Biotransformation of 8:2 fluorotelomer alcohol using microbial communities from AFFF-impacted soils

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Acknowledgements

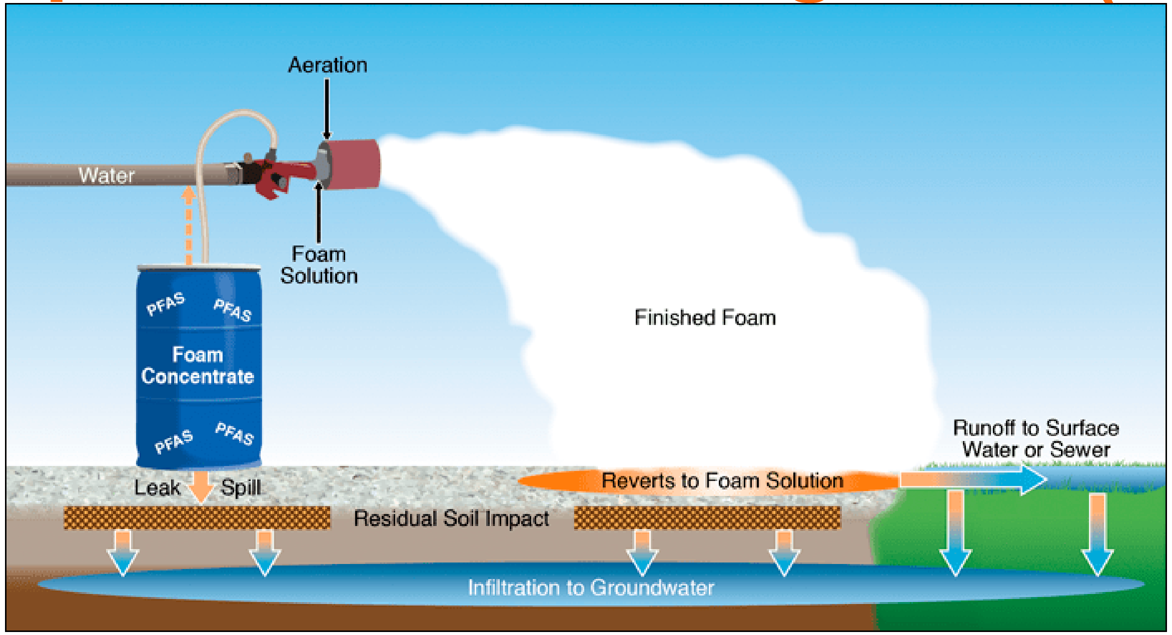
Dr. Sheng Dong and Dr. Pengfei Yan (postdoctoral fellows)


Dr. Chen Liu, Dr. Matthew Woodcock, Dr. Katherine E. Manz, Dr. Linda M. Abriola, and Dr. Kurt D. Pennell

Dr. Melissa P. Mezzari

Strategic Environmental Research and Development Program (SERDP) under Project ER18-1149: Development and Laboratory Validation of Mathematical Modeling Tools for Prediction of PFAS Transformation, Transport, and Retention in AFFF Source Areas.

Aqueous film forming foam (AFFF)



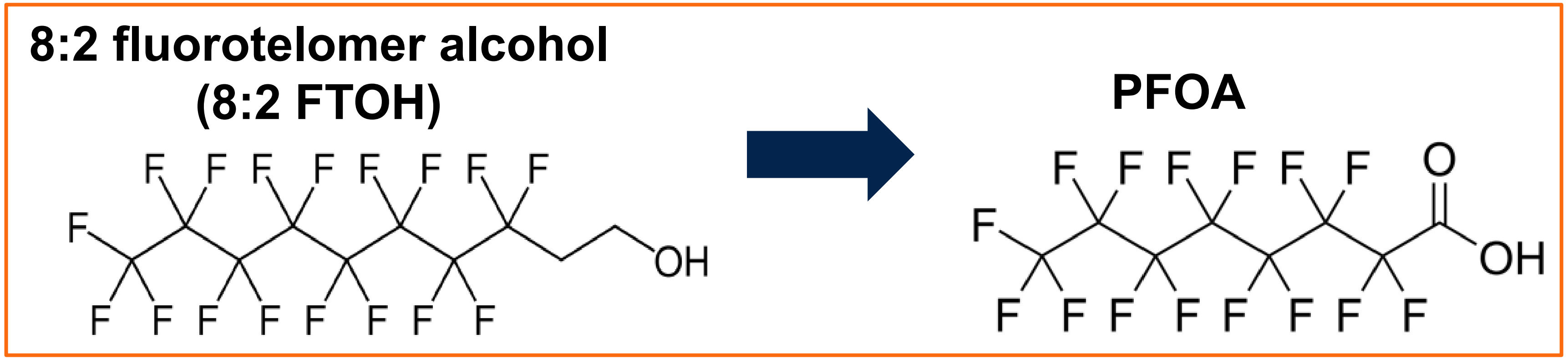
- A wide variety of perfluoroalkyl acids (PFAAs) and PFAA precursors (i.e., polyfluoroalkyl substances) identified in various AFFF formulations
- Repeated application of AFFFs at fire training areas and airports have resulted in particularly high PFAS contamination in soil & groundwater

Little is known about the environmental fate and transformation of PFAA precursors at AFFF-impacted sites

Biotransformed by native microbes? aerobes or anaerobes?

https://cen.acs.org/environment/persistent-pollutants/California-bans-PFAS-firefighting-foams/98/i38
https://coyotegulch.blog/2021/07/15/epa-identifies-drinking-water-contaminants-for-potential-regulation/

Background and Motivation

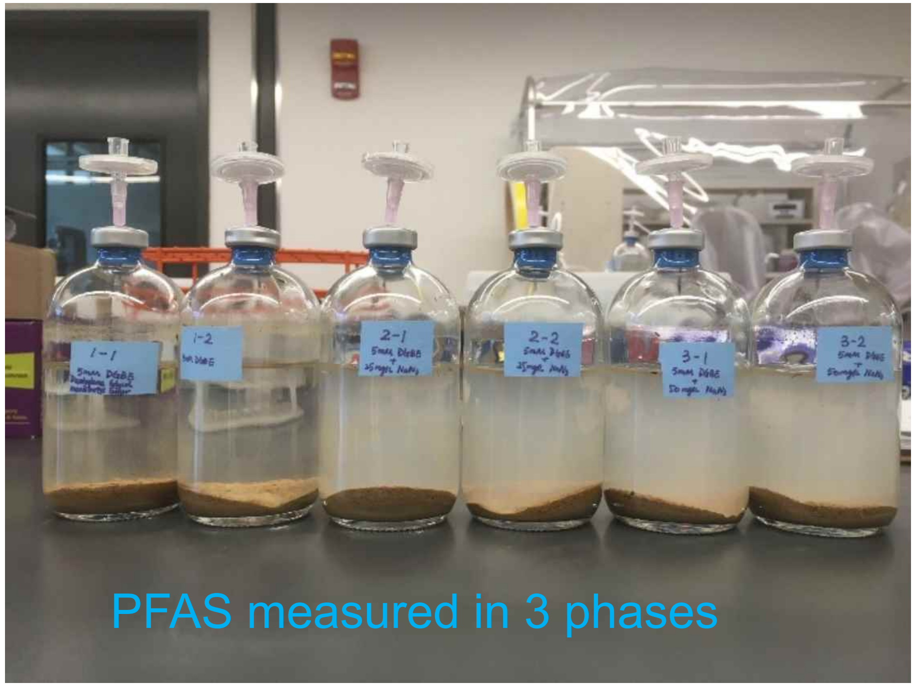


- Present at 8.0 - 26.5 mg/L in FT-based AFFFs[1,2]
- Also, likely present as a byproduct during synthesis of FT-based precursors

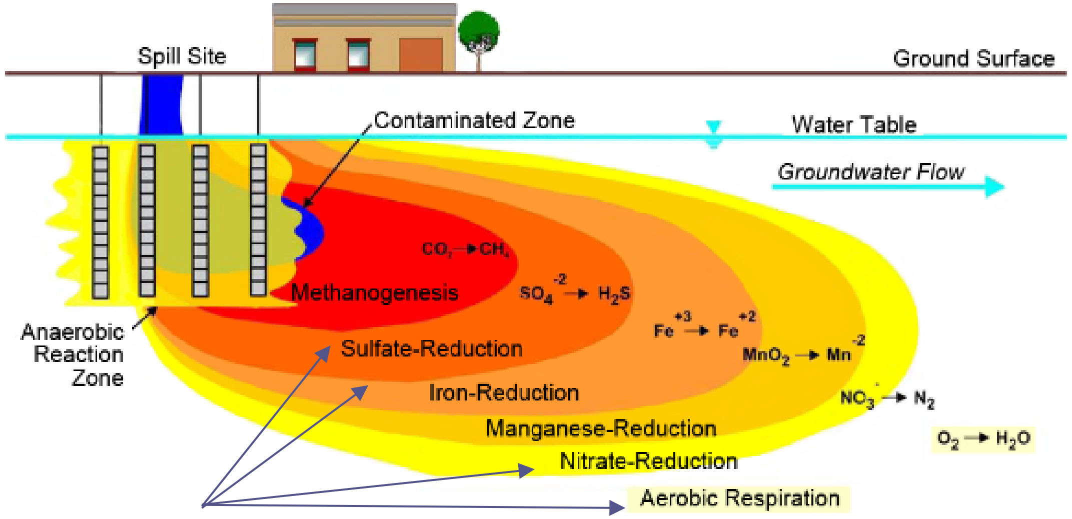
- Previous studies mostly under oxic conditions using microbial communities from WWTP, pure cultures, pristine soils, wetlands, etc.
- Few studies have used AFFF-impacted soil

(1) Herzke et al. *Chemosphere* 2012, *88* (8), 980–987.
(2) Favreau, et al. Chemosphere 2017, 171, 491–501.

Objective: To assess the biotransformation (BTF) potential of 8:2 FTOH in AFFF-impacted soil under various redox conditions.



PFAS measured in 3 phases



Electron Acceptor Conditions were screened

Former Loring AFB (ME)

Robins AFB (GA)

Experimental Setup

- 1:10 ratio of solid to synthetic groundwater
- Soils from the former Loring and Robins AFBs
- Electron Donor = Diethylene glycol butyl ether (DGBE, solvent in AFFF), and lactate for biostimulation
- 8:2 FTOH spiked at 170 µg/L
- Sodium azide added to create bacteriostatic conditions

8:2 FTOH BTF under Aerobic Conditions

Profile of 8:2 FTOH

7.2 %

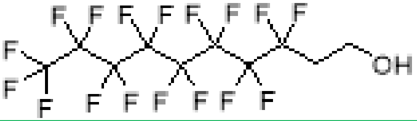
Targeted Metabolite Formation

21.9%

7.7%

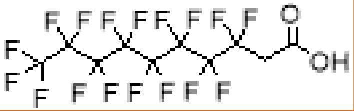
6.0%

8:2 FTOH

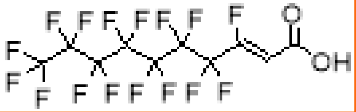


Intermediates

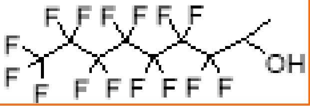
8:2 FTCA



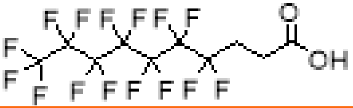
8:2 FTUA



7:2 sFTOH

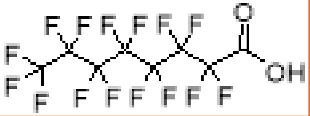


7:3 acid



Terminal product

PFOA



- Abiotic control: 85–127 %
- Live treatment: ~7% remaining after 90 d; half-life <5 d

- 58.5 mol% of initial added 8:2 FTOH recovered in live treatment as byproducts

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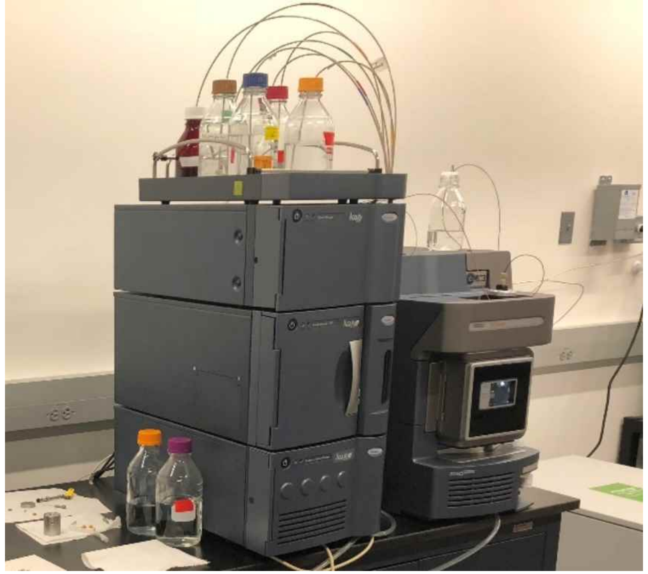
High Resolution Mass Spectrometry

Waters uHPLC Xevo TQ-S

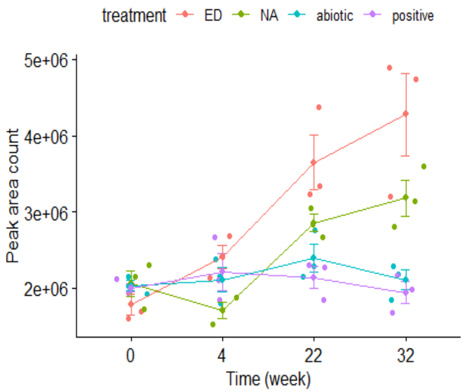


Thermo GC QExactive Orbitrap

Thermo LC QExactive HFX Orbitrap

NSF-CBET 1919870 (Pennell)

- Targeted analysis of 44 PFAS using Waters uHPLC-TQS (EPA 537.1 and draft method1633)
- Non-targeted PFAS analysis using high resolution liquid- and gas-chromatograph Thermo Orbitrap mass spectrometers to detect reaction byproducts
    - Performed non-targeted analysis in Thermo Compound Discoverer Software



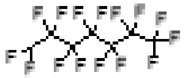
Transformation Products increased in active microcosms

Potential 8:2 FTOH Aerobic BTF identified by LC-HRMS analysis

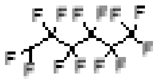
Tentative name	Identification confidence level	Tentative formula	Mass error [ppm]	Theoretical m/z	Observed m/z	Identified in microcosms
1H-perfluoroheptane	1	C7 H F15	0.14	368.9766	368.9764	Loring[a] and Robins
3-OH-7:3 acid	2	C10 H5 F15 O3	0.36	456.9926	456.9930	Loring[b]
1H-perfluorohexane	3	C6 H F13	-0.33	318.9798	318.9795	Loring[a]
Perfluoroheptanal	3	C7 H F13 O	-0.25	346.9747	346.9745	Loring[a] and Robins
7:3 u acid	3	C10 H3 F15 O2	0.24	438.9821	438.9822	Loring[b] and Robins
3-fluoro-7:3 acid	3	C10 H4 F16 O2	0.67	458.9883	458.9885	Loring[b]
6:2 FTCA	3	C8 H3 F13 O2	0.29	376.9853	376.9691	Loring[b]
7:3 u amide	4	C10 H4 F15 N O	-0.05	437.9981	437.9975	Loring[b] and Robins
6:2 FTUA	4	C8 H2 F12 O2	-0.09	356.9790	356.9785	Loring[b]
6:3 acid	4	C9 H5 F13 O2	1.25	391.0009	391.0009	Loring[b]

a. Identified in both low-dosed and high-dosed treatment
b. Identified in high-dosed treatment only

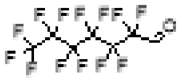
1H-perfluoroheptane



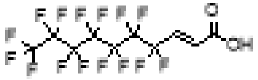
1H-perfluorohexane



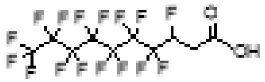
Perfluoroheptanal



7:3 uacid

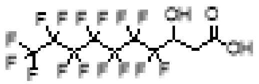


3-fluoro-7:3 acid

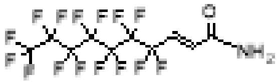


6:2 FTCA

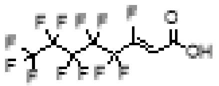
3-OH-7:3 acid



7:3 u amide



6:2 FTUA



6:3 acid

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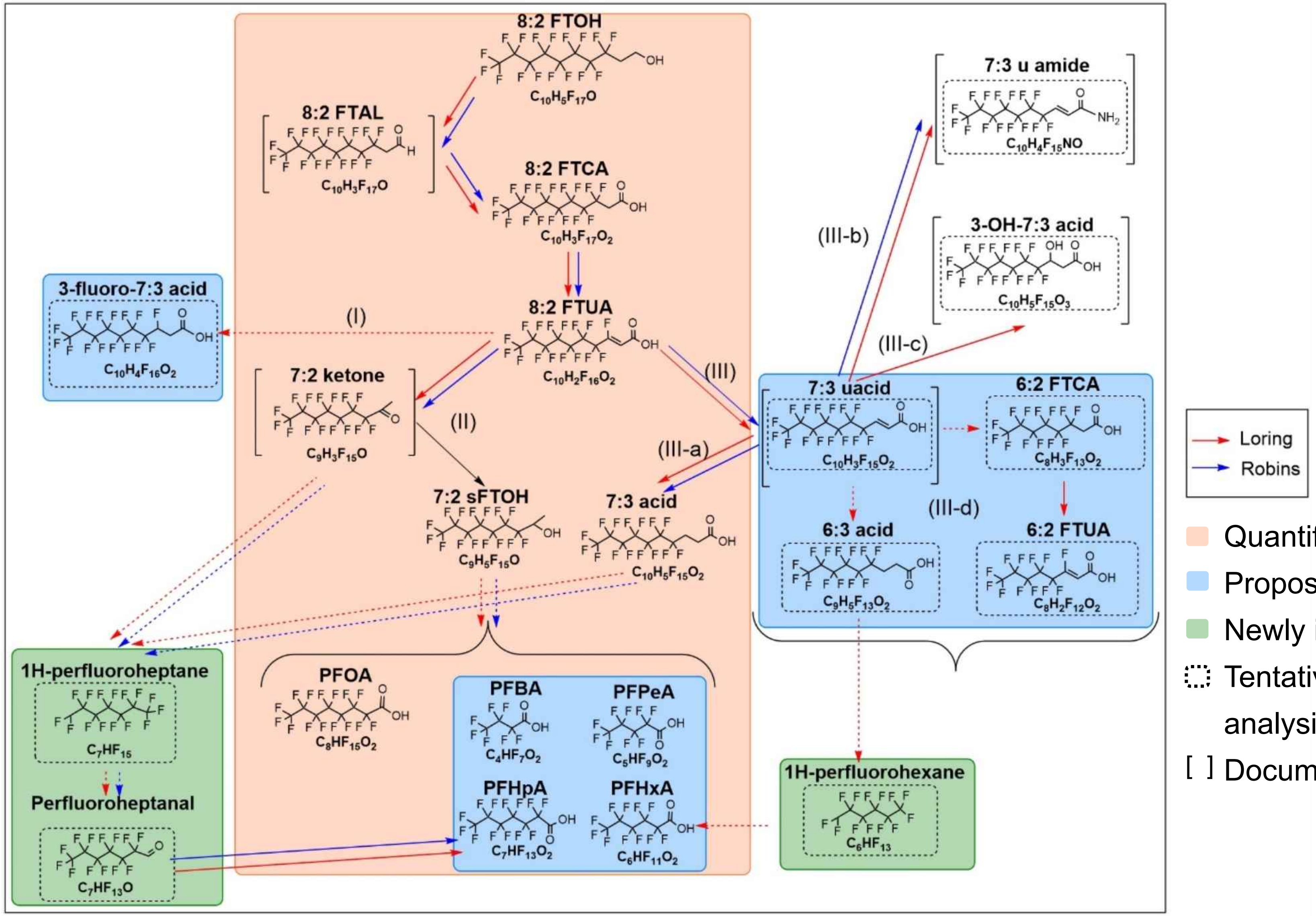
Proposed Aerobic BTF Pathways of 8:2 FTOH



Quantified by LC-MS/MS in this study, except [ ]

Proposed based on prior literature

Newly identified in this study

Tentative BTF products identified in non-targeted analysis in this study

[ ] Documented BTF products in prior literature

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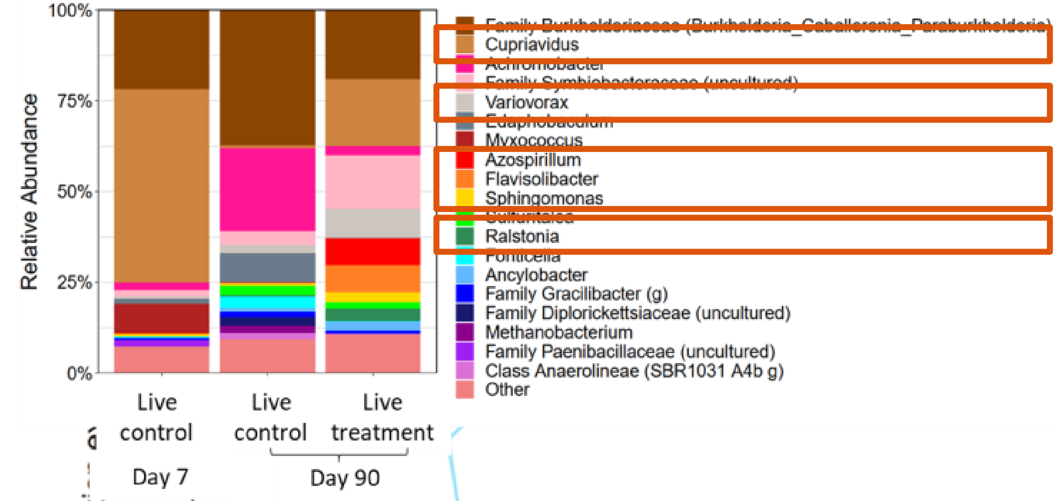
Aerobic Microbial Community Composition Shifts in Robins and Loring AFB Soils

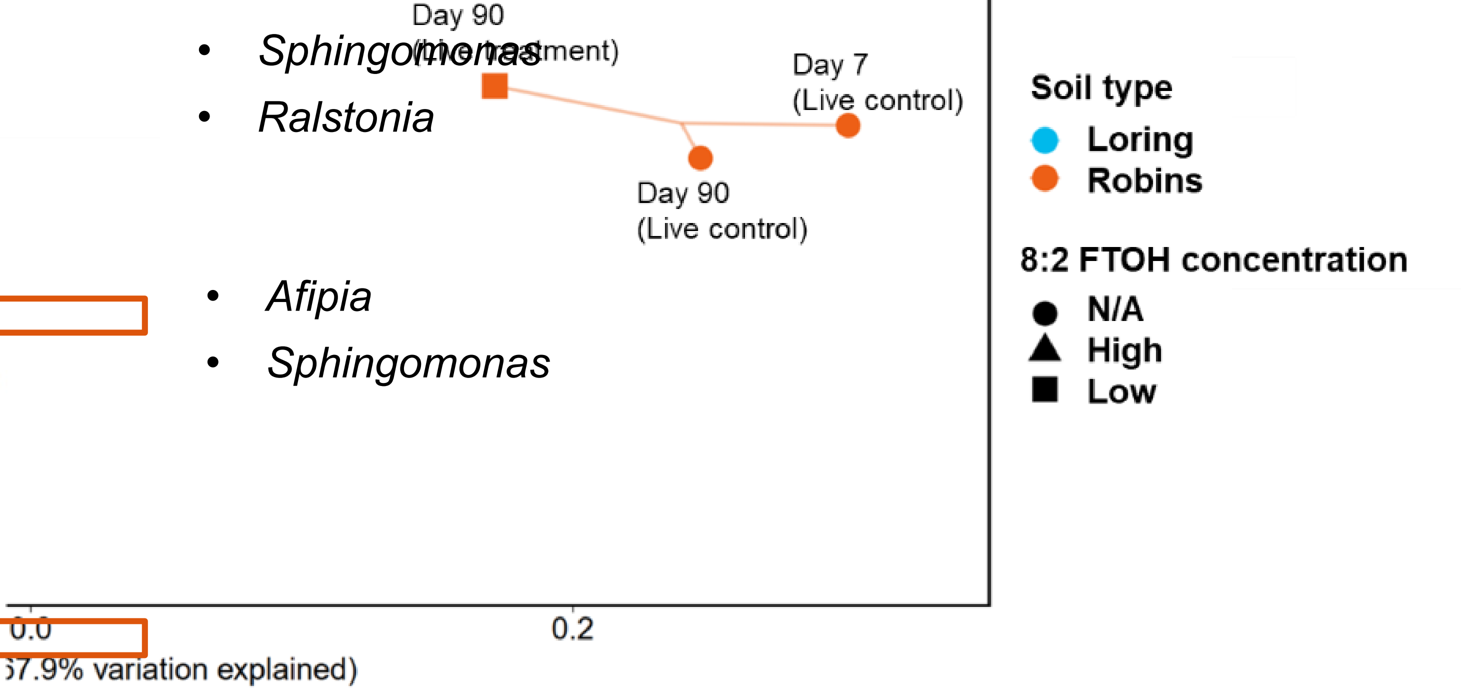
Robins



microbial community changes across

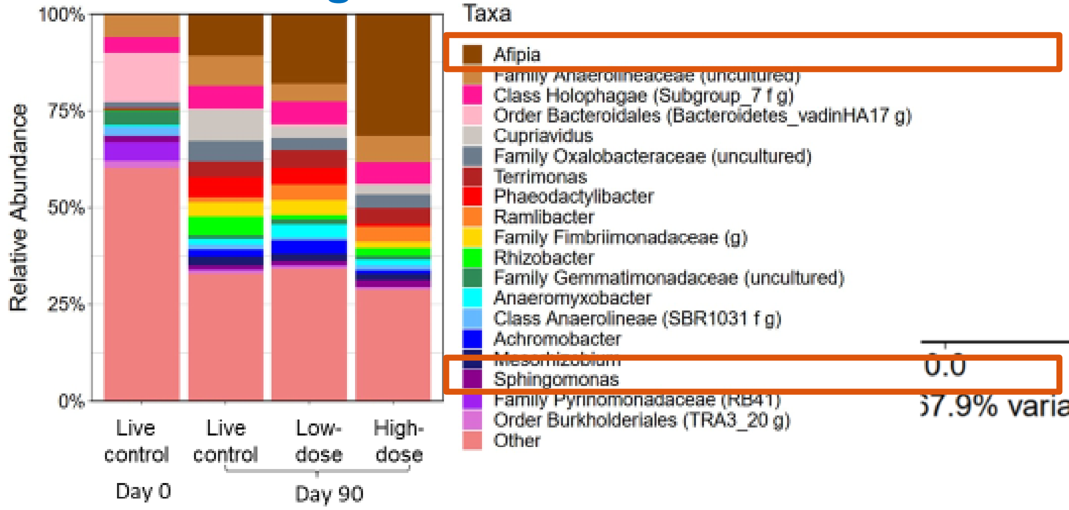
or Robins AFB soil.

- *Cupriavidus*
- *Variovorax*
- *Azospirillum*
- *Flavisolibacter*
- *Sphingomonas*
- *Ralstonia*



- *Afipia*
- *Sphingomonas*

Loring



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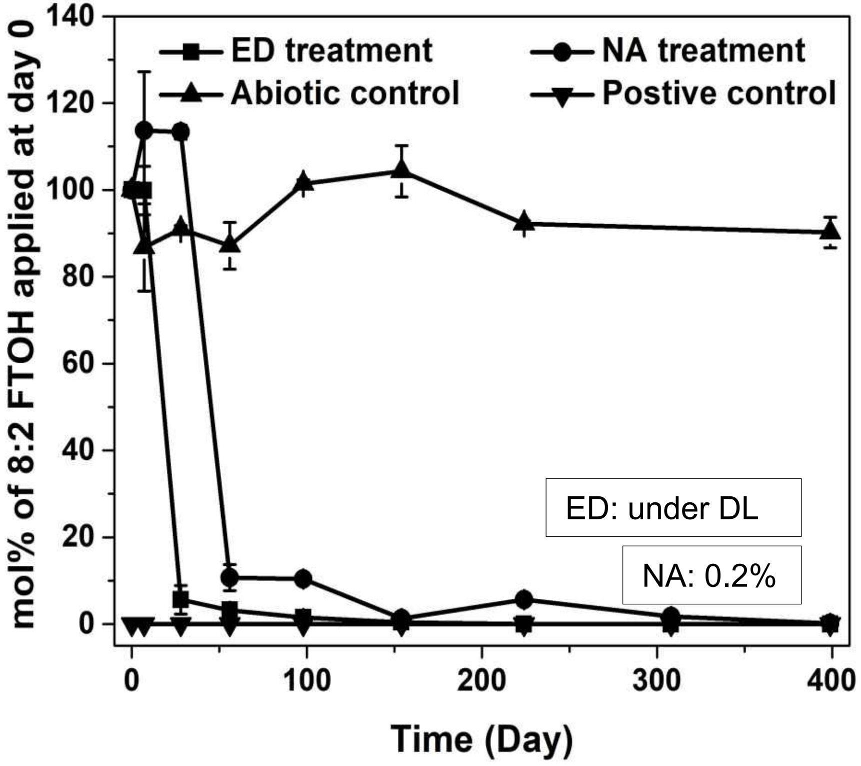
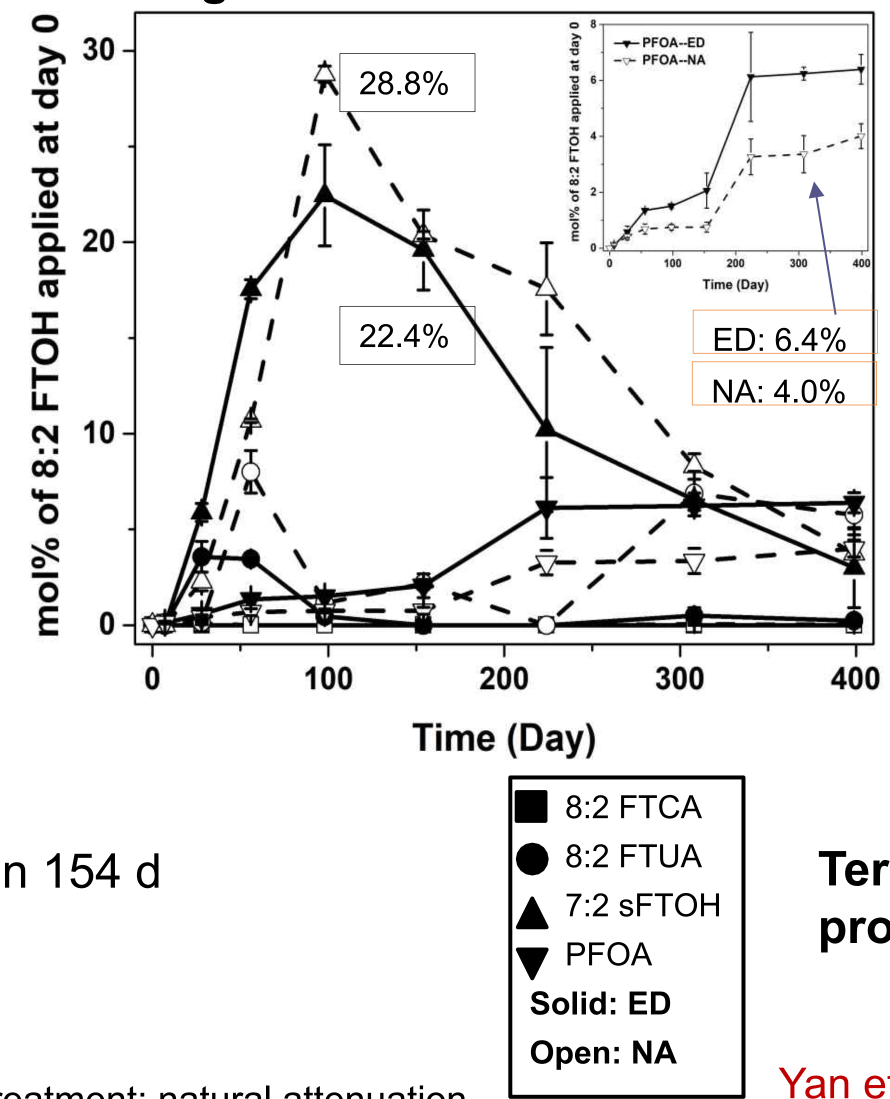
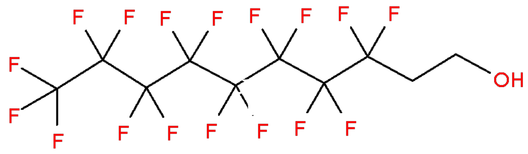
8:2 FTOH BTF under Nitrate-Reducing Condition

Profile of 8:2 FTOH



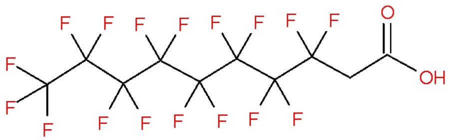
Targeted Metabolite Formation



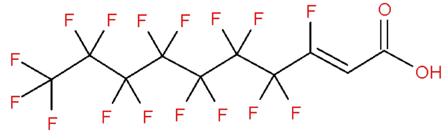


8:2 FTOH

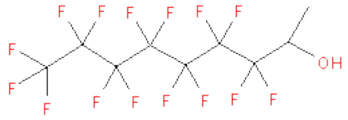
Intermediates



8:2 FTCA

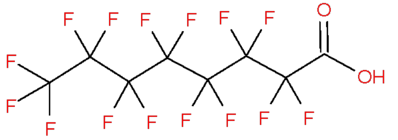


8:2 FTUA



7:2 sFTOH

Terminal product



PFOA

- > 98% of 8:2 FTOH was biotransformed within 154 d
- Half-life (ED): 12.5 d
- Half-life (NA): 36.5 d

* ED treatment: biostimulation w/ lactate as e- donor; NA treatment: natural attenuation

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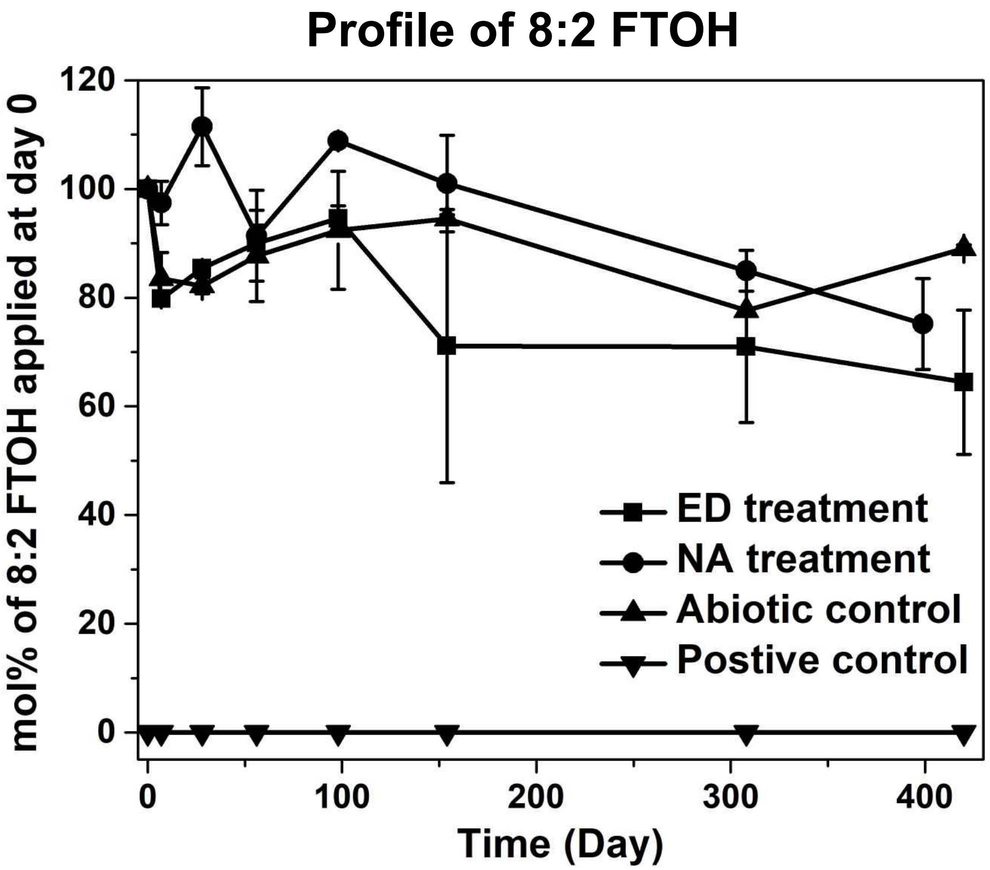
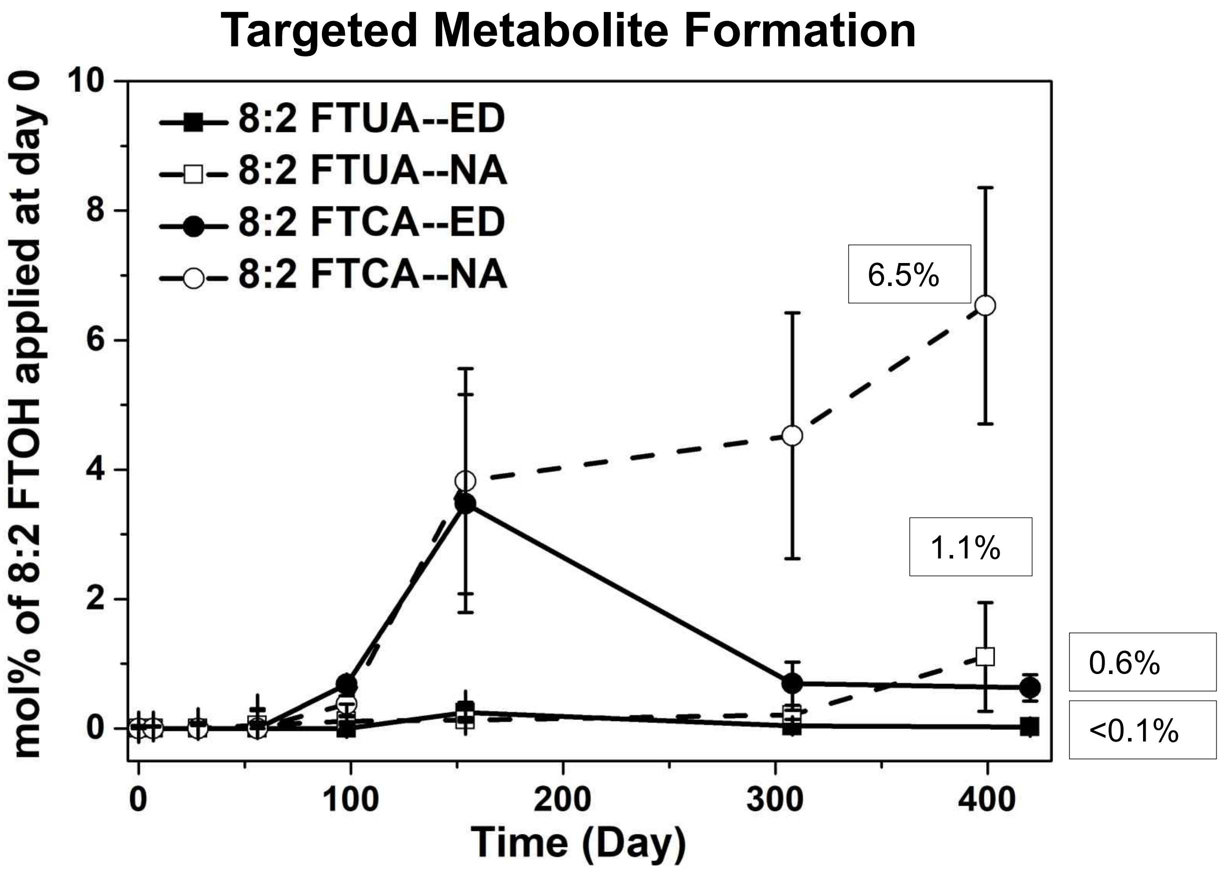
8:2 FTOH BTF under Sulfate-Reducing Condition



- 64.4% remained in ED treatment
- 75.2% remained in NA treatment



- Small amount of polyfluorinated **8:2 FTCA** and **8:2 FTUA** were detected as transformation products.

* ED treatment: biostimulation w/ lactate as e- donor; NA treatment: natural attenuation

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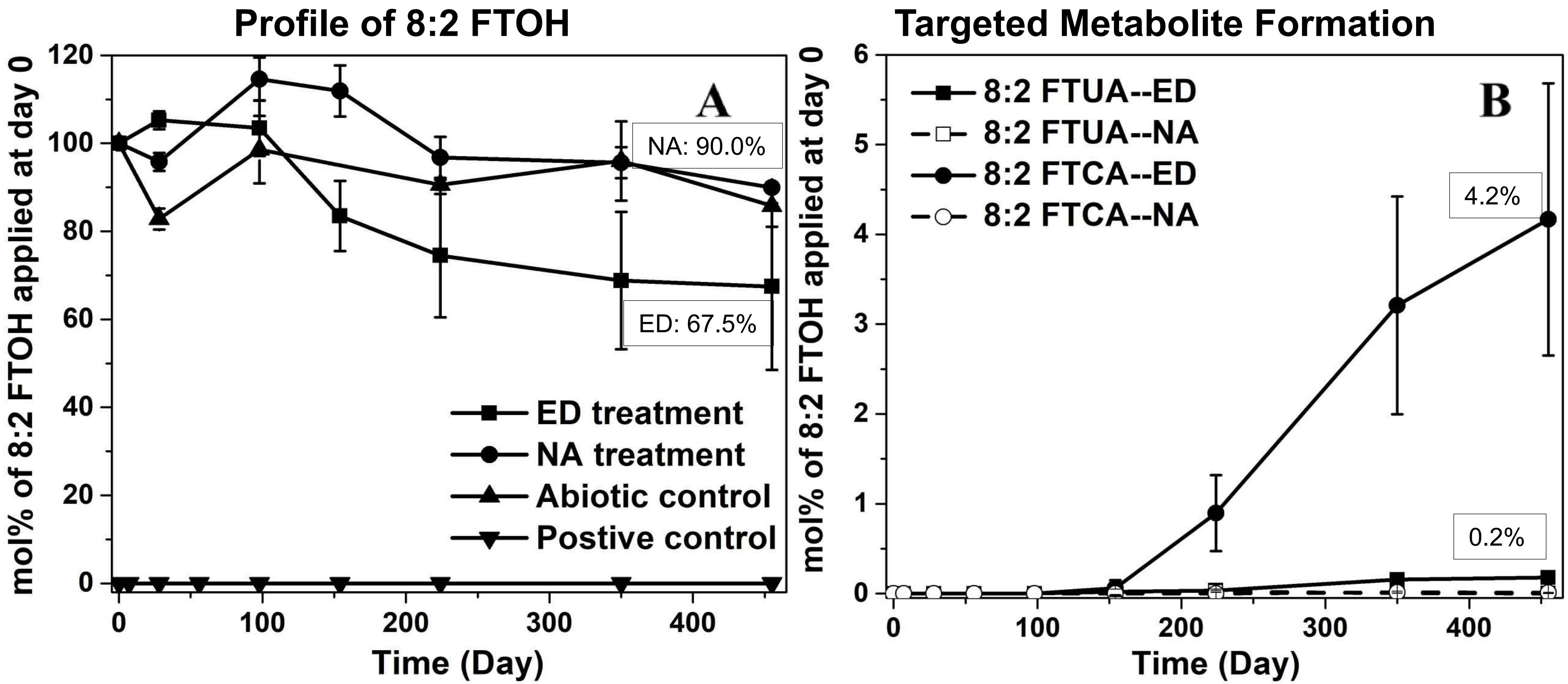
8:2 FTOH BTF under Iron-Reducing Condition



- Biotransformation of 8:2 FTOH was not observed till 154 d (ED) and 224 d (NA).
- Small amount of polyfluorinated **8:2 FTCA** and **8:2 FTUA** were detected as transformation products.

* ED treatment: biostimulation w/ lactate as e- donor; NA treatment: natural attenuation

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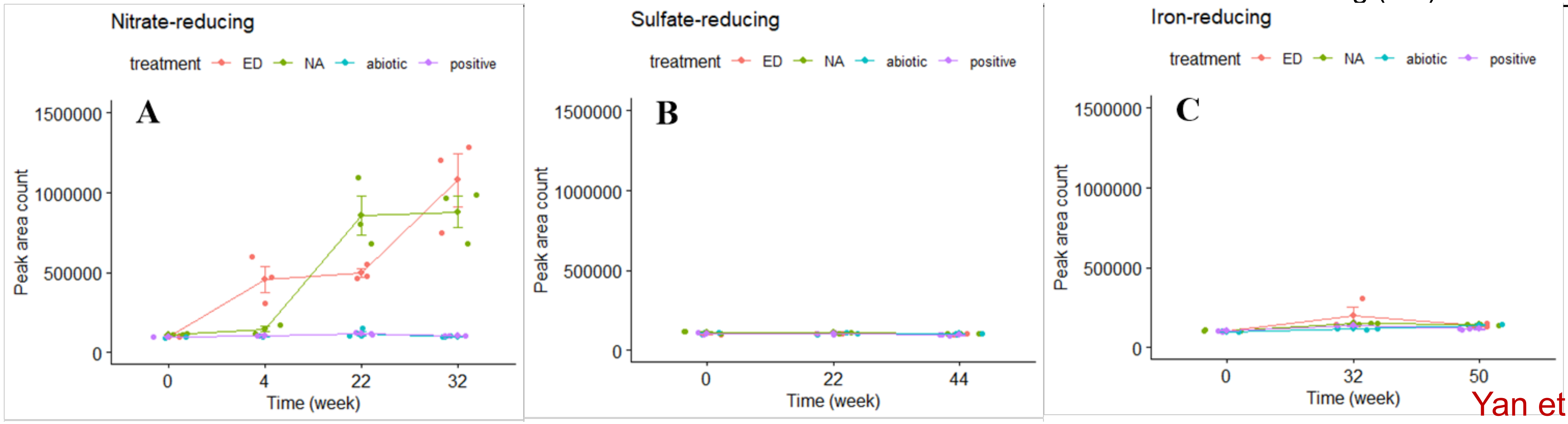
Potential Anaerobic 8:2 FTOH BTF Products Identified by LC-HRMS Analysis

Abbreviated name	Formula	Mass (m/z)	Mass error [ppm]	Level of confidence	Identified in microcosms
1H-perfluoroheptane	C_7HF_{15}	368.9764	0.14	1	Nitrate-reducing (ED & NA)
3-OH-7:3 acid	$C_{10}H_5F_{15}O_3$	456.9930	0.36	2	
7:3 U acid	$C_{10}H_3F_{15}O_2$	438.9822	0.24	3	
7:3 U amide	$C_{10}H_4F_{15}NO$	437.9975	-0.05	4	
3-F-7:3 acid	$C_{10}H_4F_{16}O_2$	458.9885	0.67	3	Sulfate-reducing (ED & NA), iron-reducing (ED)



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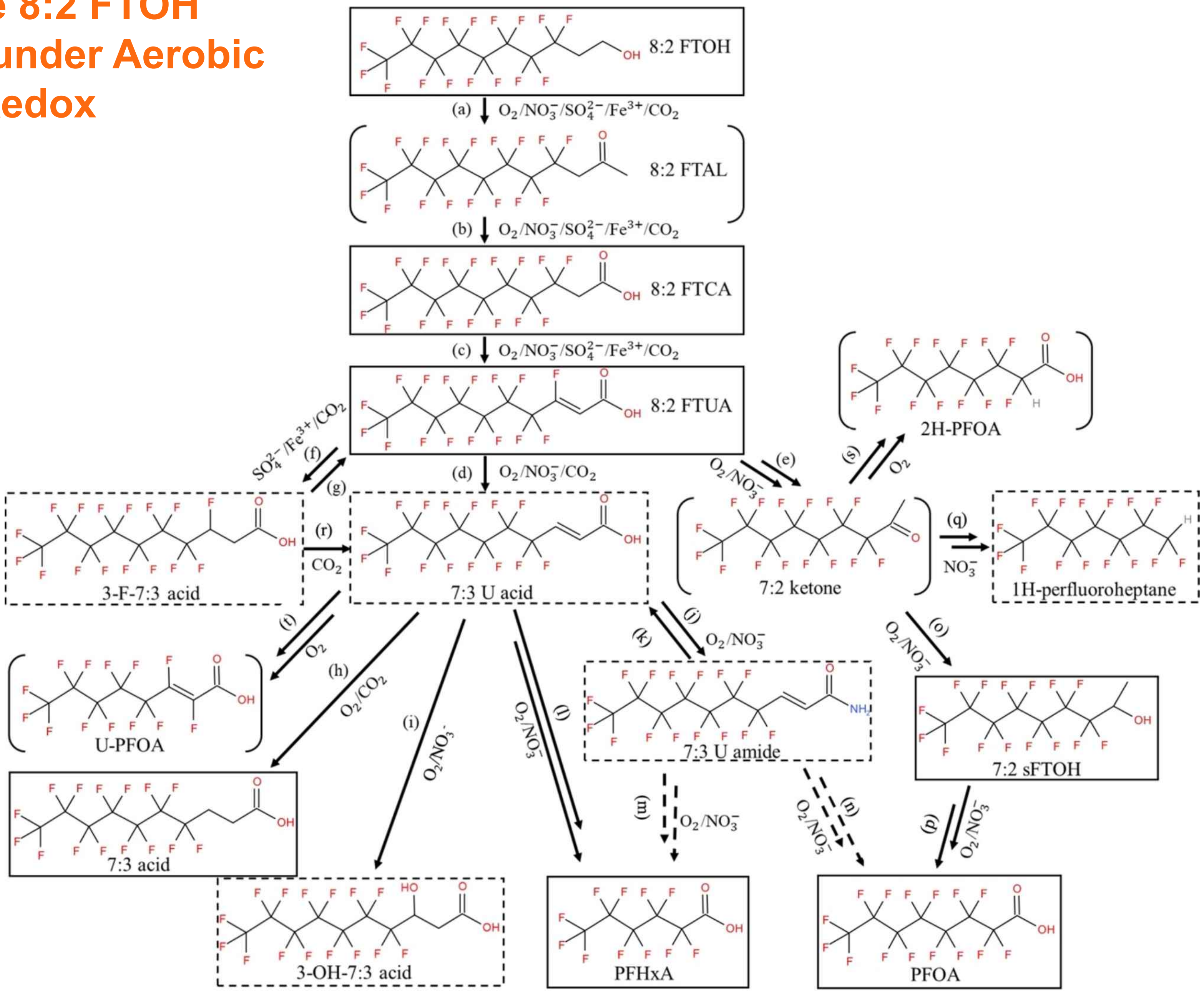
The time trend of 7:3 U acid during 8:2 FTOH biotransformation in each treatment under (A) nitrate-reducing; (B) sulfate-reducing; and (C) iron-reducing conditions based on peak areas of extracted ion chromatograms.

Comprehensive 8:2 FTOH BTF pathways under Aerobic and Anerobic Redox Conditions



Targeted analyzed by LC-MS/MS

Non-targeted identified by LC-HRMS

Compound proposed and/or detected in previous studies

Reaction expected to occur

Potential reaction that may or may not occur

Double arrows indicate multiple steps involved

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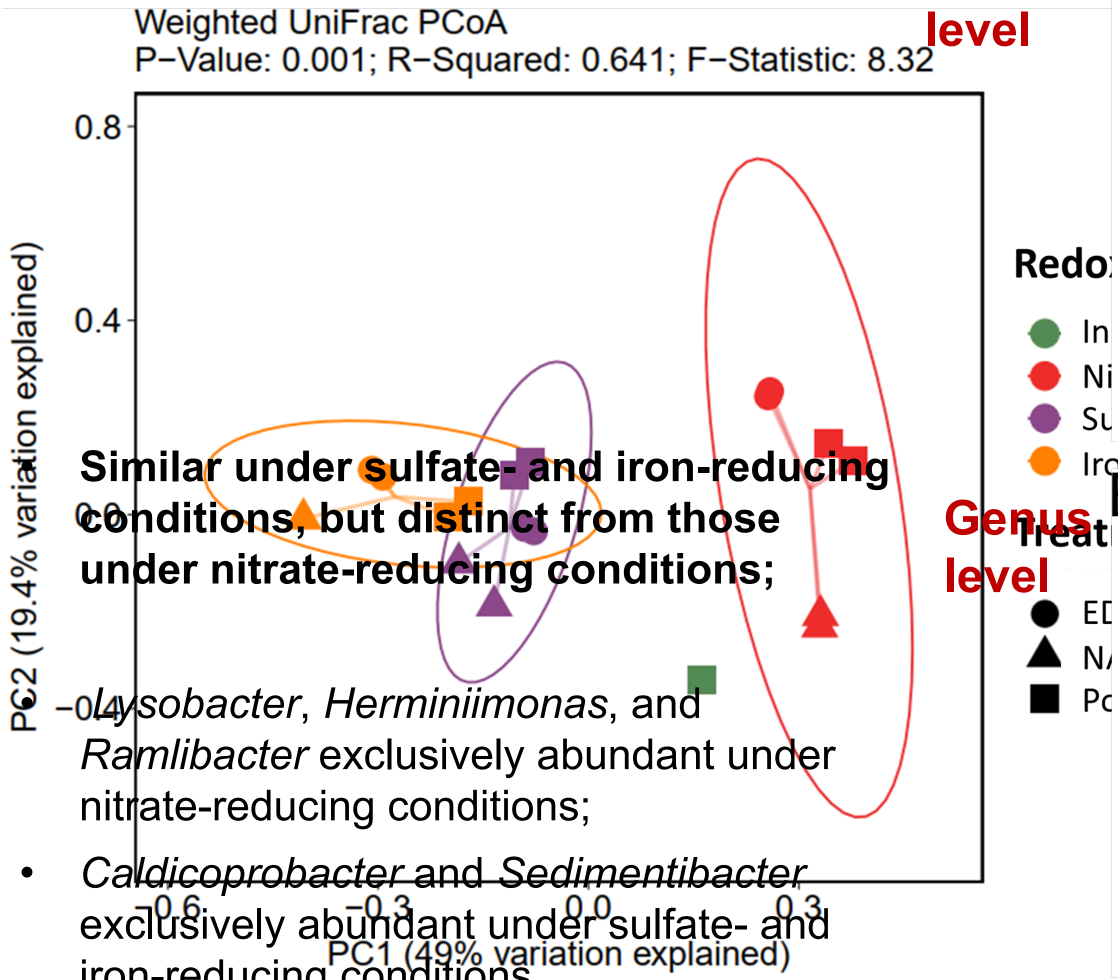
Why biotransformation of 8:2 FTOH differs under various redox conditions?

Microbial Communities

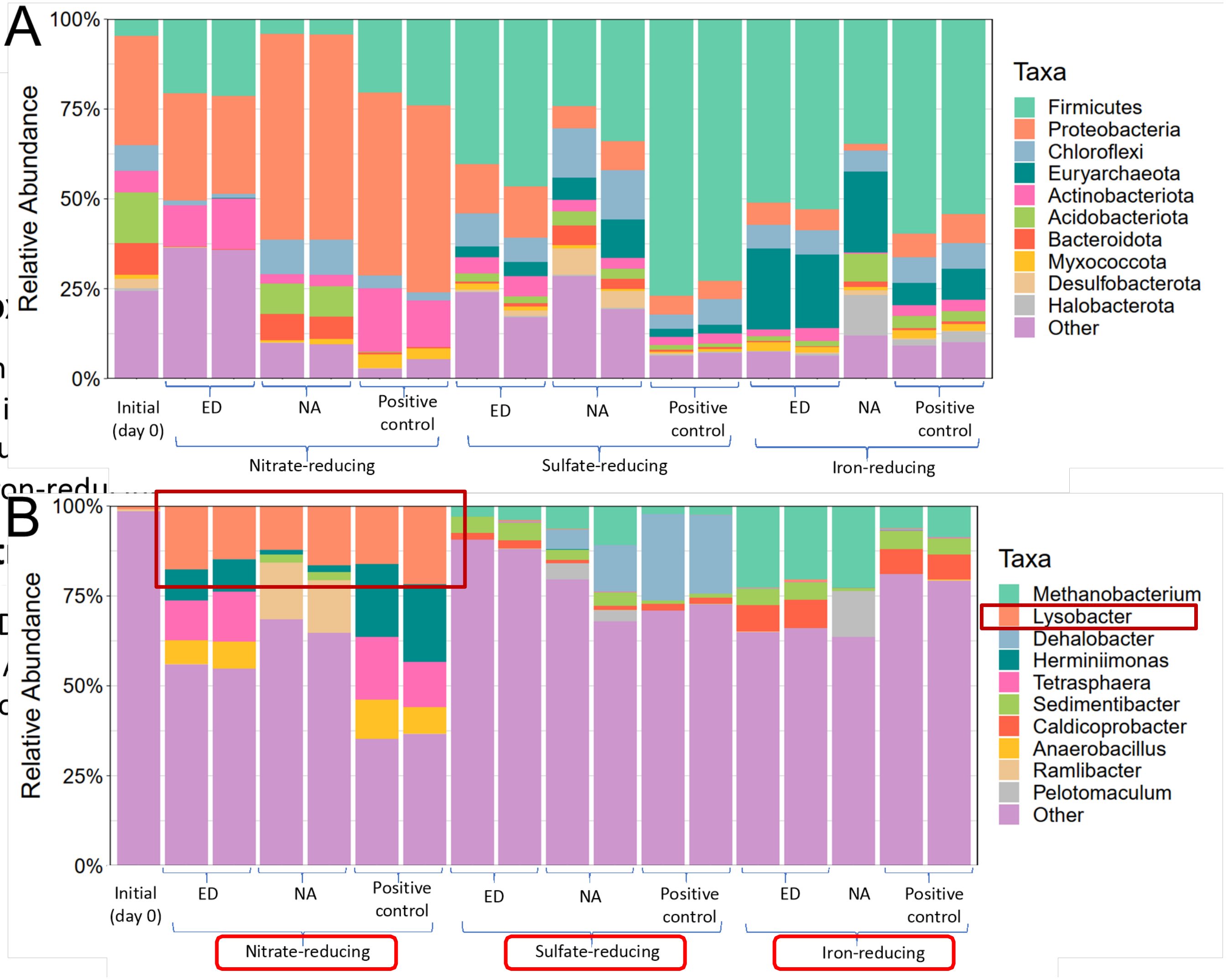


Similar under sulfate- and iron-reducing conditions, but distinct from those under nitrate-reducing conditions;

- *Lysobacter*, *Herminiimonas*, and *Ramlibacter* exclusively abundant under nitrate-reducing conditions;
- *Caldicoprobacter* and *Sedimentibacter* exclusively abundant under sulfate- and iron-reducing conditions.

Phylum level

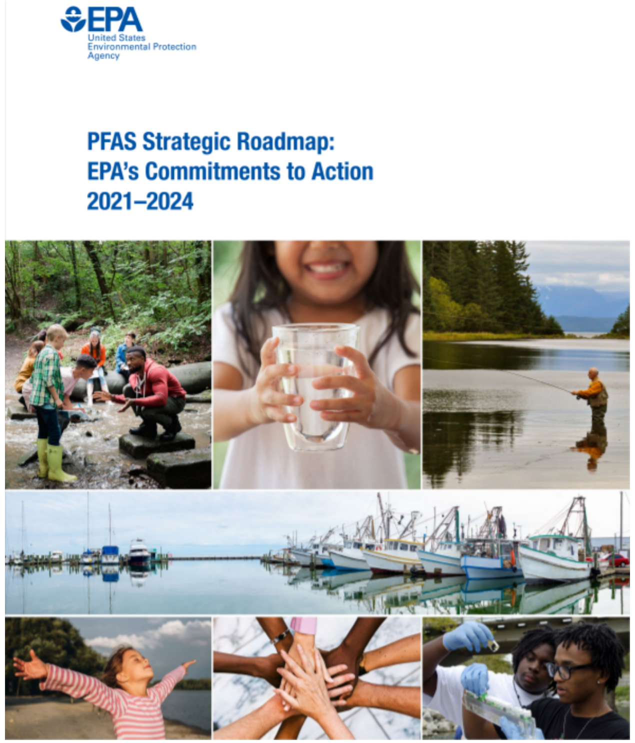
Genus level



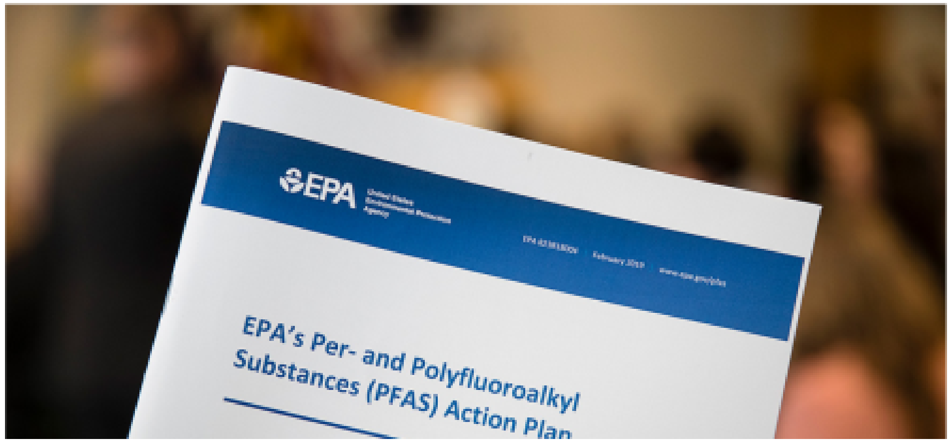
Principal coordinate analysis (PCoA) plot of phylogenetic microbial community changes among the microcosms under different redox conditions.

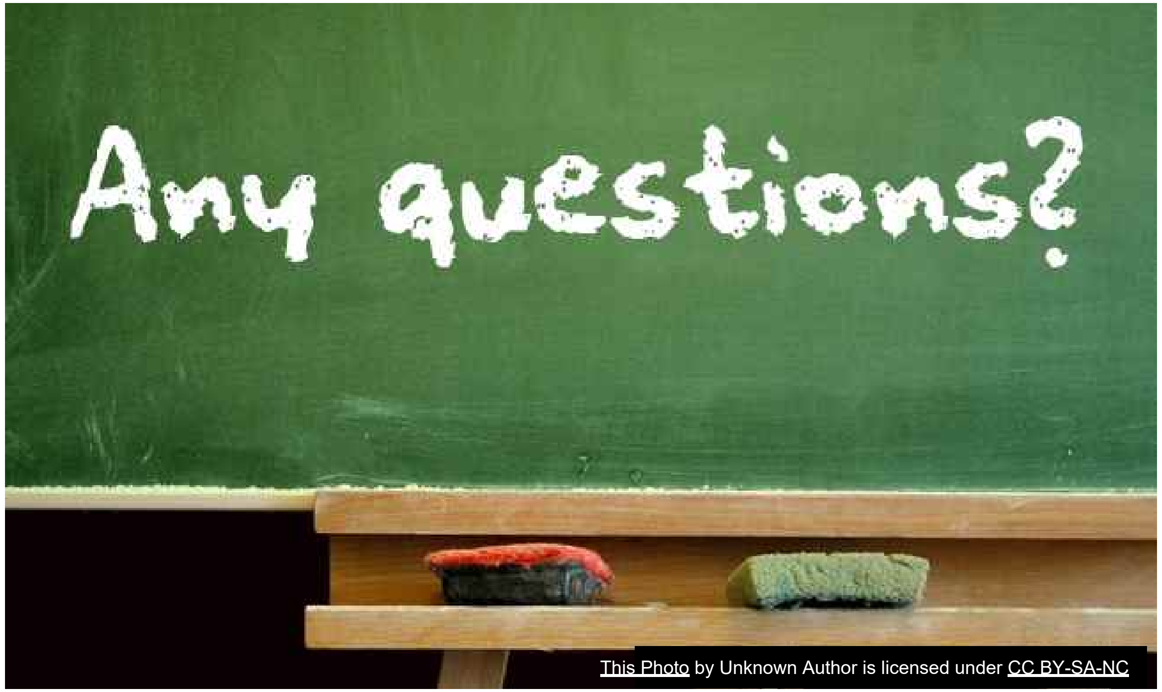
Key points

- 8:2 FTOH was demonstrated to be **amendable to biotransformation** by the native soil microbial communities from AFFF-impacted soils.
- 8:2 FTOH biotransformation **(e.g., rate, pathway, extent)** was **microbial community and redox condition specific**.
    - Only under aerobic and nitrate-reducing conditions, significant PFOA was formed
- Perfluoroheptanal, 1H-perfluoroheptane, 1H-perfluorohexane, and 3-F-7:3 acid were identified as novel 8:2 FTOH biotransformation products.



Biden admin launches plan to regulate PFAS





This work was supported by the Strategic Environmental Research and Development Program (SERDP) Project ER18-1149: Development and Laboratory Validation of Mathematical Modeling Tools for Prediction of PFAS Transformation, Transport, and Retention in AFFF Source Areas.

SERDP
DOD ▪ EPA ▪ DOE

Yan, P.F., Dong, S., Manz, K.E., Liu, C., Woodcock, M.J., Mezzari, M.P., Abriola, L.M., Pennell, K.D. and Cápiro, N.L., 2022. Biotransformation of 8: 2 Fluorotelomer Alcohol in Soil from Aqueous Film-Forming Foams (AFFFs)-Impacted Sites under Nitrate-, Sulfate-, and Iron-Reducing Conditions. *Environmental Science & Technology*, 56(19), pp.13728-13739. https://doi.org/10.1021/acs.est.2c03669

Dong, S., Yan, P.F., Liu, C., Manz, K.E., Mezzari, M.P., Abriola, L.M., Pennell, K.D. and Cápiro, N.L., 2023. Assessing aerobic biotransformation of 8: 2 fluorotelomer alcohol in aqueous film-forming foam (AFFF)-impacted soils: Pathways and microbial community dynamics. *Journal of Hazardous Materials*, 446, p.130629. https://doi.org/10.1016/j.jhazmat.2022.130629

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