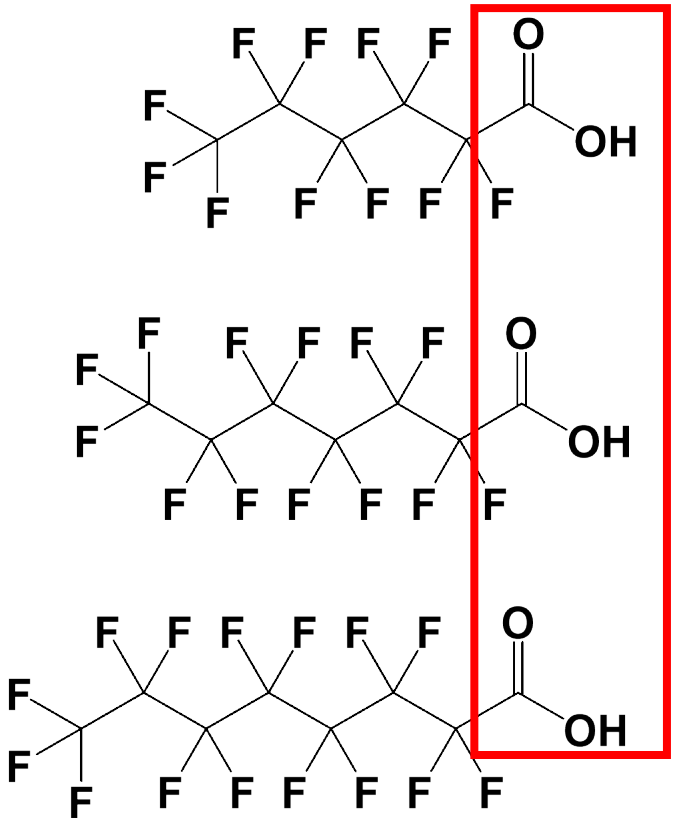
Aerobic Biotransformation and Biodefluorination of Fluorotelomer Carboxylic Acids (FTCAs) in Municipal Wastewater Treatment Sludge

Chen Wu, Qi Wang, Hao Chen, Mengyan Li
Department of Chemistry and Environmental Science
New Jersey Institute of Technology

2022 Chlorinated Conference
05/23/2022

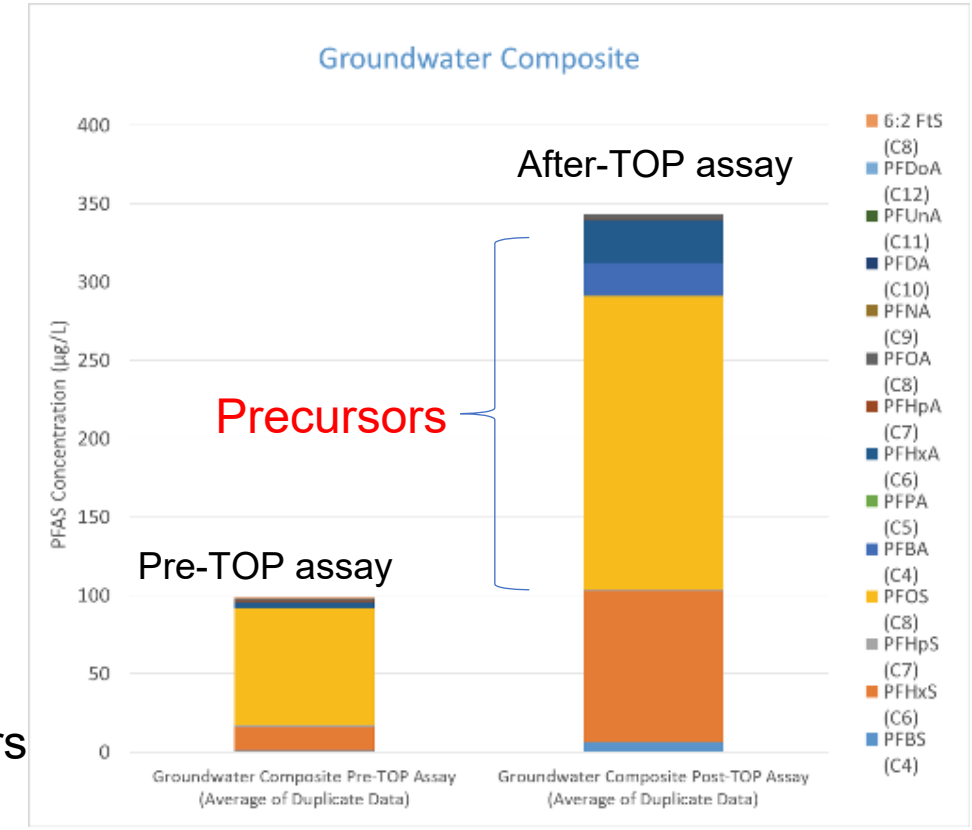
PFCAs and Their Precursors

PFCAs: Perfluorinated Carboxylic Acids

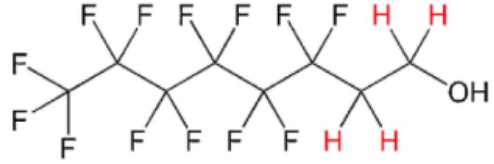


Total Oxidizable Precursors (TOP) Assay

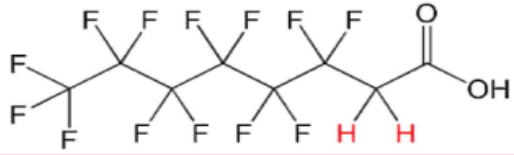
PFCAs ← PFCA precursors



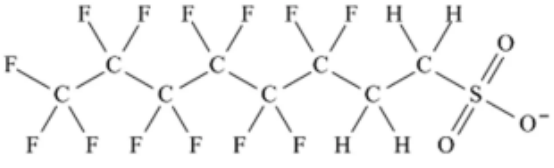
FTCAs: Fluorotelomer Carboxylic Acids



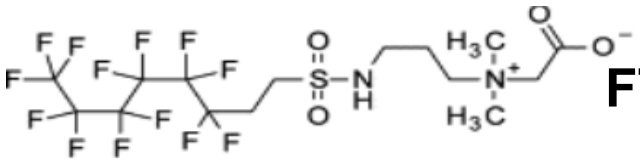
FTOH



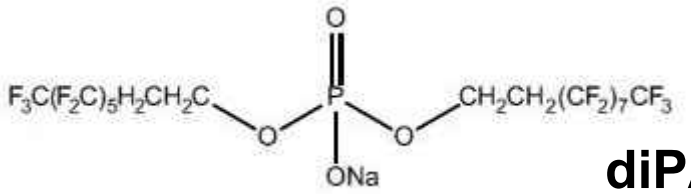
FTCA



FTS

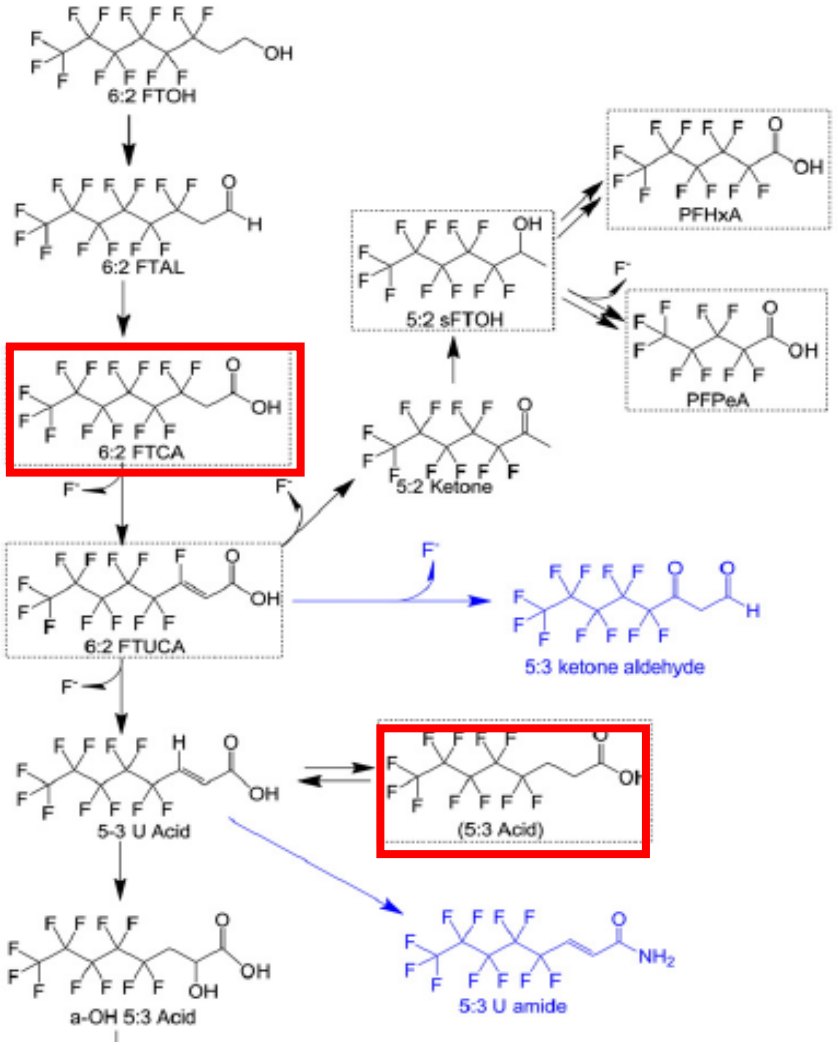


FTAB

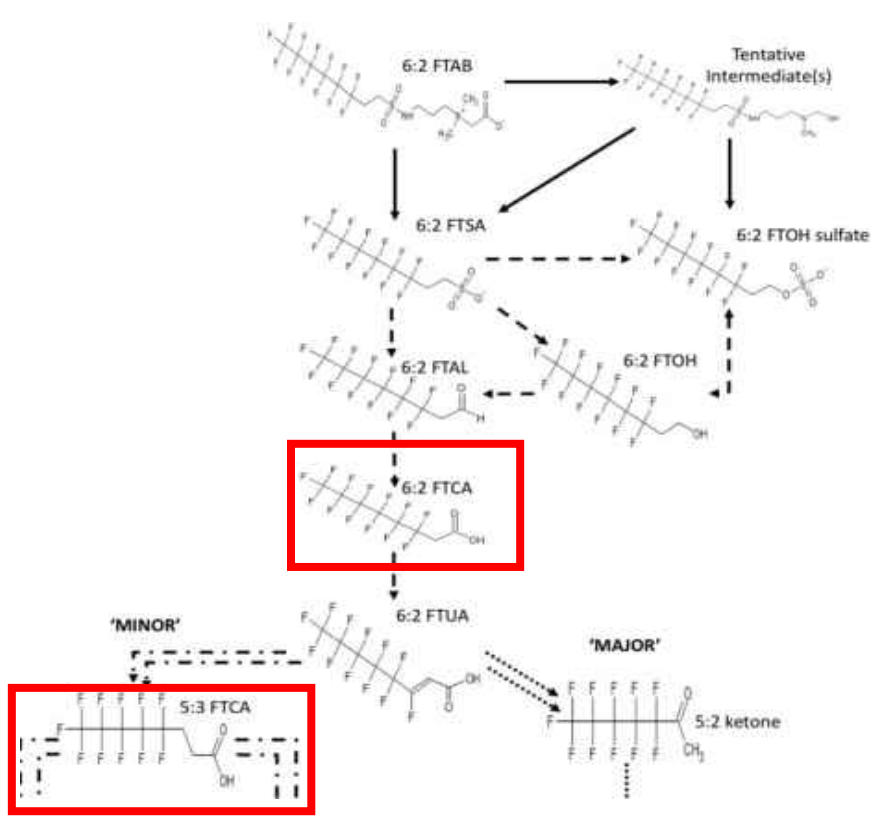


diPAP

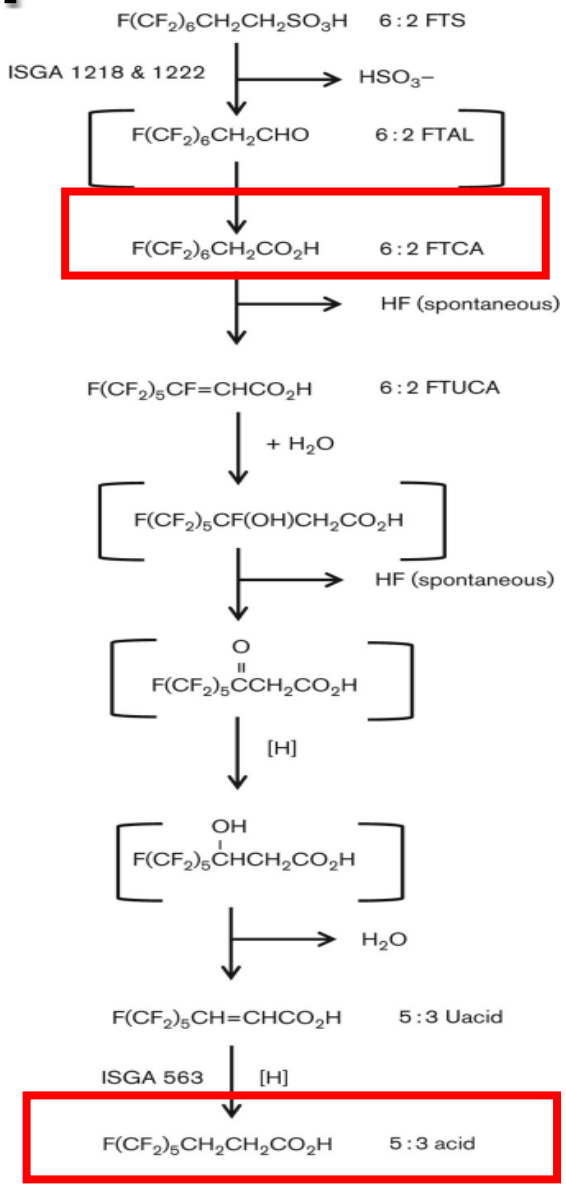
FTCAs as Key Intermediates of PFCA Precursor Biotransformation



J Liu, SM Avendaño, Environment international, 2013

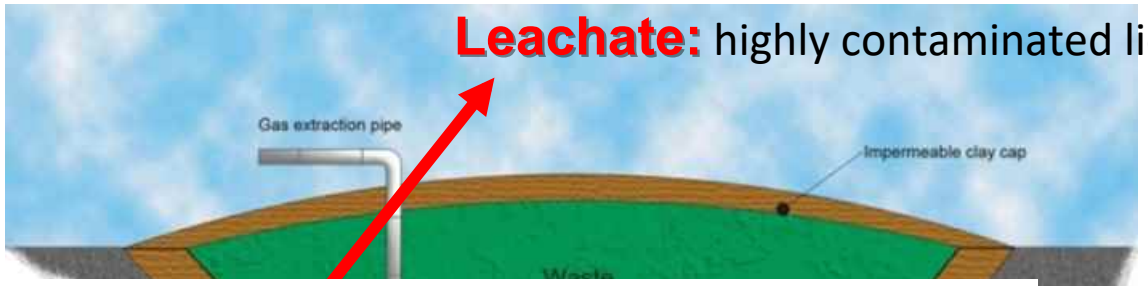


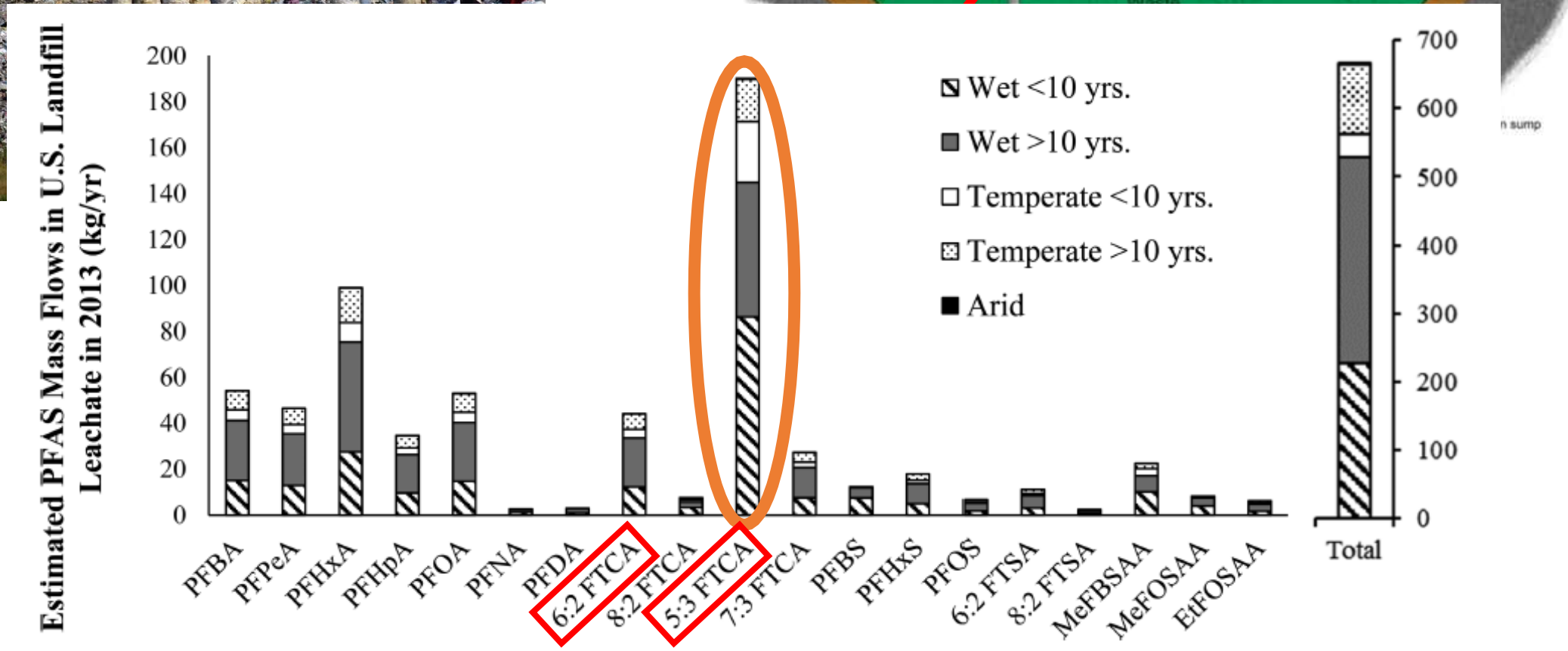
Dayton M.J. Shaw, et al, Science of The Total Environment, 2019



Jonathan D.V. Hamme, et al, Microbiology, 2013

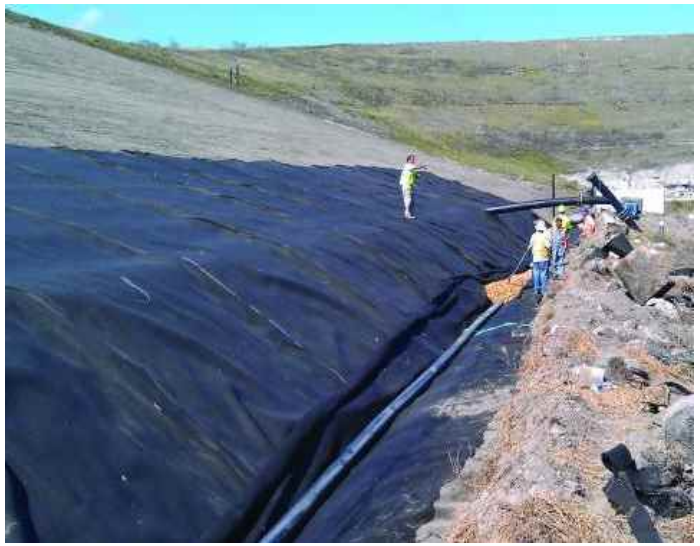
FTCAs Are Dominant in Landfill Leachates





Johnsie Lang, Jennifer Field, et,al., Environ. Sci. Technol, 2017

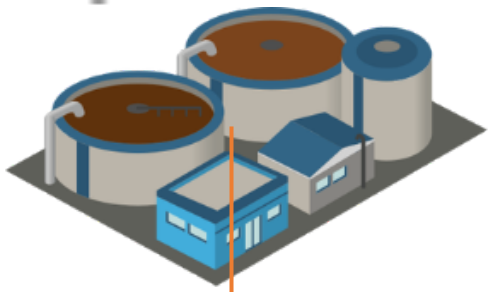
FTCAs Can Enter WWTPs via the Discharge of Landfill Leachates

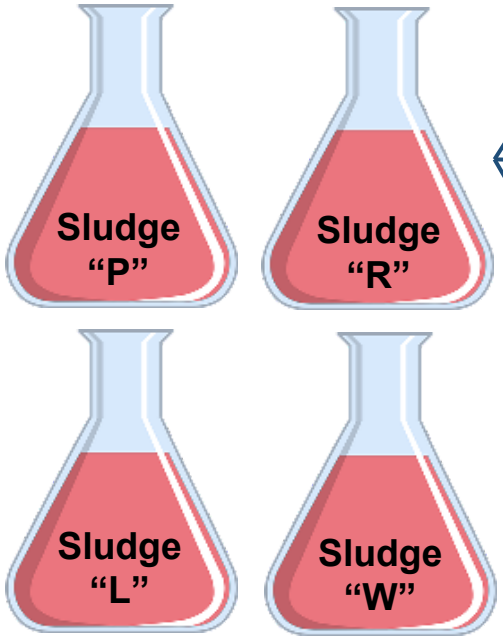


discharge

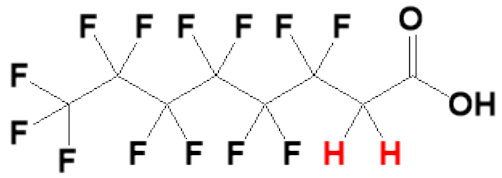
- How are FTCAs transformed over the municipal wastewater treatment train?
- What are the transformation products of FTCAs?
- How do FTCAs affect the performance of activated sludge?

Experimental Workflow

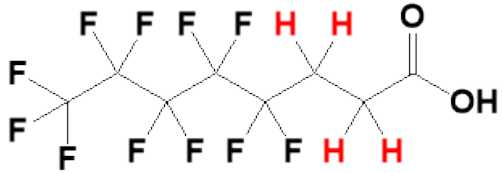




6:2 FTCA Treatment



5:3 FTCA Treatment



Microbial Control
live sludge

Analytical Control
FTCA

Abiotic Control
FTCA + autoclaved sludge

Sludge Treatment
FTCA + live sludge

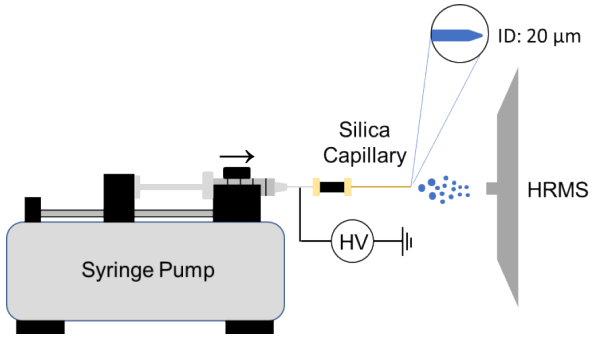
- Washed by PBS
- Incubated in synthetic wastewater (SWW)

Experimental Workflow

- F^- releasing

Fluoride probe

- FTCAs removal and target PFAS generation
- Novel transformation products identification



Nano-ESI HRMS

Thermo Scientific Q Exactive Plus MS

- Microbial community analysis

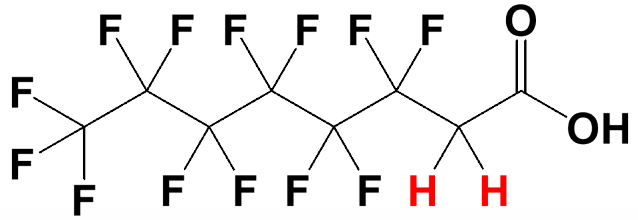
16S rRNA sequencing

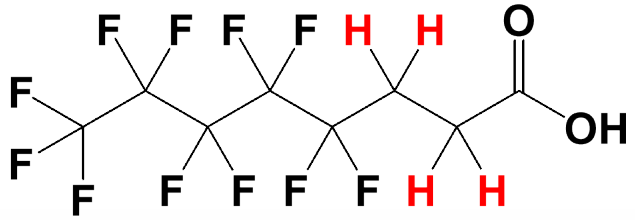
Analytical Control
FTCA

Abiotic Control
FTCA + autoclaved sludge

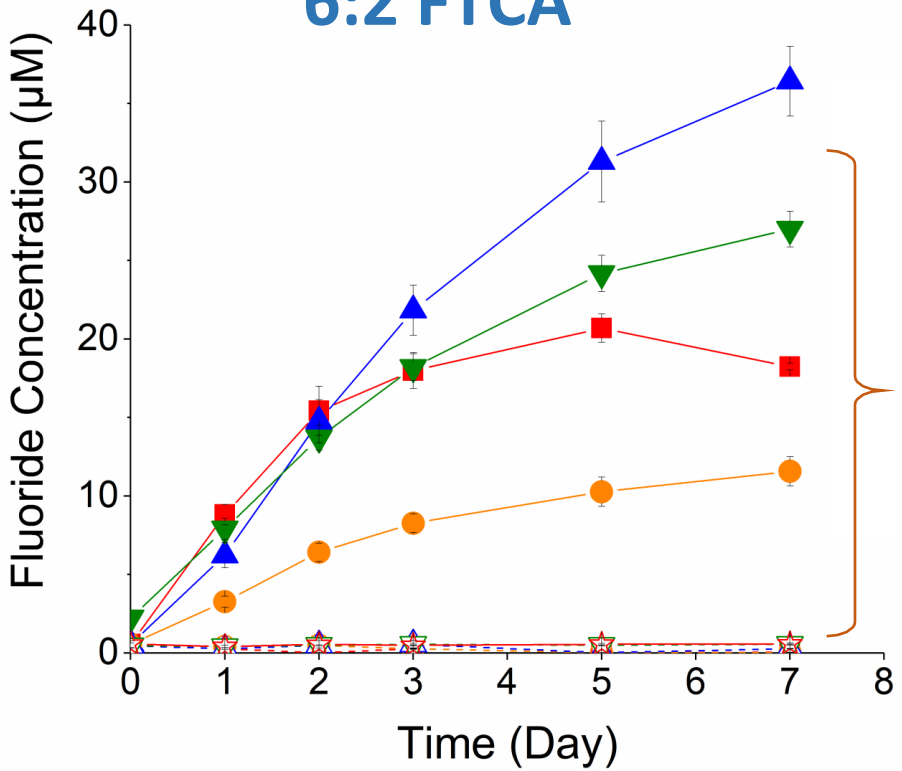
Sludge Treatment
FTCA + live sludge

FTCAs Exhibited Distinct Defluorination Potential

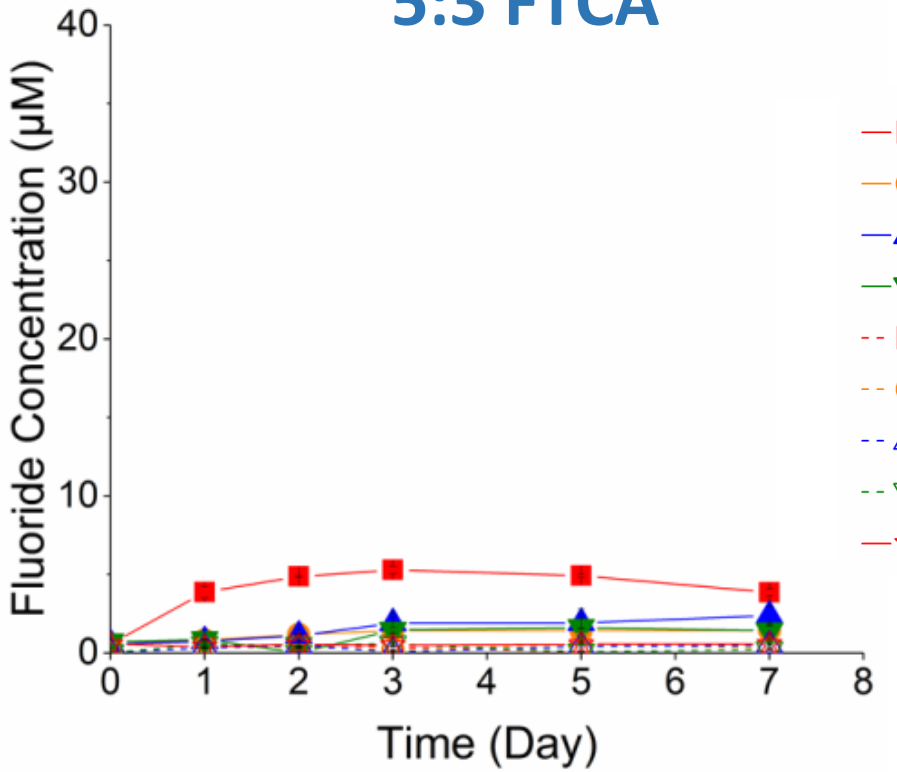


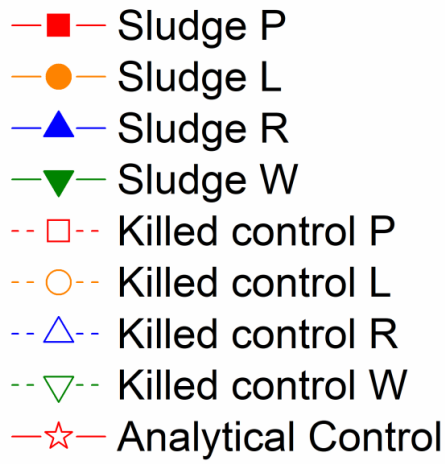


6:2 FTCA



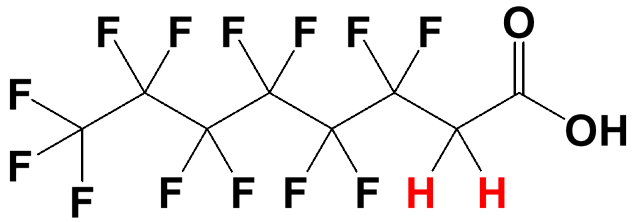
5:3 FTCA

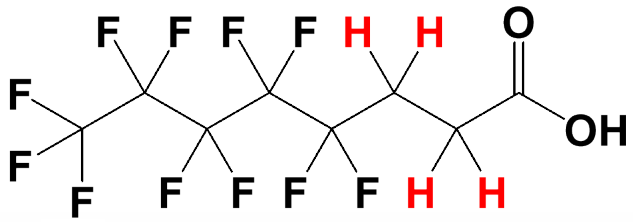


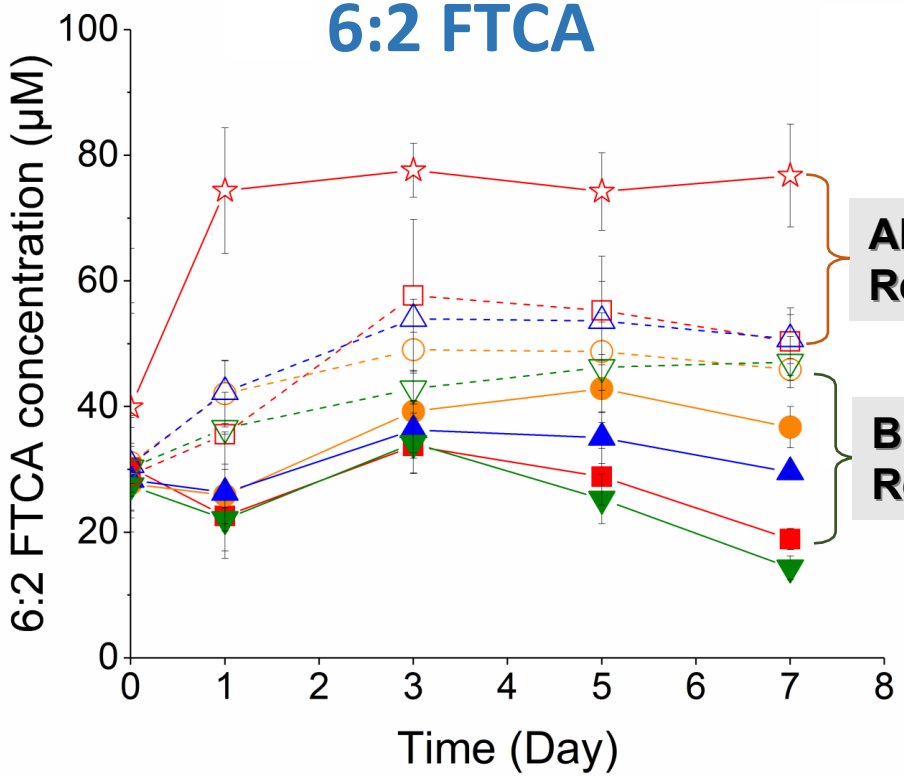


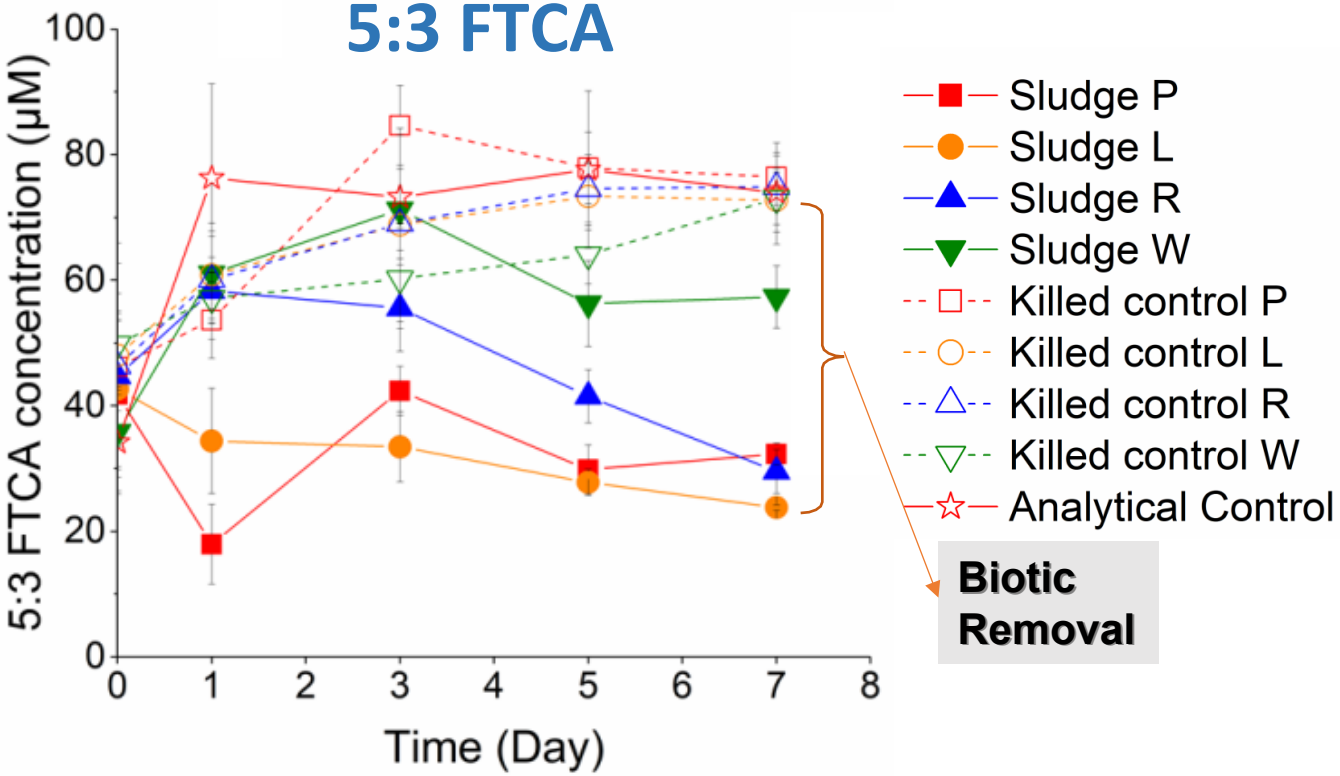
Significant F^- release was only observed in 6:2 FTCA treatments.

FTCAs Exhibited Distinct Biotic and Abiotic Removal



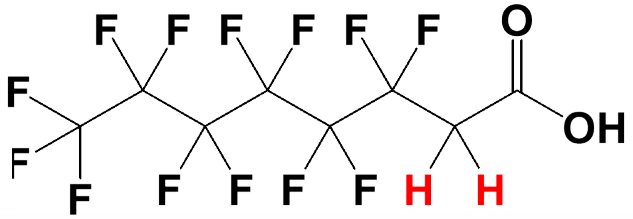




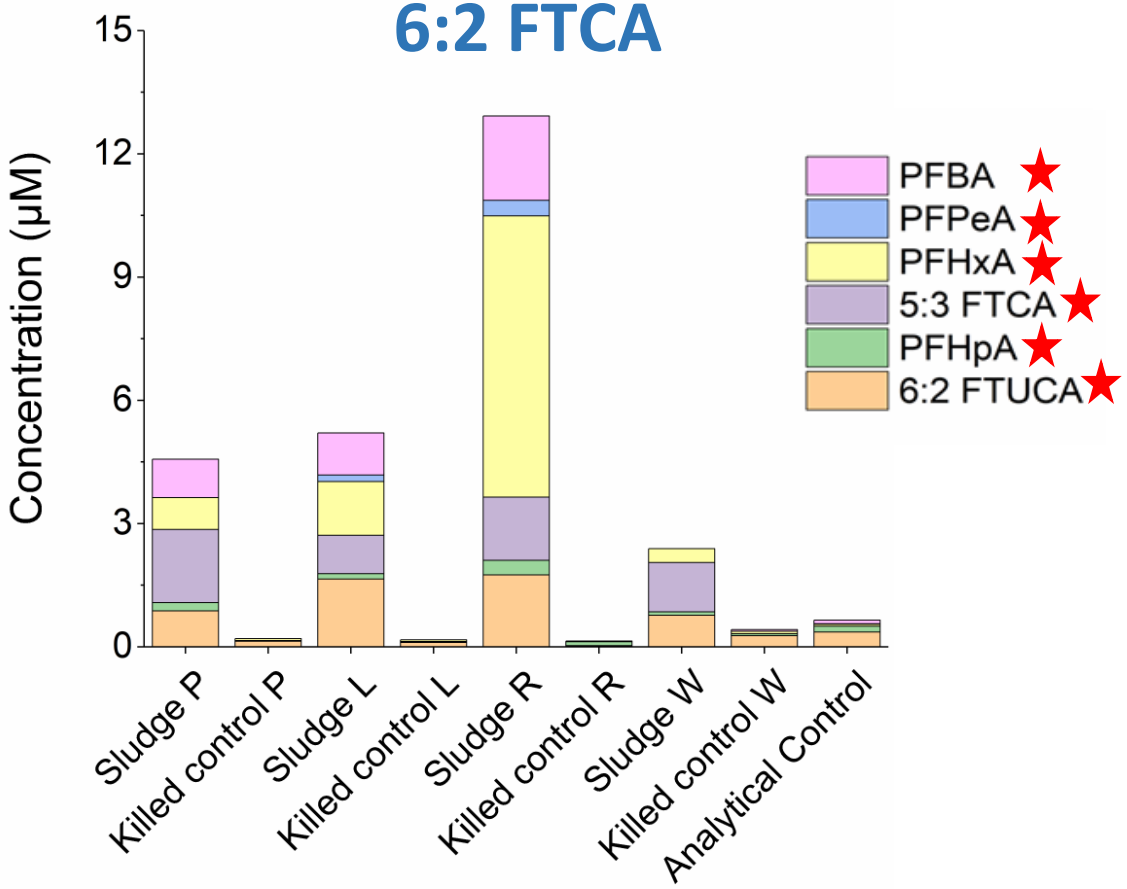


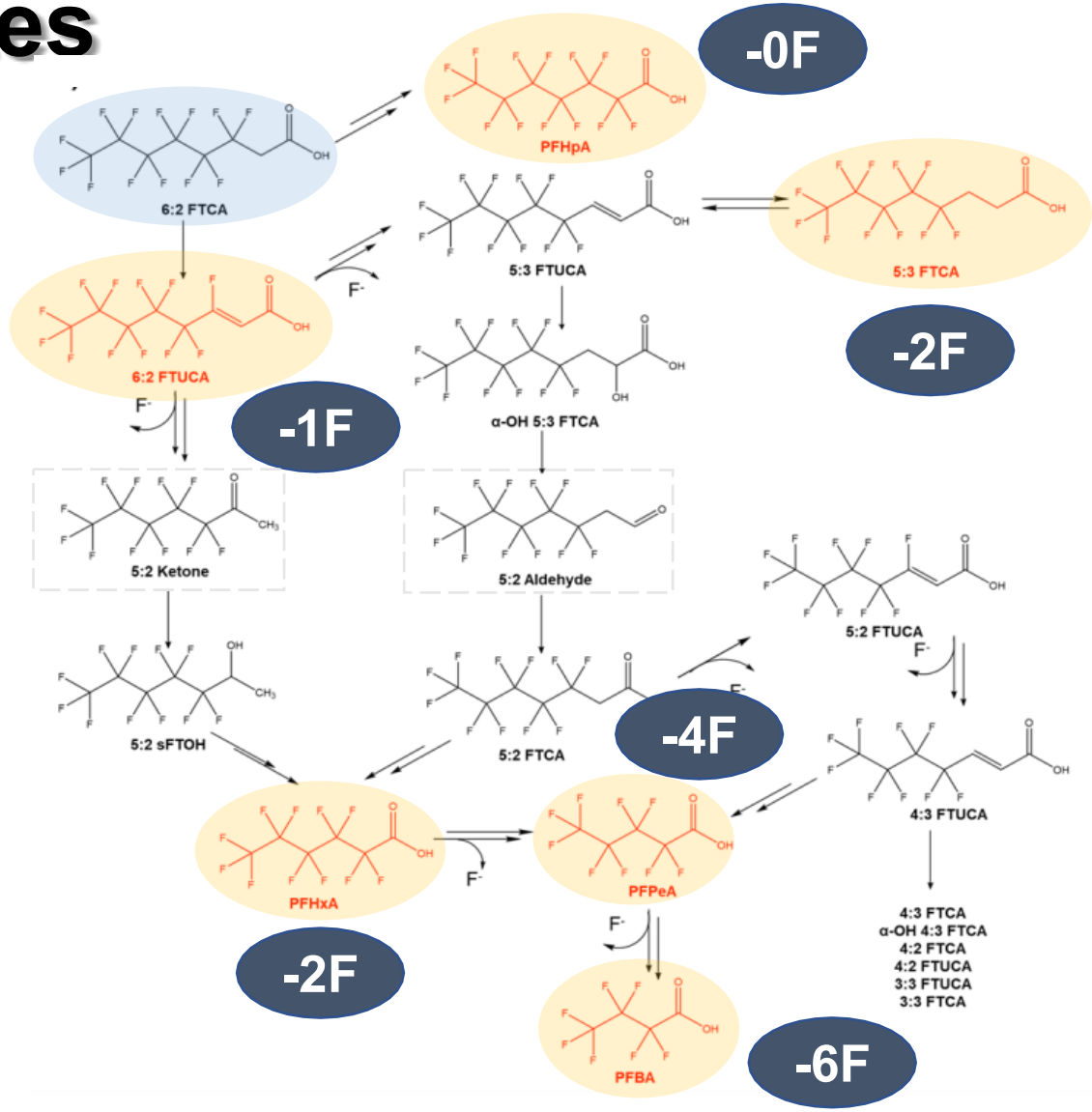
6:2 FTCA was removed abiotically and biotically, while 5:3 FTCA was removed biotically.

Biodefluorination of 6:2 FTCA Was Evident by Its Biotransformation Metabolites



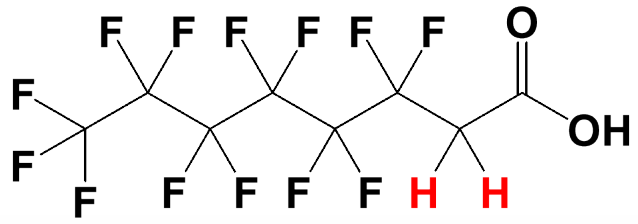
6:2 FTCA



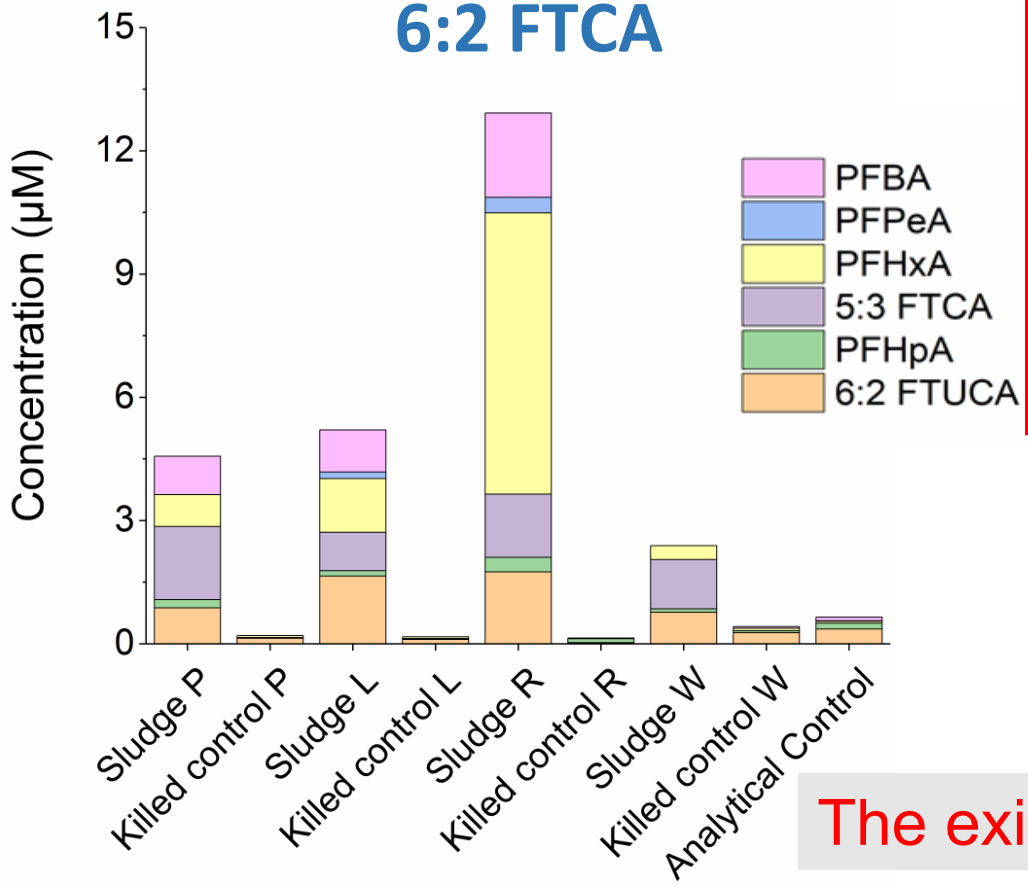


Target transformation products (TPs)

Biodefluorination of 6:2 FTCA Was Evident by Its Biotransformation Metabolites



6:2 FTCA



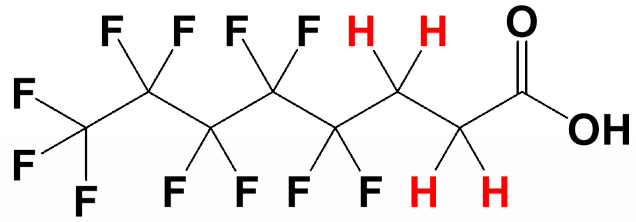
	Sludge P	Sludge L	Sludge R	Sludge W
Biotic Δ6:2 FTCA (μM)	29.6	11.8	19.0	34.2
Target TPs (μM)	4.6	5.2	12.9	2.4
Theoretical F release from Target TPs (μM)	8.9	8.6	27.9	1.3
Detected F^- (μM)	18.2	11.6	36.4	27.0
F- / biotic Δ6:2 FTCA	0.56	0.84	1.83	0.74

Biotic 6:2 FTCA removal > Target TPs formation

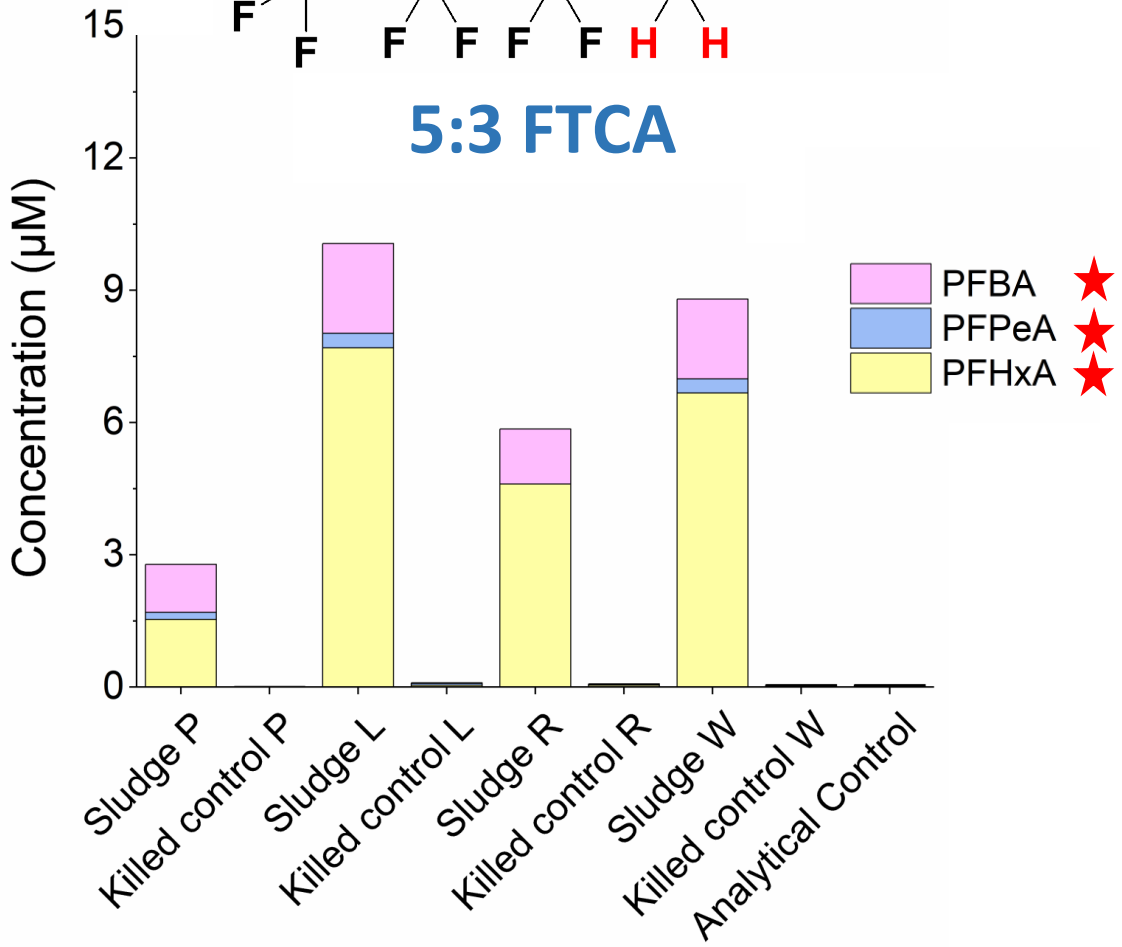
Theoretical F release from target TPs < Detected F^-

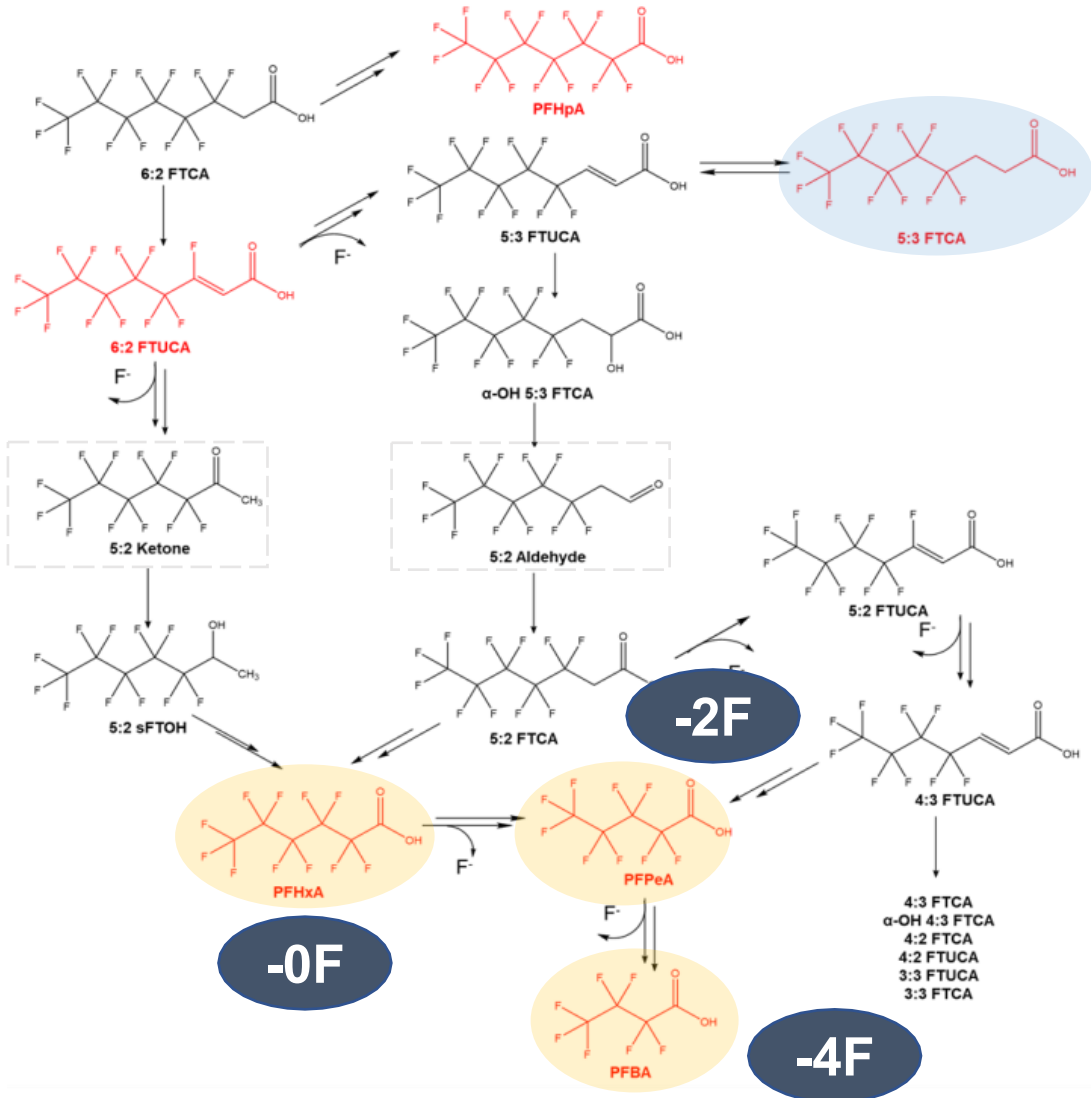
The existence of non-target TPs correlates with F^- release.

Formation of PFBA Was Contradictory to No Fluoride Release during 5:3 FTCA Biotransformation



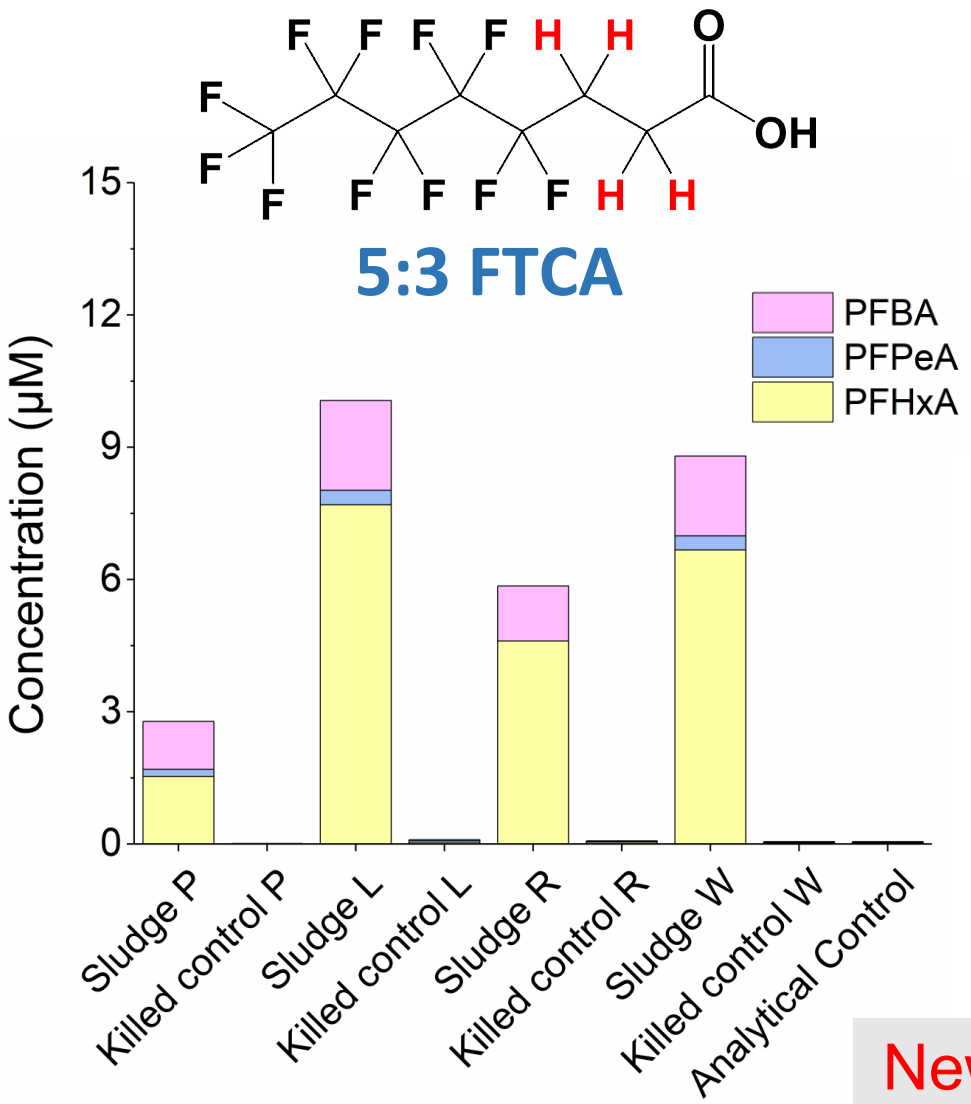
5:3 FTCA





Target transformation products (TPs)

Formation of PFBA Was Contradictory to No Fluoride Release during 5:3 FTCA Biotransformation



	Sludge P	Sludge L	Sludge R	Sludge W
Biotic Δ5:3 FTCA (μM)	41.6	50.2	44.4	16.6
Target TPs (μM)*	2.8	10.1	5.8	8.8
Theoretical F release from Target TPs (μM)	4.7	8.8	5.0	7.9
F- (μM)	1.4	3.9	1.4	2.4
F- / biotic Δ5:3 FTCA	0.01	0.06	0.01	0.09

Biotic 5:3 FTCA removal > Target TPs formation

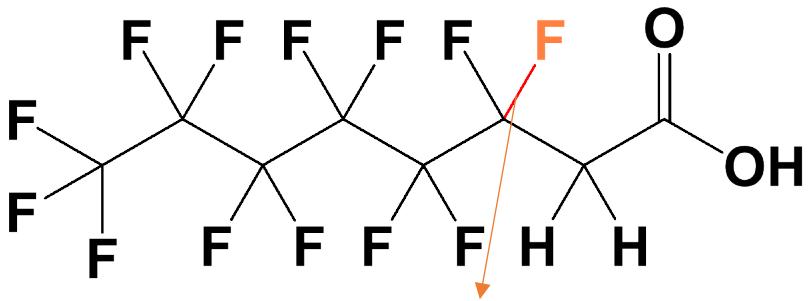
Theoretical F release from target TPs > Detected F^-

New non-fluoride releasing biodefluorination pathways?

Distinct Biotransformation Behavior of FTCAs

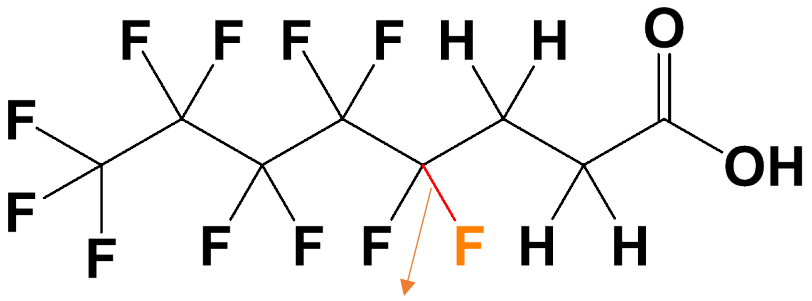
	6:2 FTCA	5:3 FTCA
Abiotic removal	+	-
F^- accumulation	+	-
Non-target TPs	+	+

6:2 FTCA



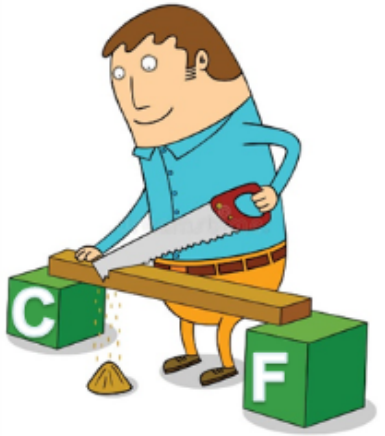
BDE: 105.3 kcal/mol

5:3 FTCA



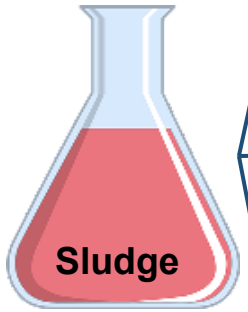
BDE: 107.7 kcal/mol

Defluorination



Bond Dissociation Energies (BDE) were calculated by DFT

Shifting of Dominant Taxa by FTCAs

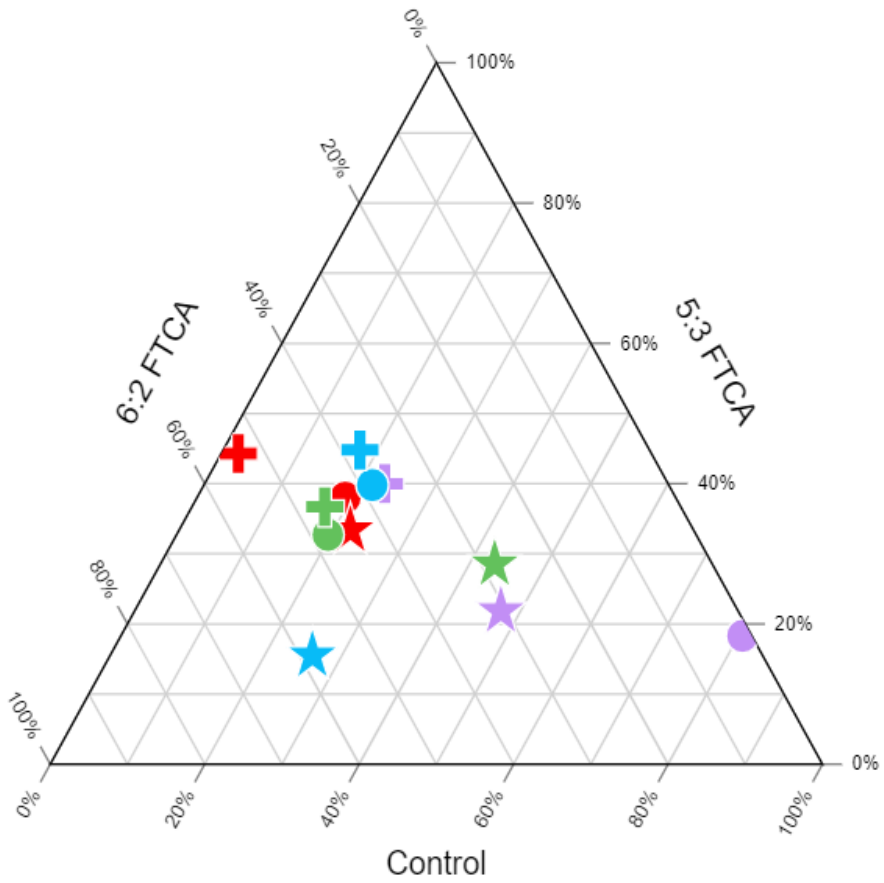


6:2 FTCA Treatment
live sludge + 6:2 FTCA

5:3 FTCA Treatment
live sludge + 5:3 FTCA

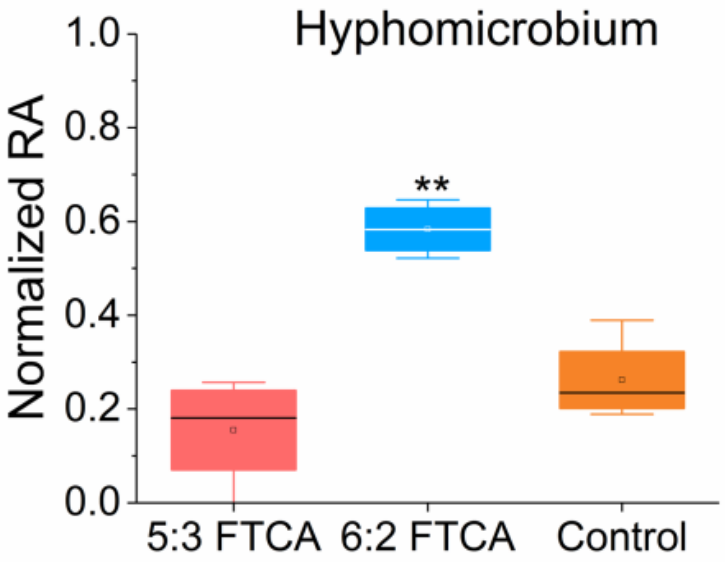
Microbial Control
live sludge

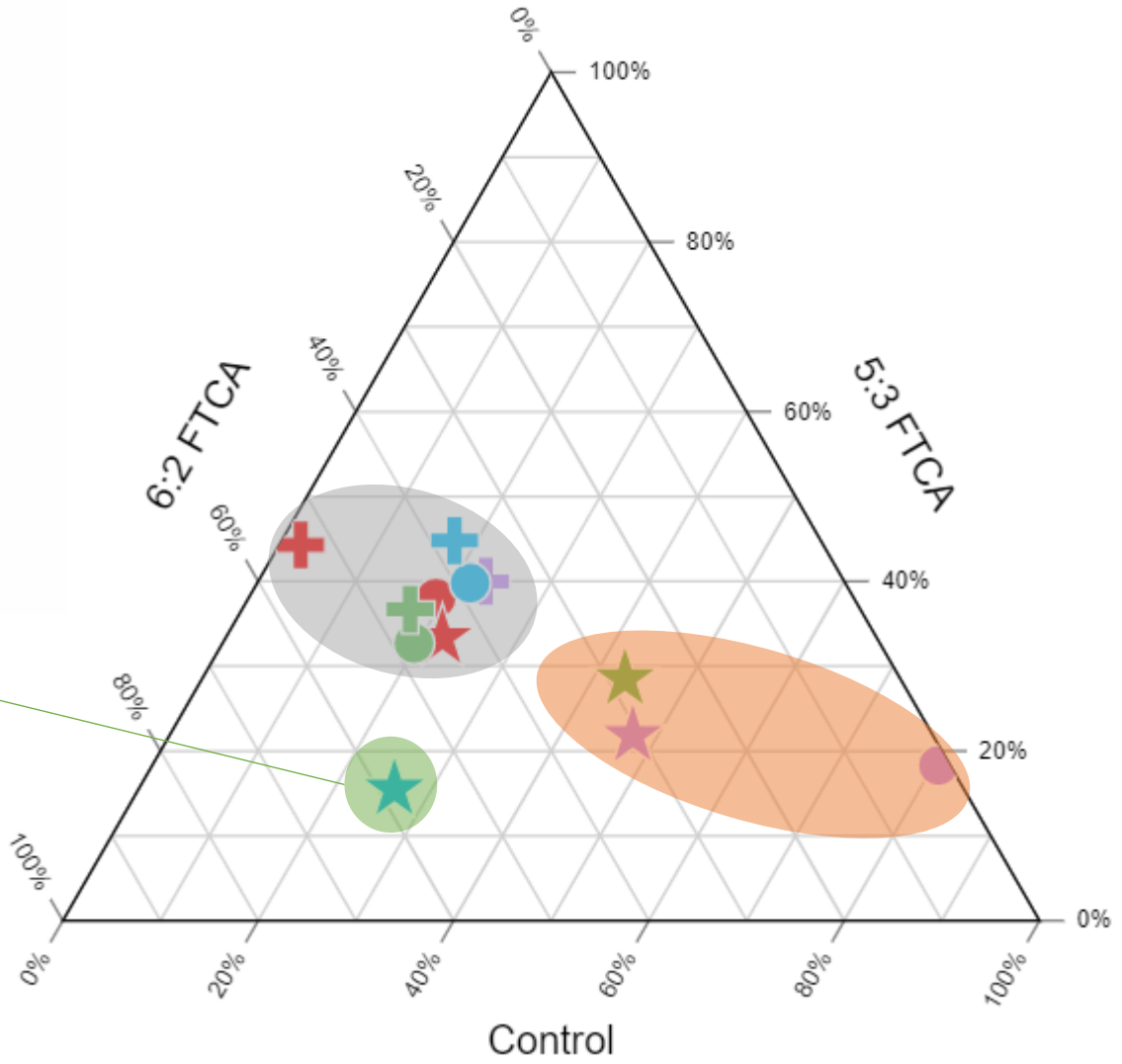
7 days incubation



- Candidatus Accumulib
- Methyloversatilis
- Zoogloea
- Turneriella
- Propionicimonas
- Leptothrix
- Thermomonas
- Nitrospira
- Hyphomicrobium
- Dechloromonas
- Sphingobium
- Methylibium

Shifting of Dominant Taxa by FTCAs

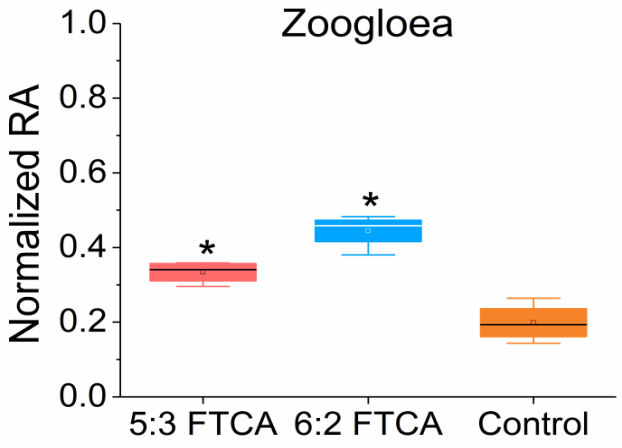




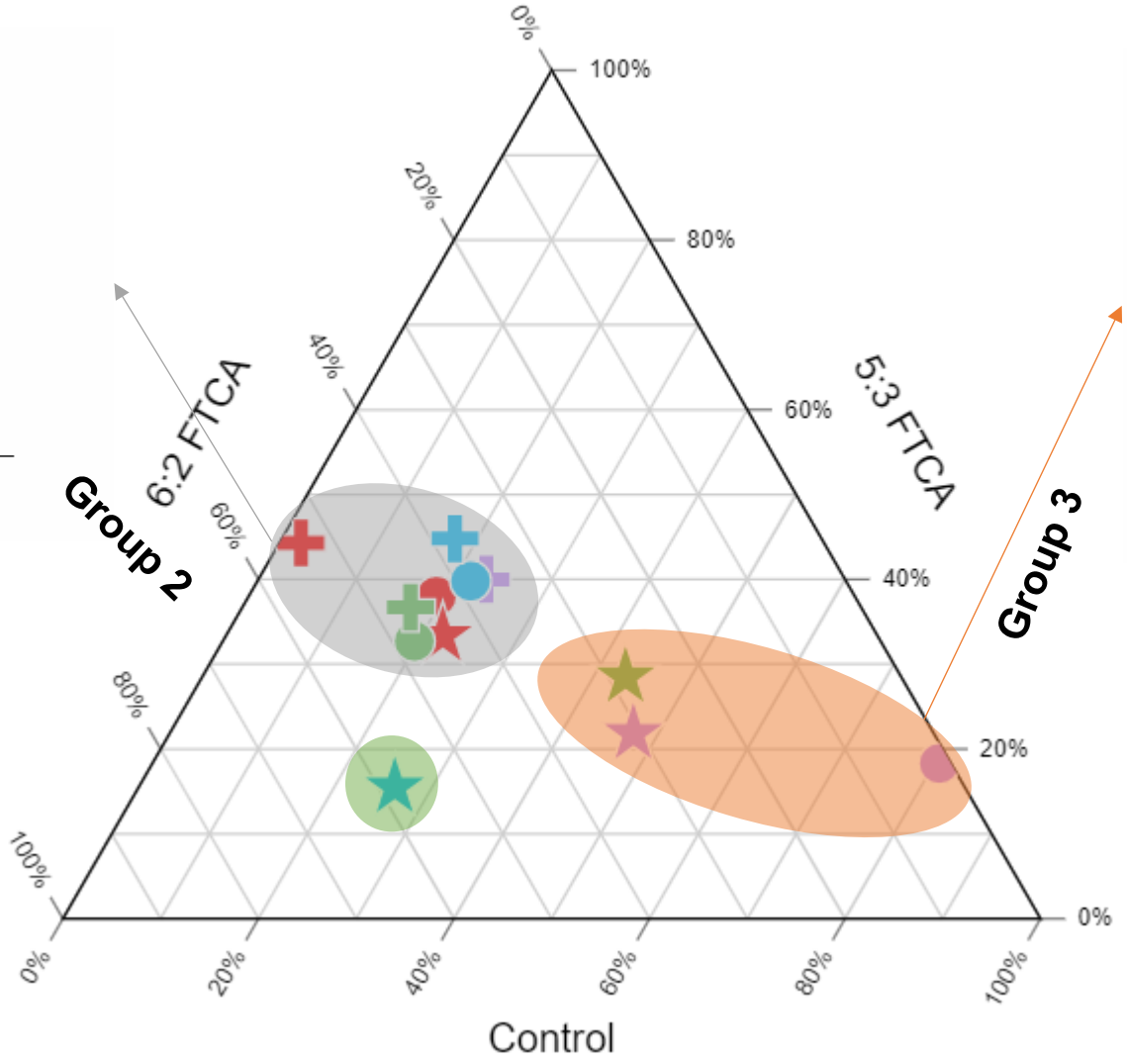
Group 1

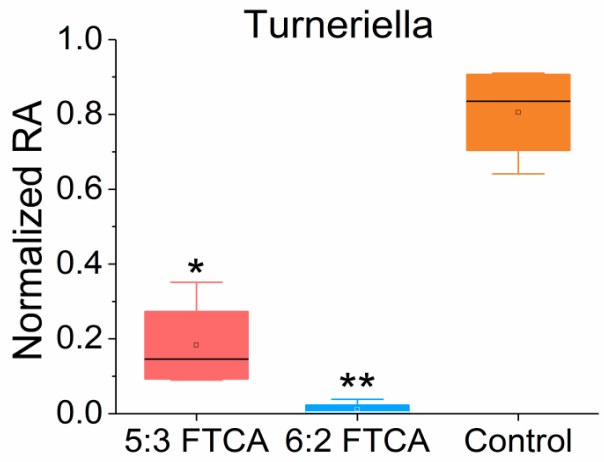
Fluoride release?

Shifting of Dominant Taxa by FTCAs



FTCA biotransformation?

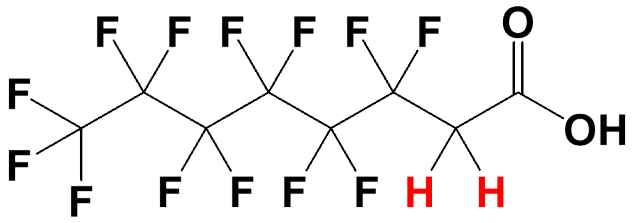




Sensitive to FTCAs exposure

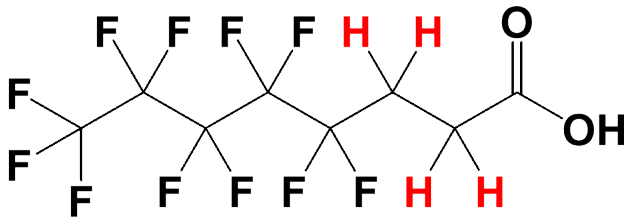
Implications

6:2 FTCA

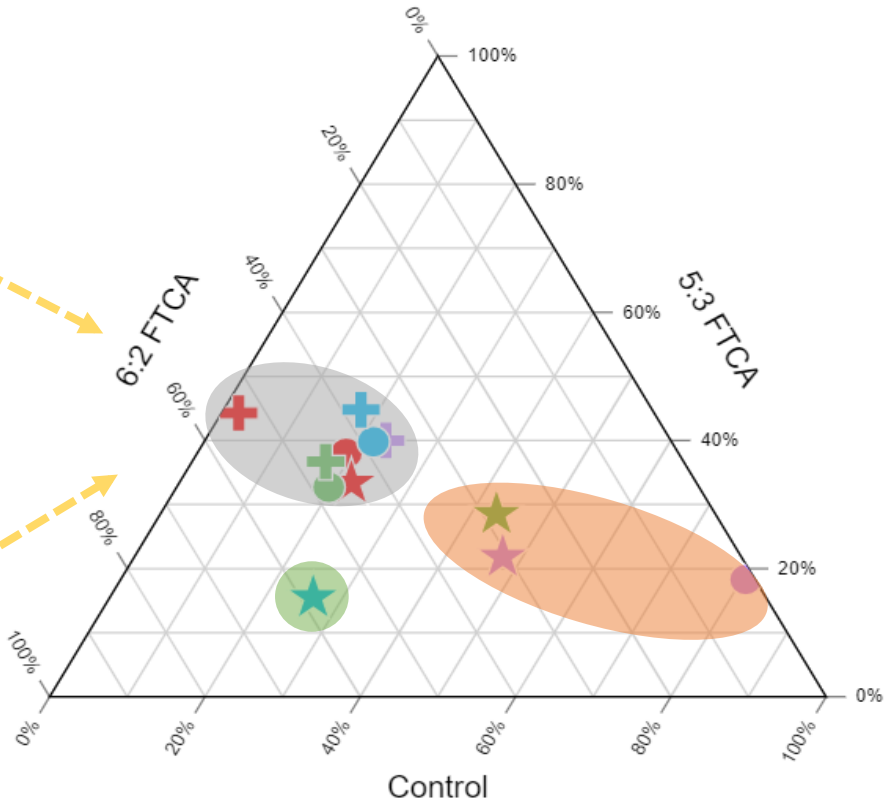


- Abiotic & biotic removal
- F^- releasing biotransformation

5:3 FTCA



- Non-fluoride releasing biodefluorination
- Biotic removal



Welcome to our platforms/posters on PFASs

Title	Presenter	Location and Time
Rapid Quantitative Analysis and Suspect Screening of Per- and Polyfluorinated Alkyl Substances (PFASs) in Aqueous Film-Forming Foams (AFFFs) by Nano-ESI HRMS.	Chen Wu NJIT	Smoketree Monday 12:35 pm
Aerobic Biotransformation and Biodefluorination of Fluorotelomer Carboxylic Acids (FTCAs) in Municipal Wastewater Treatment Sludge.	Chen Wu NJIT	Smoketree Monday 3:30 pm
Effective Adsorption Removal of Polyfluoroalkyl and Perfluoroalkyl Substances (PFASs) by Reed Straw-derived Biochar (RESCA).	Mengyan Li NJIT	Smoketree Wednesday 3:30 pm
Target and Suspect Screening of Per- and Polyfluorinated Alkyl Substances (PFASs) in Municipal Wastewater Samples by Nano-ESI-HRMS.	Chen Wu NJIT	Poster #225 Monday 4:30 pm

Welcome to our platforms/posters on 1,4-Dioxane and Microplastics

Title	Presenter	Location and Time
Untangling the Robust Catalytic Versatility of Soluble Di-iron Monooxygenases in Initiating the Biotransformation of Legacy and Emerging Groundwater Pollutants.	Mengyan Li NJIT	Catalina Tuesday 8:00 am
Biodegradation of 1,4-Dioxane by Psychrophilic Propanotrophs.	Jose Antunes NJIT	Poster #360 Monday 4:30 pm
Synchronous Biodegradation of 1,4-Dioxane and TCE by *Mycobacterium* sp. DT1.	Jose Antunes NJIT	Poster #361 Monday 4:30 pm
Sequential Anaerobic and Aerobic Bioaugmentation for Commingled Groundwater Contamination of Trichloroethene and 1,4-Dioxane.	Mengyan Li NJIT	Poster #367 Monday 4:30 pm
Microplastics as Hubs Enriching Antibiotic-resistant Bacteria and Pathogens in Municipal Activated Sludge.	Mengyan Li NJIT	Poster #323 Wednesday 4:30 pm

Acknowledgements

Advisor: Dr. Mengyan Li

Current PhD students
- Dung Pham
- Jose Antunes
- Sumbel Yaqoob
- Chao Li
- Boyuan Su

Previous members:
- Dr. Fei Li
- Dr. Na Liu
- Dr. Daiyong Deng

Collaborators:
- Dr. Hao Chen
- Qi Wang