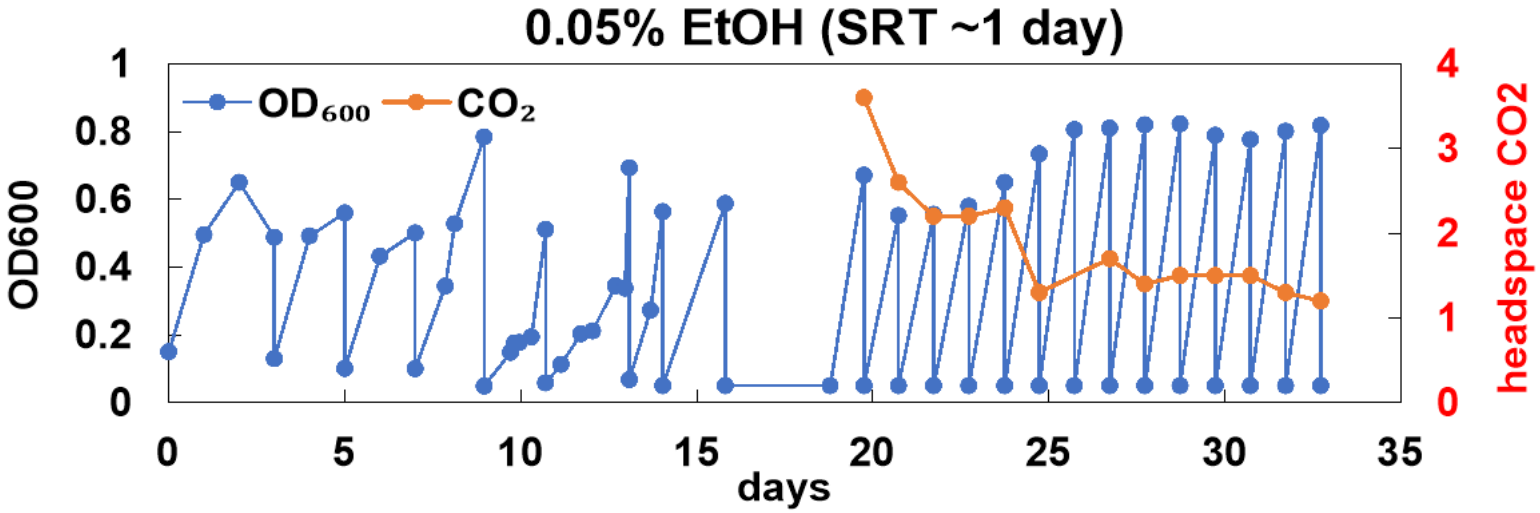
CPB

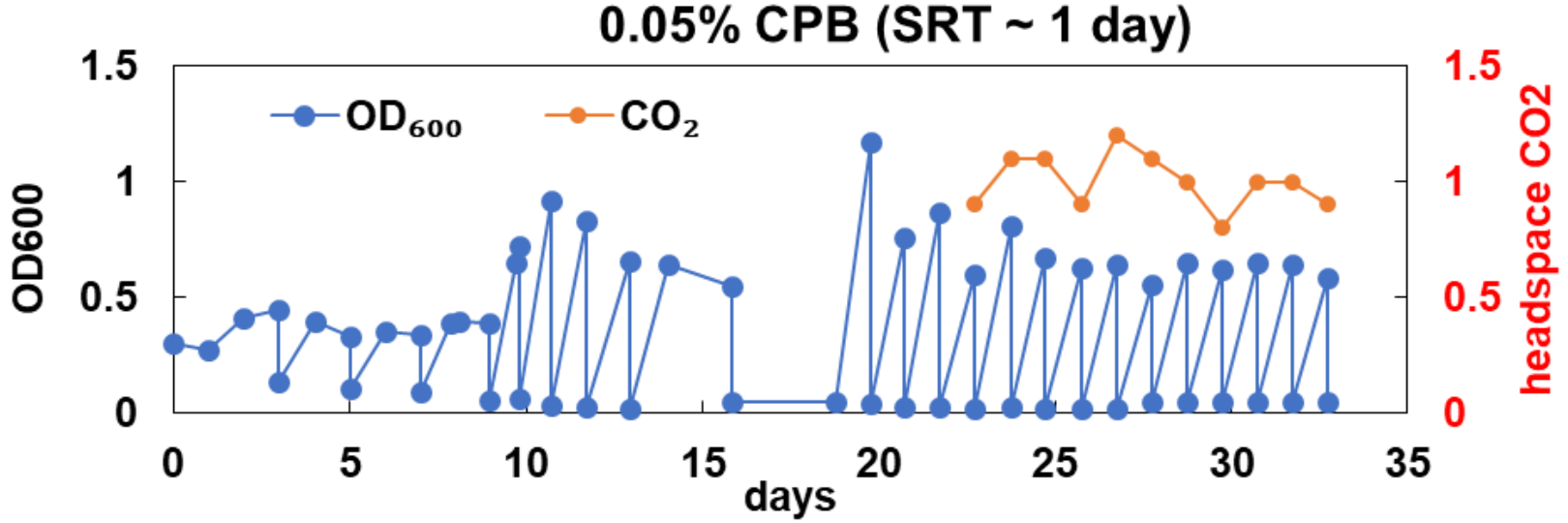
- **A zwitterionic surfactant**
- **Present in AFFF formula : 1-5% w/w.**



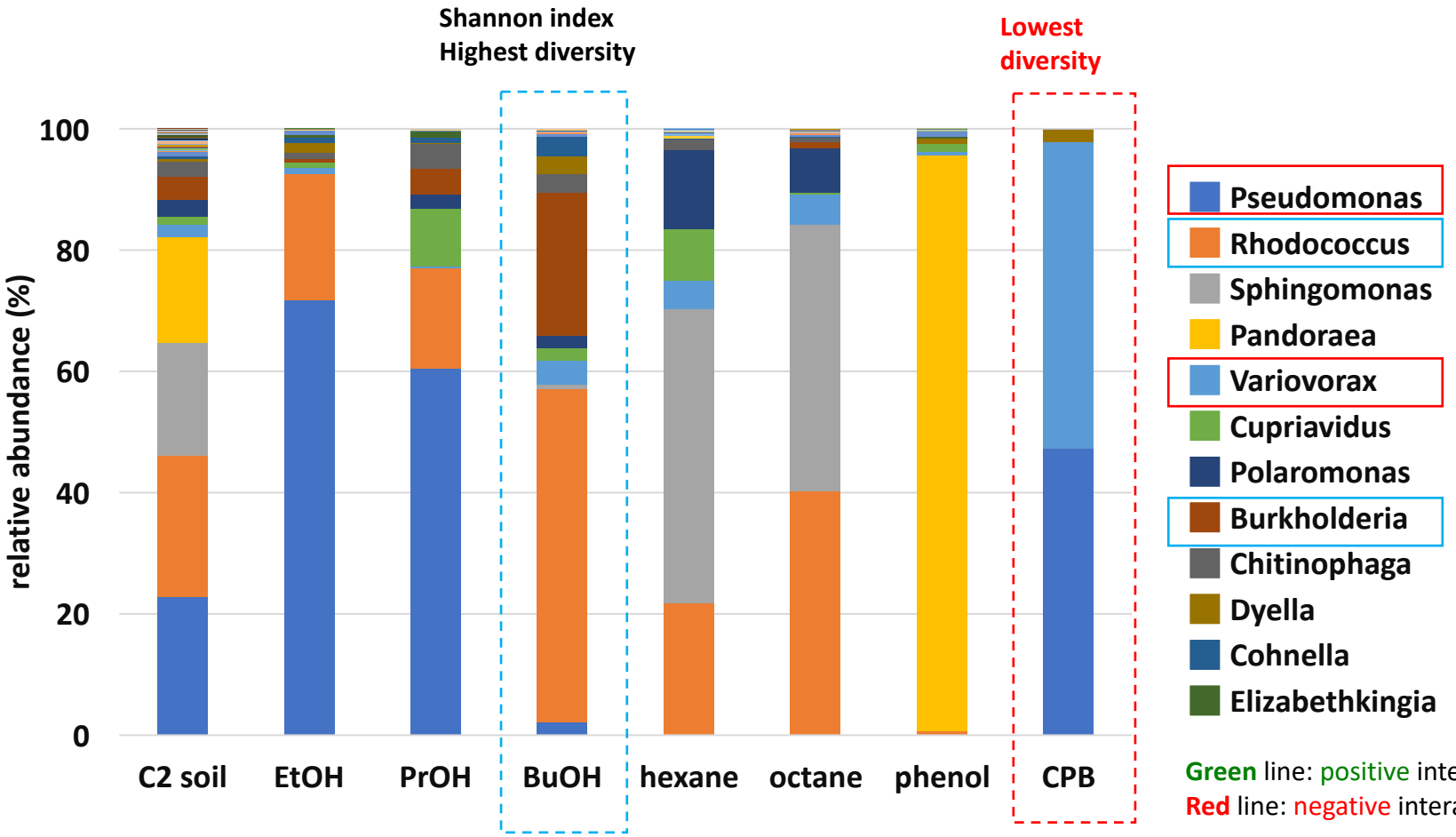
- **Ammonia mineral salts (AMS)**
- **Room Temp, 150 rpm**

Enrichments in Sequential Batch Reactors

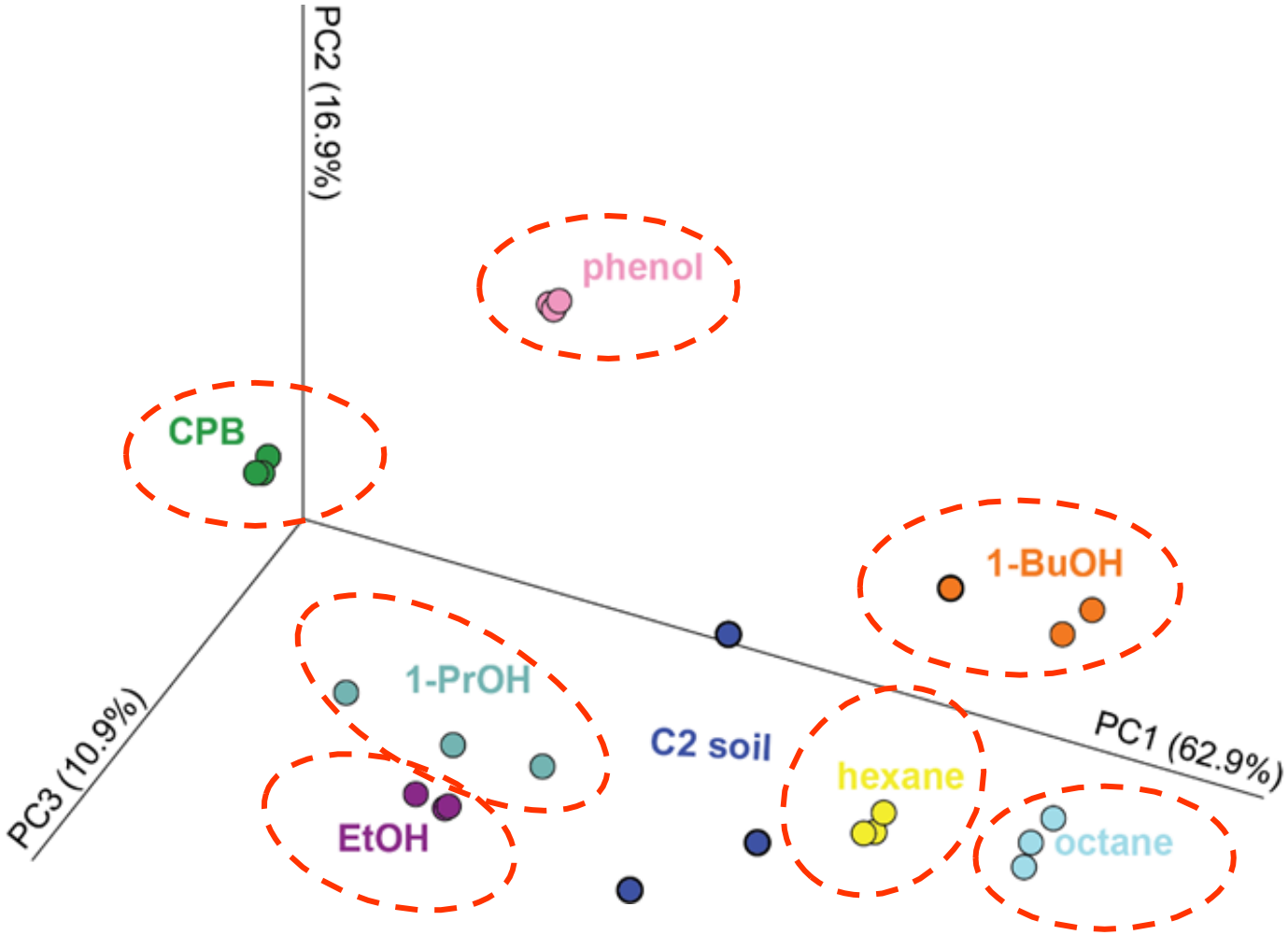




Microbial Communities of the Enrichments

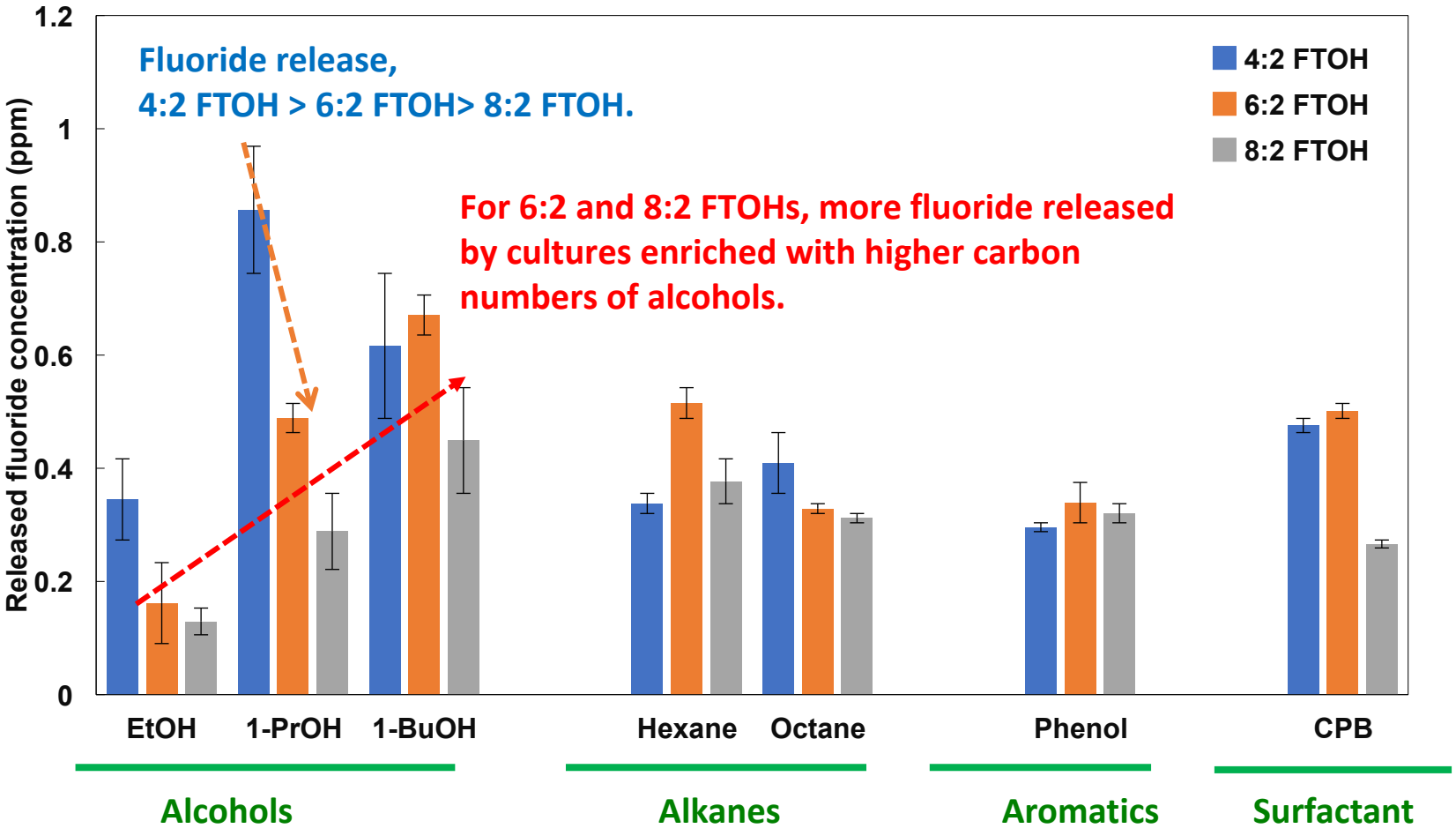


Carbon Sources are the Drivers of Different Microbial Communities of the Enrichments



Principle coordinate analysis (PCoA) plot on the weighted UniFrac distance matrix referring beta-diversity of C2 soil and enrichment sample microbial communities from respective carbon sources with sequence depth of 33,000.

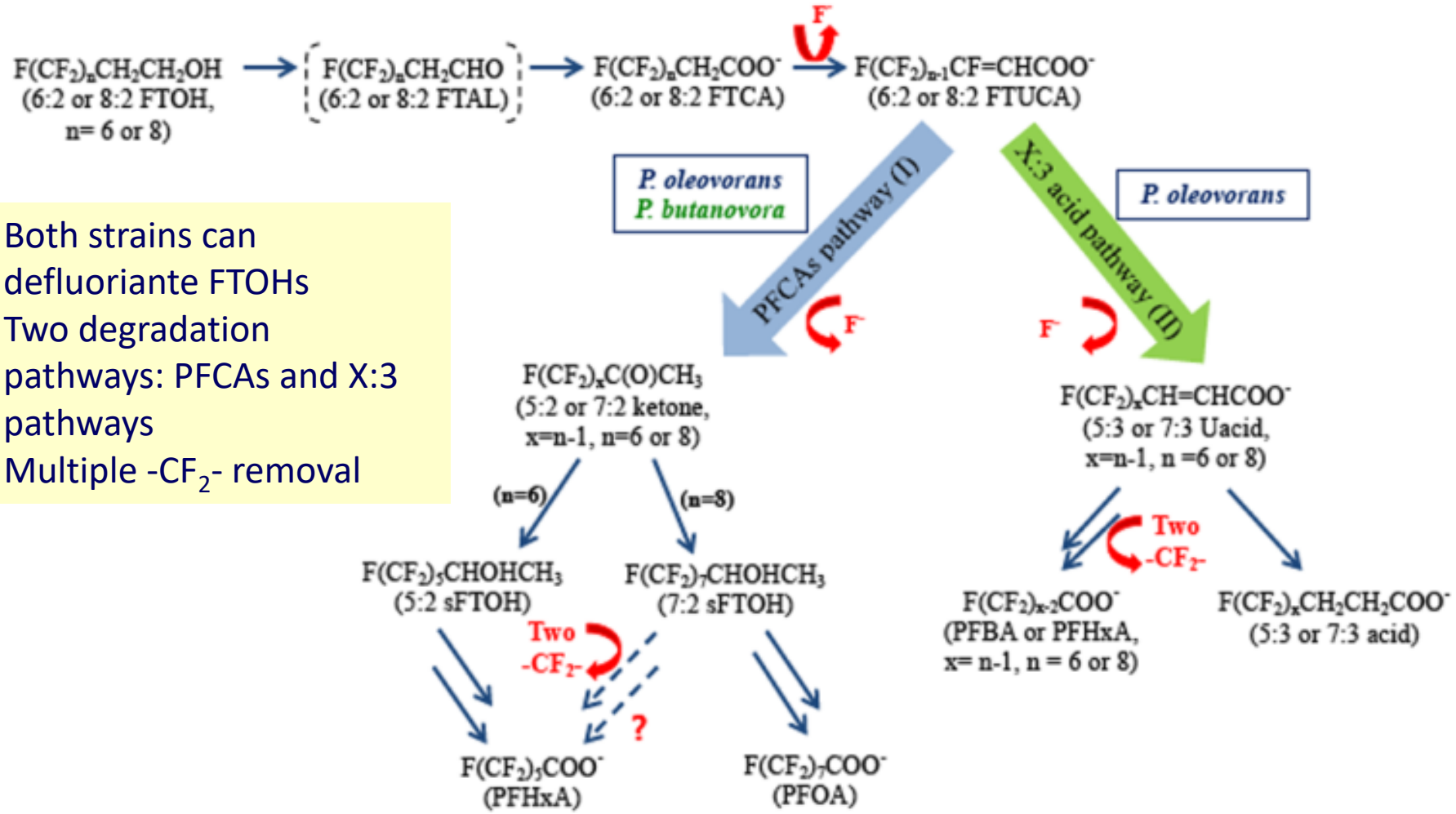
Biodegradation of FTOHs by the Enrichments



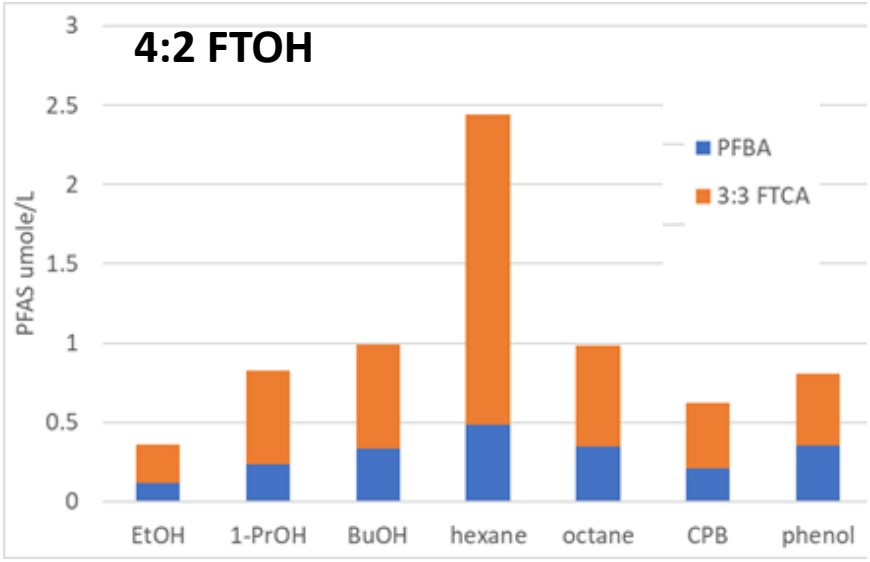
- All the enrichment cultures were able to degrade FTOHs.
- No chain-length dependent defluorination of FTOHs was observed for alkane- phenol- and CPB-enriched cultures.

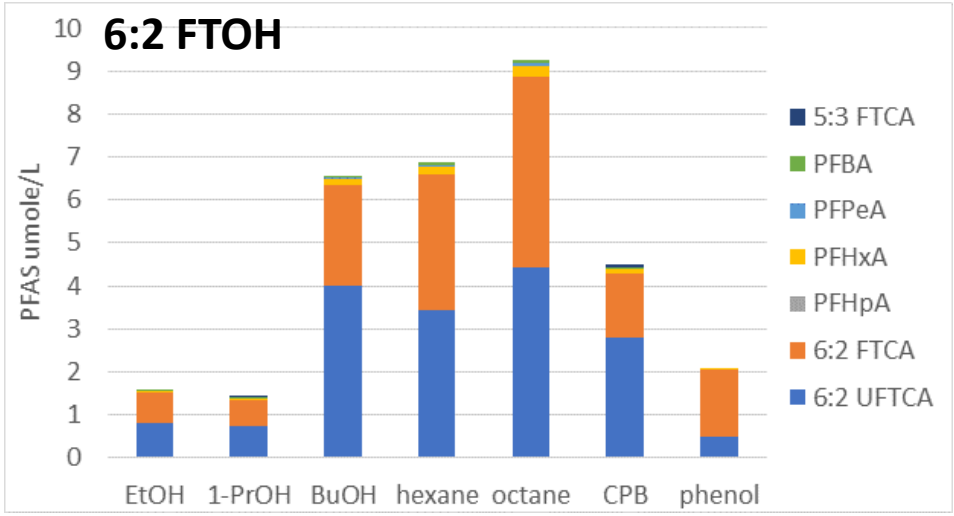
Two Pathways for FTOH Biodegradation

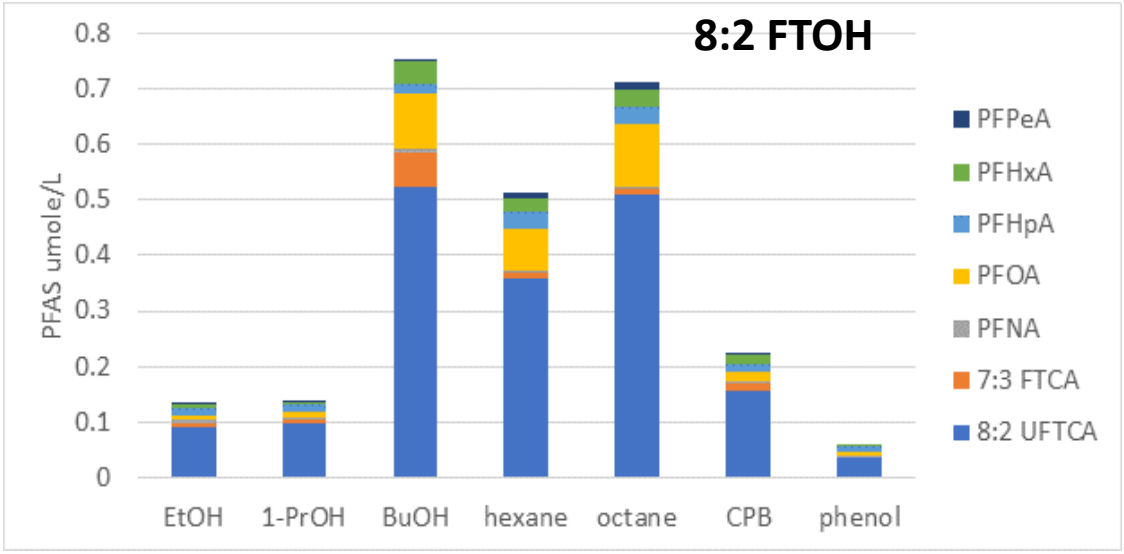
- Both strains can defluoriante FTOHs
- Two degradation pathways: PFCAs and X:3 pathways
- Multiple -CF_2- removal



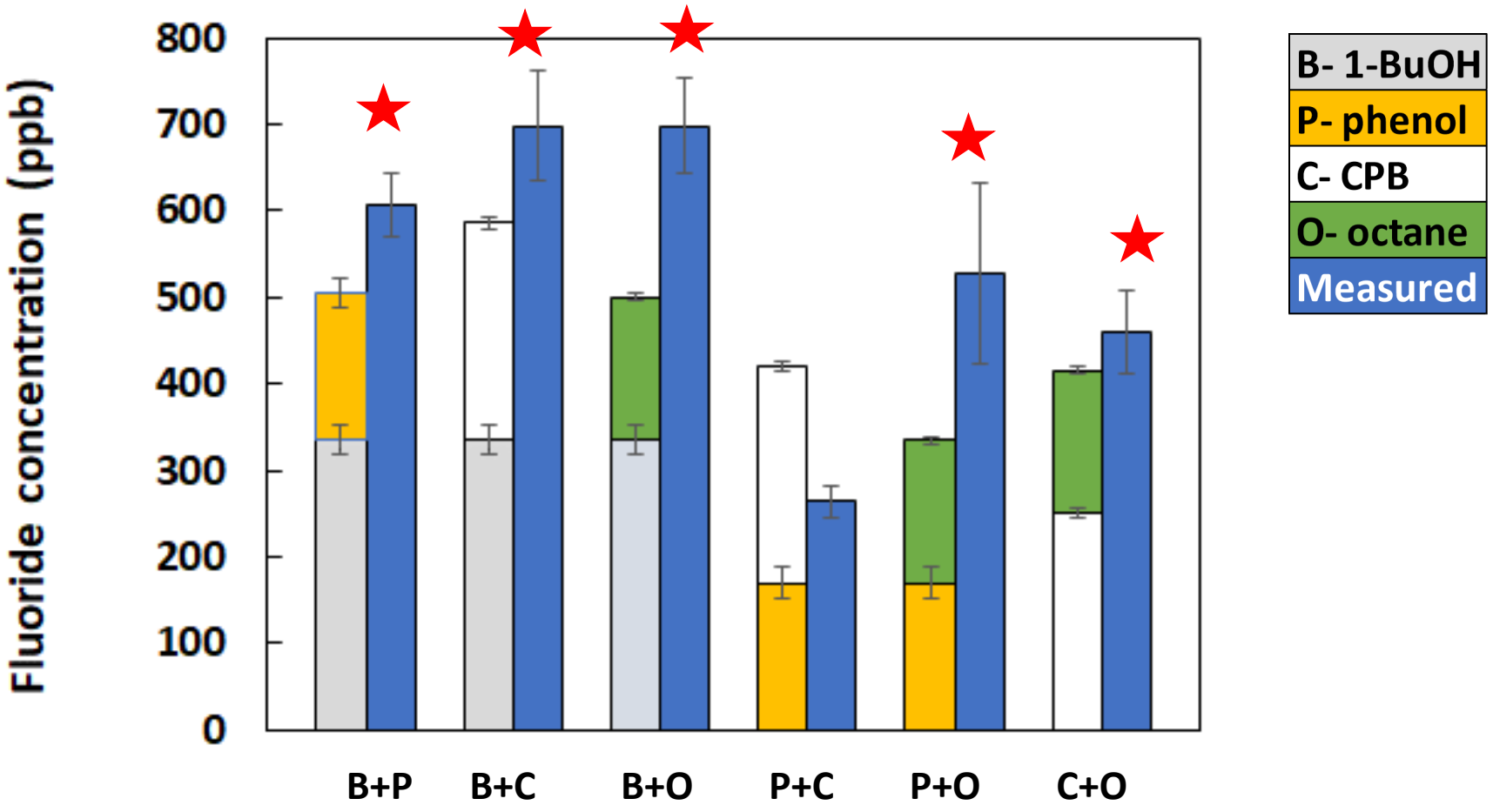
Biodegradation Metabolites of FTOHs







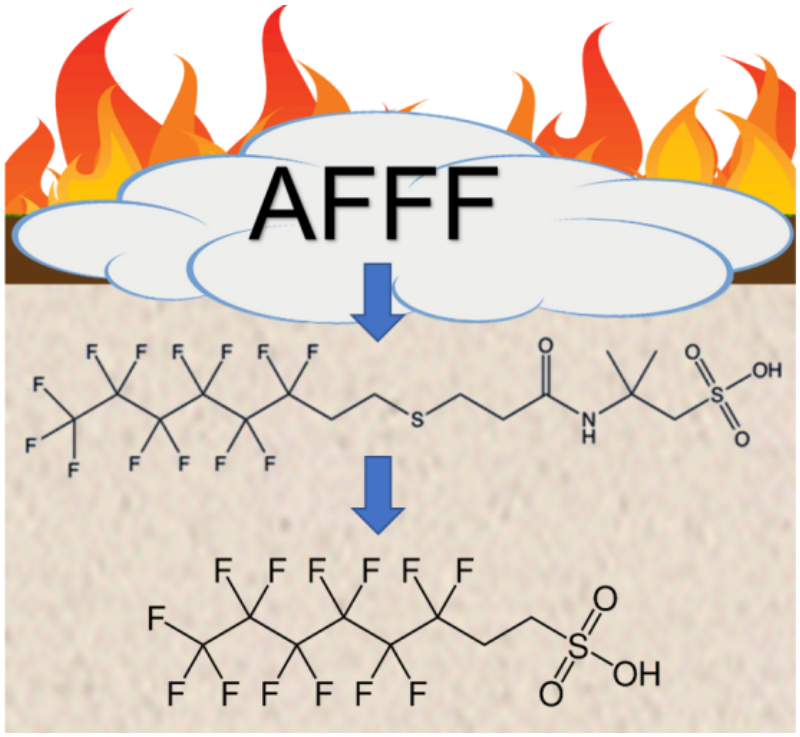
Enhanced Defluorination of 6:2 FTOH by Dual Enrichments



- Higher 5:3 FTCA found in combinations with CPB-enriched culture

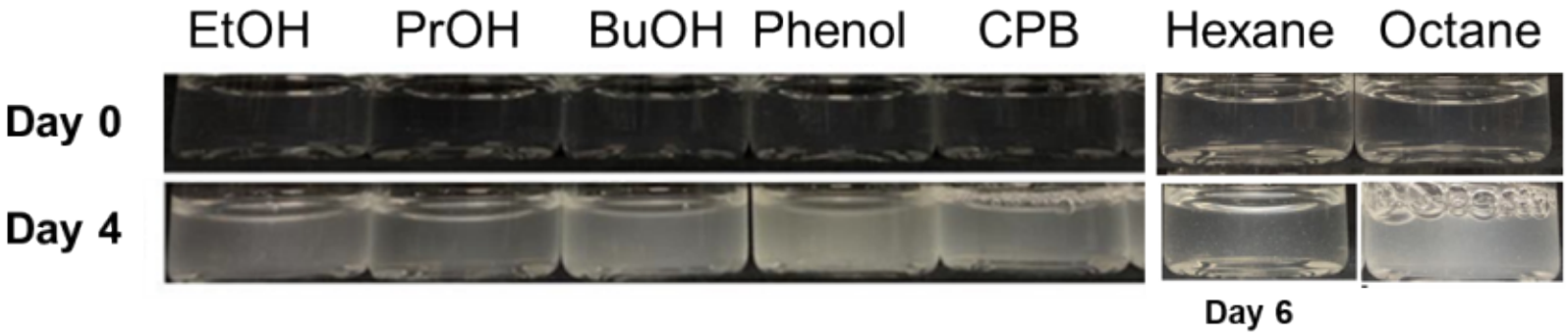
6:2 FTSA in AFFF-impacted Soil

- 6:2 Fluorotelomer sulfonates (FtS, FTS, or FTSA)
  - as ingredients in aqueous film-forming foams (AFFFs)
  - as transformation metabolites from precursors in AFFFs
- Known Precursors to fluorotelomer sulfonates
  - fluorotelomer thioether amido sulfonate (FtTAoS)
  - fluorotelomer sulfonamide betaines (such as 6:2 FtSaB)

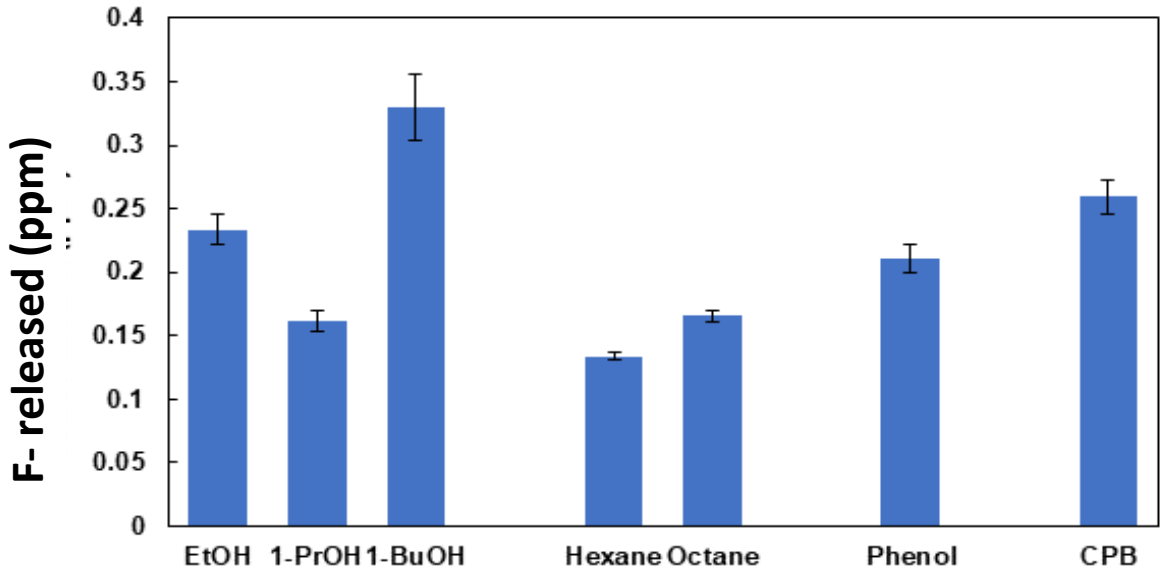


- 6:2 FTSA found in high levels in AFFF-impacted soils and groundwater
  - AFFF-impacted soil: 612-2,101 µg/kg
- 6:2 FTSA is also detected in
  - River, groundwater and wastewater: 1.6-37.9 ng/L
  - Landfill leachate: 582 ng/L

Enrichments Used 6:2 FTSA as S Source

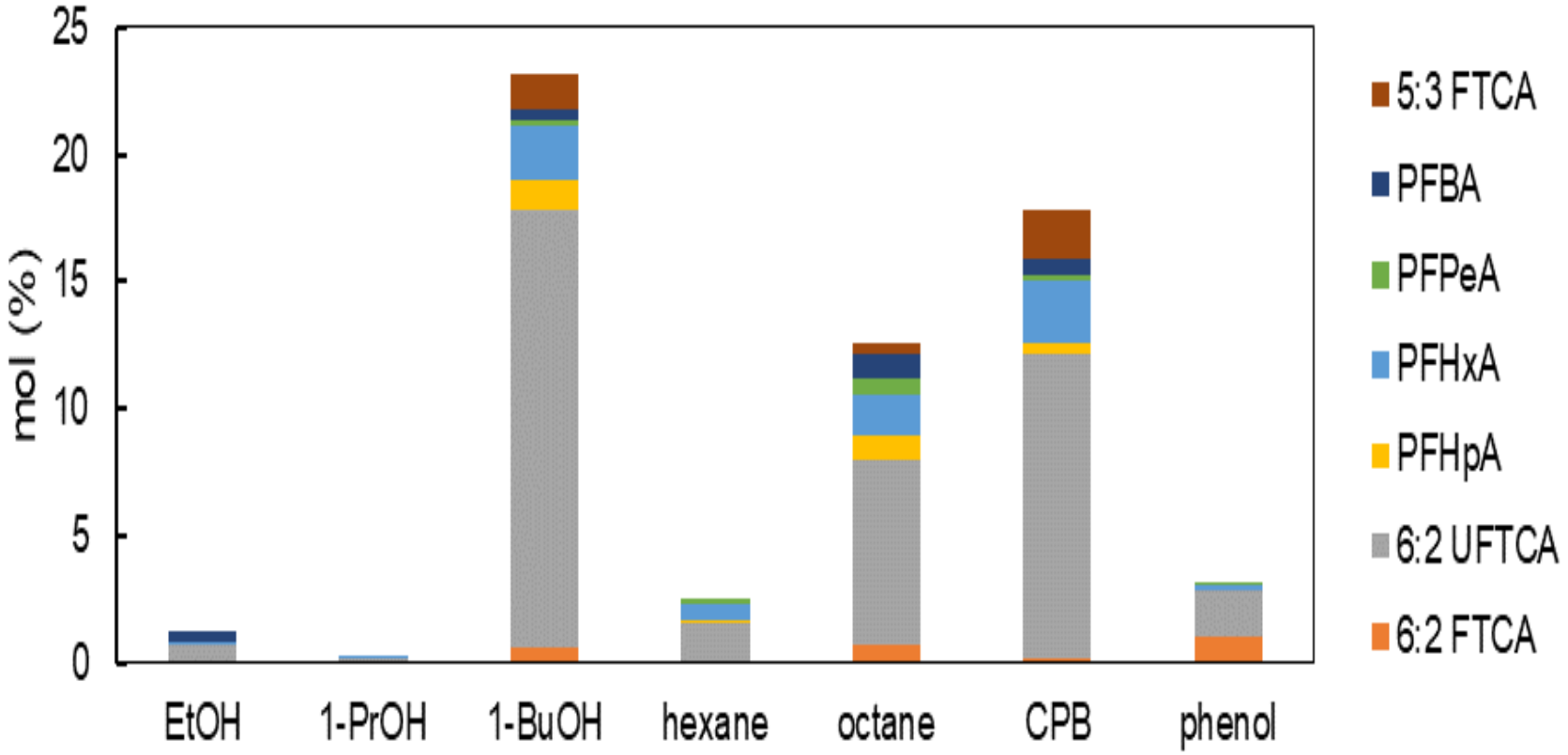


- **F^- released in spent growth medium (initial 6:2 FtS =20 ppm)**



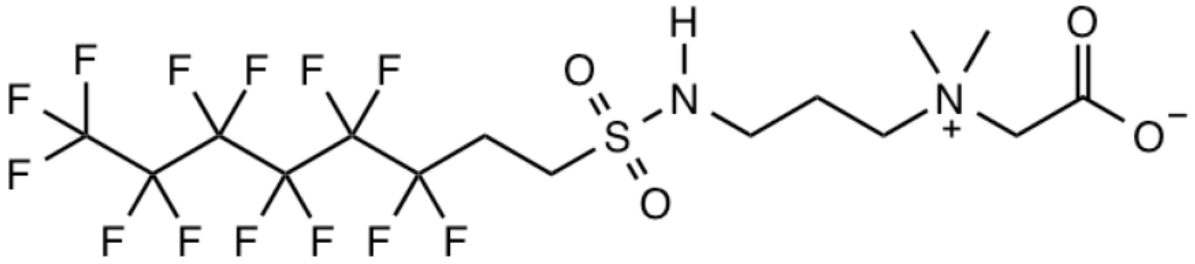
Metabolites of 6:2 FTSA when 6:2 FTSA was used as S source by the Enrichments

- **Metabolites (initial 6:2 FtS concentration = 4 ppm)**



Can Enrichments Degrade 6:2 FtSaB?

- **6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FtSaB or 6:2 FTAB)**
  - a novel perfluorooctane sulfonate alternative
  - induced developmental toxicity in zebrafish embryos
  - 6:2 FTSA can be produced as its metabolite

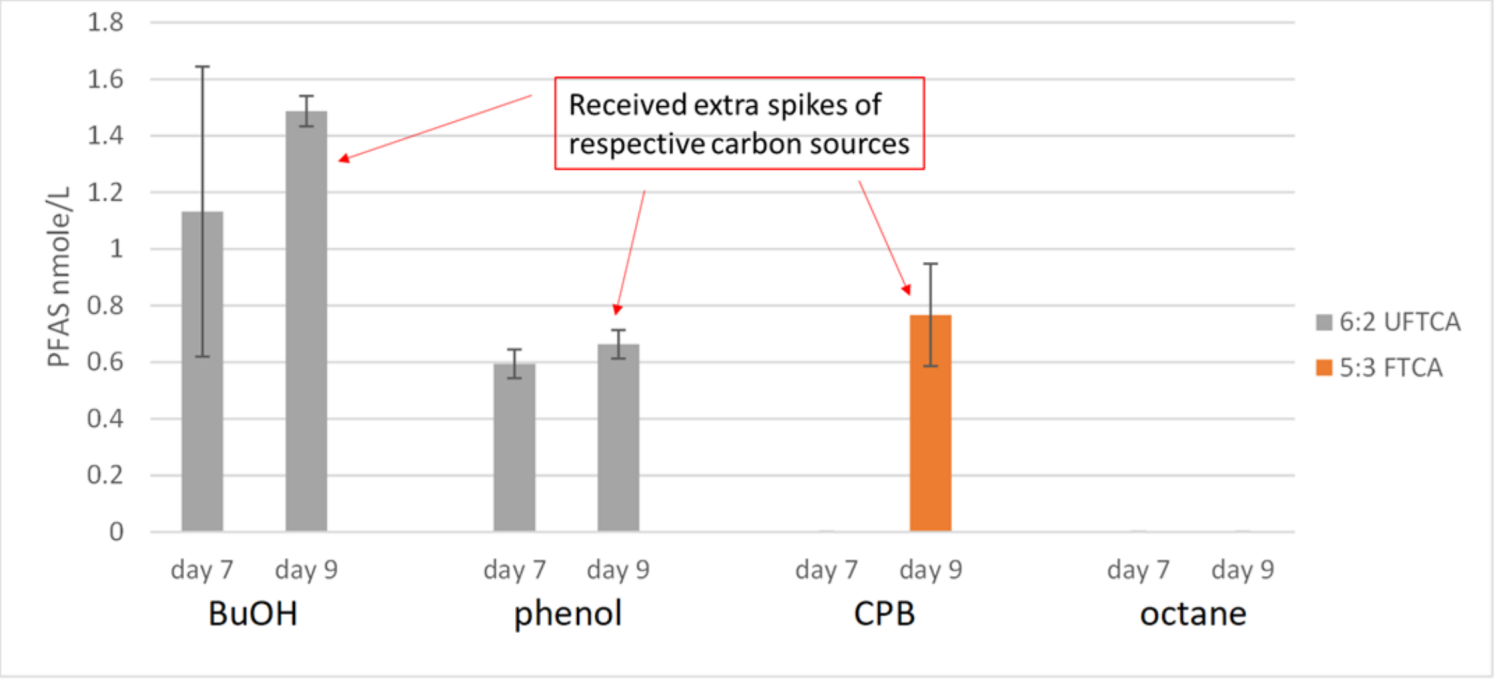


- Under sulfur-rich conditions, no fluoride release was detected after two weeks when 6:2 FtSaB was spiked into the enrichment cultures.

Can enrichments use 6:2 FtSaB for Growth?

Exp. Setup:

- Butanol-, octane-, phenol- and CPB-enriched cultures + 4 mg/L of 6:2 FtSaB + respective carbon source in S-free medium on day 0.
- Two additional carbon source spikes on day 3, and day 7 for butanol-, phenol- and CPB-enrichment cultures.
- One additional carbon source spike on day 5 for octane-enrichment culture.



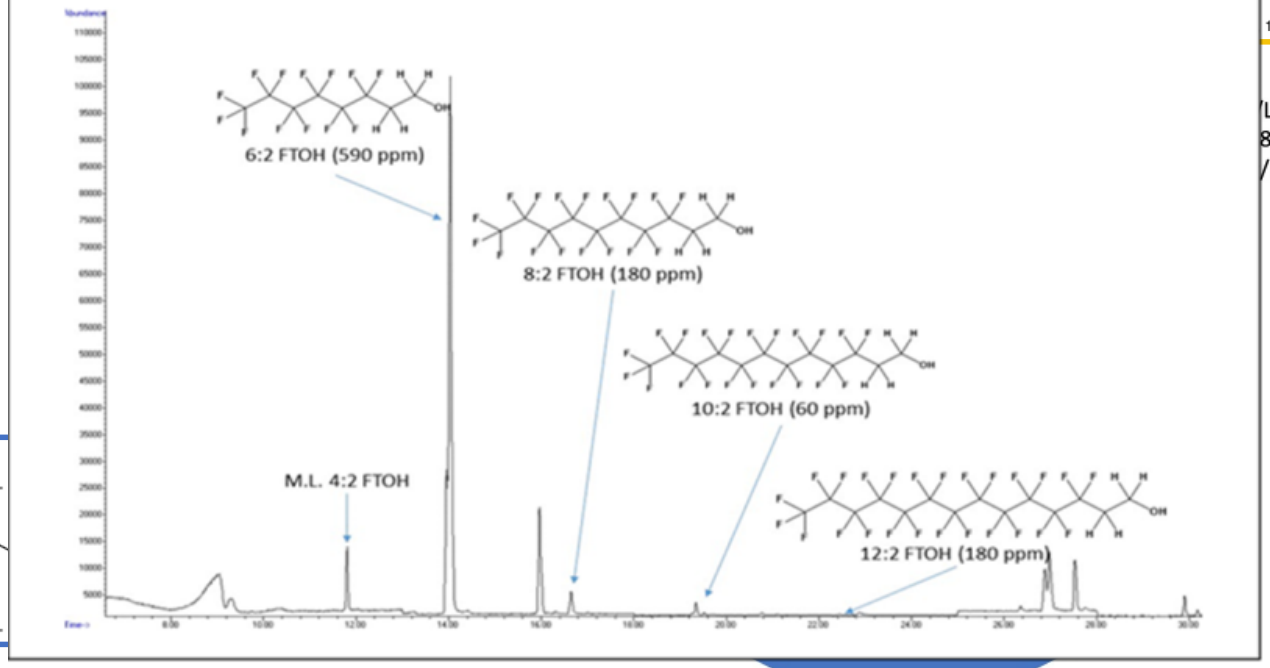
Capstone 1157

Capstone 1157: a complex commercial reference material comprised of:

- **Non-volatile PFAS:**
  - **6:2 – 12:2 FtSaBs (1 target)**
  - **6:2 – 8:2 FtSaAms (suspects)**
  - **4:2 – 10:2 FtS (targets)**
- **Volatile PFAS: 6:2 -12:2 FTOHs (targets)**

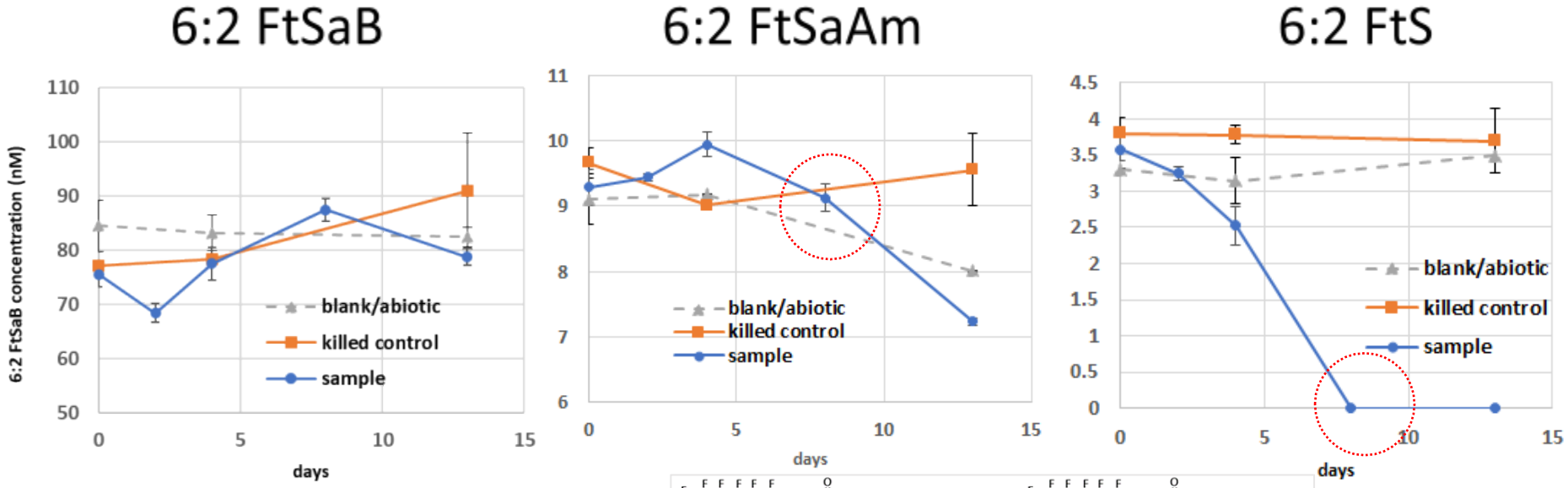
- **Gas and liquid chromatography with mass spectrometry required**
- **Combination of suspect & target data analysis**

Figure 1.1 GC-MS chromatogram indicating Capstone 1157 contains 6:2 -12:2 FTOHs.



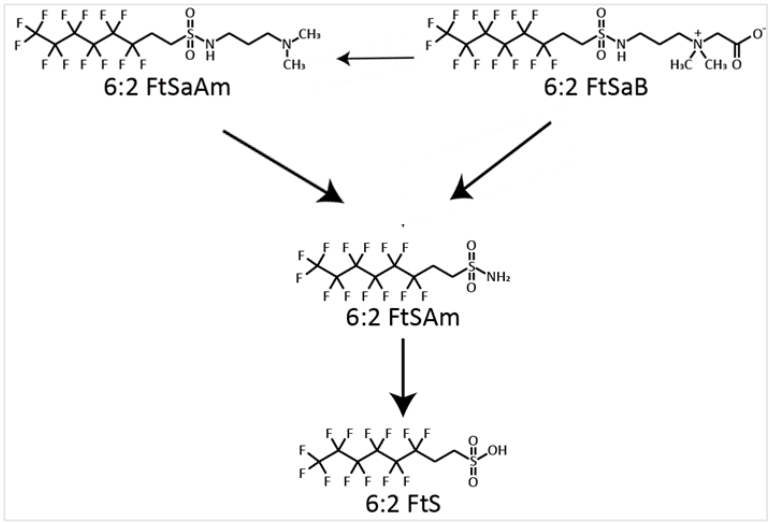
Biodegradation of Capstone 1157

- **Two enrichment cultures: CBP- and butanol-enriched cultures**
- **S-limited conditions**



- 6:2 FtSaB = ~80 nM
- 6:2 FtSaAm = 10 nM
- 6:2 FtS= 4 nM

=> CPB-enriched culture showed promise to degrade 6:2 FtSaAm



Take Home Message

- **Soil enrichments with different carbon sources (alcohols, alkanes, phenol, and CPB)**
  - Differernt carbon sources shaped different microbial community structure., with butanol-enriched cultutre showed the most diversity and CPB-enriched culture showed the least.
  - All enrichments can defluroinate FTOHs to differernt extent.
  - Chain-length dependent defluorination of FTOHs was observed for alcohol-enrichment cultures. Also, extent of defluroination of FTOHs : 4:2 > 6:2 > 8:2 FTOH.
  - enhanced F- release from 6:2 FTOH degradation by dual enrichements.

Take Home Message

- **Soil enrichments with different carbon sources (alcohols, alkanes, phenol, and CPB) (conti)**
  - All enrichment cultures can used 6:2 FtS as sole S-source and defluorinated them under S-limited conditions
  - Butanol- and CPB-enriched cultures can use 6:2 FtSaB as sole S- source and defluorinated them under S-limited conditions

- **Capstone contains both volatile and non-volatile PFAS precursors**
  - n:2 FtSaB (n= 6, 8, 12) > n:2 FtSaAm (n= 6, 8) > 6:2 FtS > 6:2 FTOH.


Questions?