NORTHEAST CONFERENCE
THE SCIENCE OF PFAS:
Public Health & The Environment
Tuesday, March 31, 2020 - Wednesday, April 1, 2020
Sheraton Framingham Hotel & Conference Center
Framingham, MA

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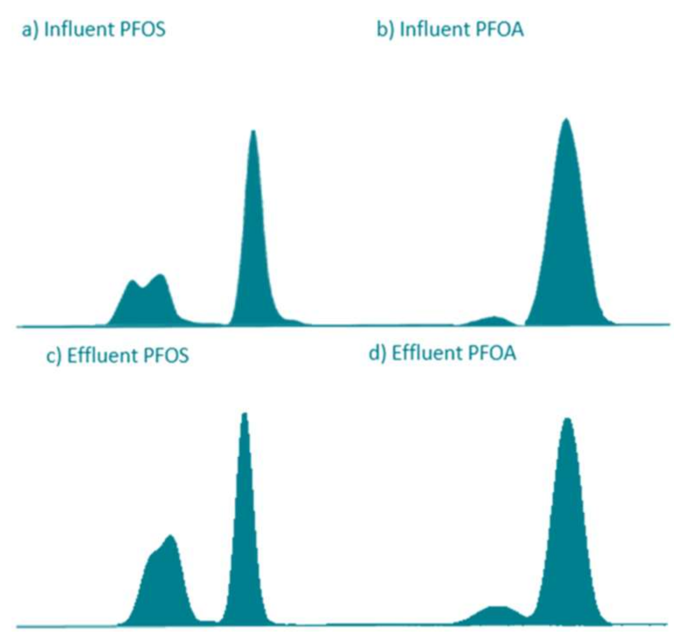
Linear vs. Branched PFAS Isomers as Preliminary Identification of PFAS Fate & Transport Processes



Dora Chiang, Ph.D., P.E.

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North Carolina State University
Dr. Detlef R. U. Knappe

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Pilot scale removal of per- and polyfluoroalkyl substances and precursors from AFFF-impacted groundwater by granular activated carbon†

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Outline

- Project Background
- PFAS Analysis and Lessons Learns
- PFAS Isomers and Implications on F&T
- Takeaways

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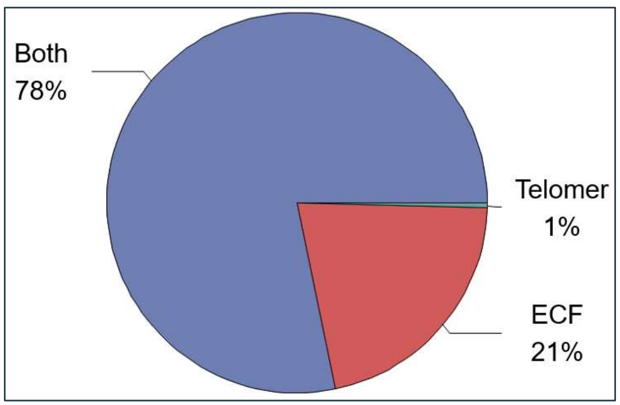
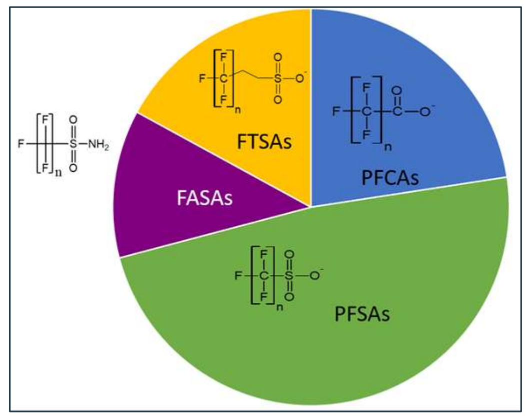
AFFF-Impacted Source Area

- Multiple types of proprietary AFFFs were used at USAF installations
- PFAS in ECF-AFFF contain approx. 70% linear and 30% branched PFAAs, similar ratio to precursors
- PFAS in FT-AFFF should be all linear (theoretically)
- When site is impacted by both formulations, the linear and branched isomer ratios become complicated



Distribution of formulations identified at AFCEC's AFFF-impacted sites
(Anderson, 2019, ITRC PFAS training)



Detections of both ECF- and FT-AFFF based PFAS in the extracted groundwater of project site

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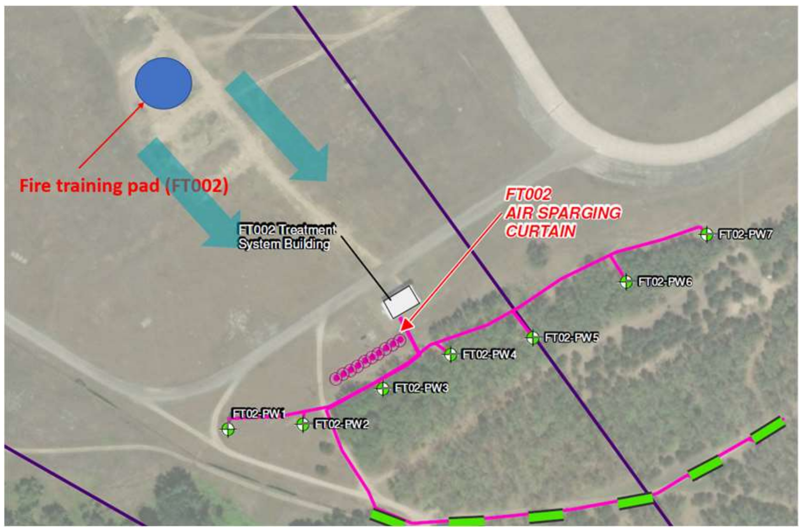
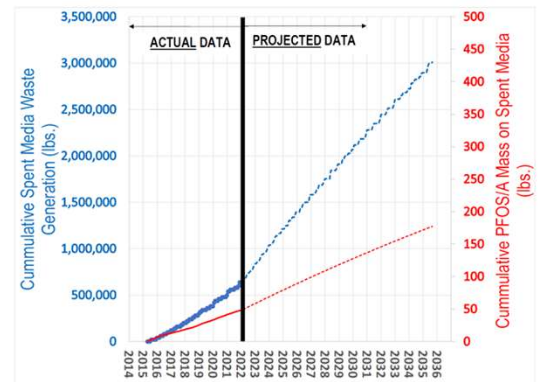
Groundwater Extraction and Treatment

Site Background

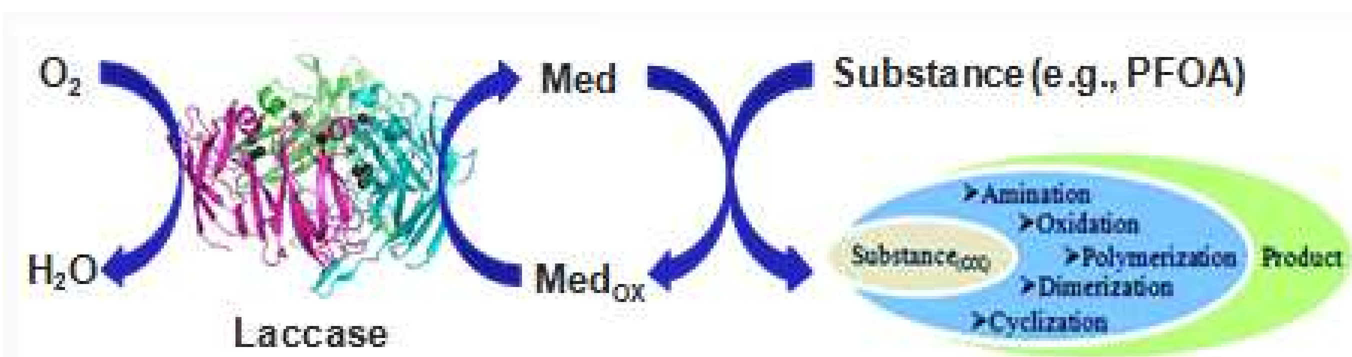


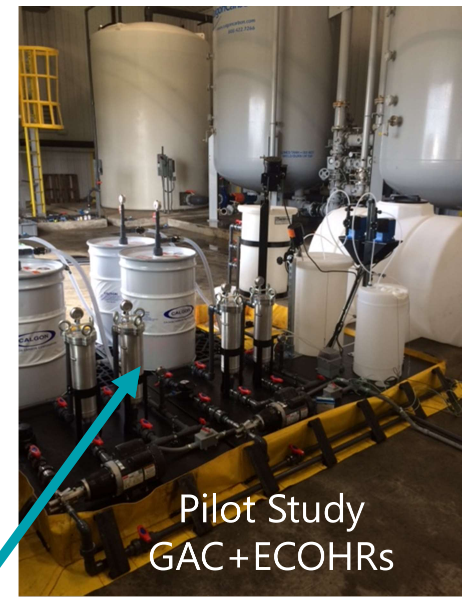


Estimated quantities of PFAS and spent media requiring waste management after 20 years of system operation

AFCEC BAA 765 Project Objectives

- To validate and demonstrate the effectiveness of reducing PFOS and PFOA concentrations in the groundwater using enzyme-catalyzed oxidative humification reactions (ECOHRs)
- To demonstrate coupling ECOHRs with GAC treatment to **delay PFAS breakthrough** and to **destroy PFAS** in the GAC vessels to the maximum extent possible





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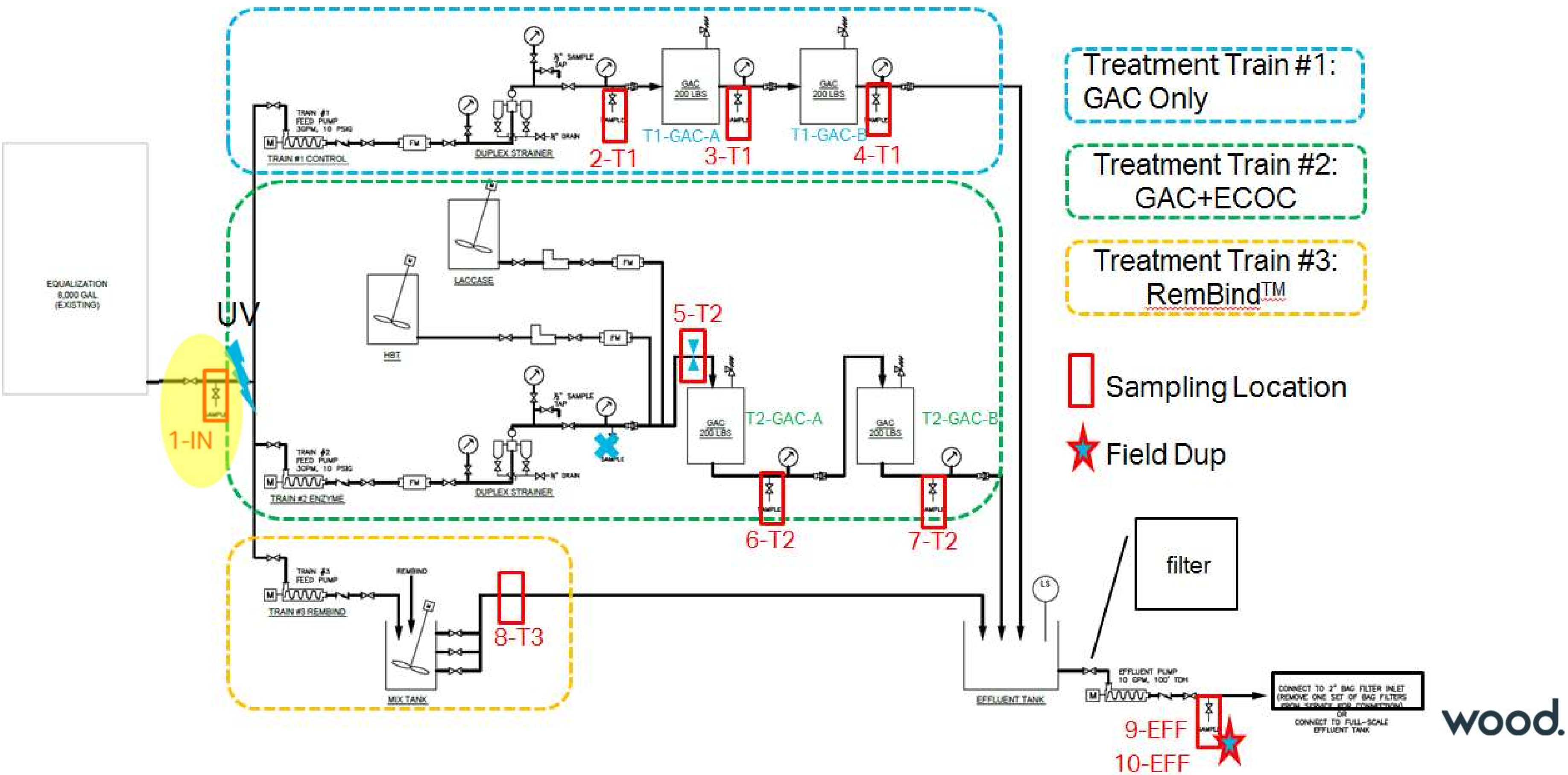
Pilot-Scale Demonstration Process Flow Diagram

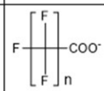
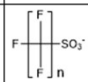
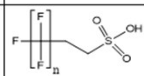
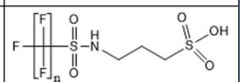
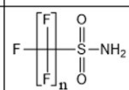
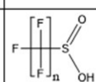
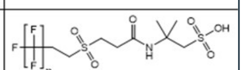
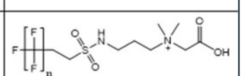
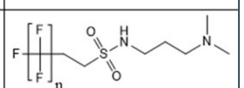


Detail Profiling of PFAS

- Weekly sampling from 9 sampling locations for 5 months

Analytical Parameter	Frequency	Laboratory	Method	Reference
PFOS and PFOA (screening purpose)	Weekly	Dr. Huang/UGA	UPLC/MS/MS	Luo et al., 2015*
Volatile Organic Compounds	Monthly	Commercial Labs	USEPA 8260B	
Total Organic Carbon	Monthly	Commercial Labs	TOC 5000A	
Fluoride	Monthly	Dr. Huang/UGA	IC-MS	
Optimized WAFB Site Specific PFAS List	Weekly	Dr. Field/OSU	Orthogonal HPLC MS/MS Quadrupole Time-of-Flight Mass Spectrometry	Backe et al., 2013* Barzen-Hanson and Field, 2015*
Total Oxidizable Precursor Assay (TOPA)	Weekly	Dr. Field/OSU	PFAS analyses, same as above	Houtz et al., 2013*
Particle-Induced Gamma-ray Emission (PIGE)	Weekly	Dr. Graham Peaslee/U of Notre Dame	PIGE	

OSU PFAS Analyses

Class #	Class	Chain length distribution observed	In method 537?	Structure
1	Perfluoroalkyl carboxylates (**PFCAs**)	C3-C9 (n=7)	C6-C14 (9 total)	
2	Perfluoroalkyl sulfonates (**PFSAs**)	C3-C8 (n=6)	C4, C6, C8 (3 total)	
3	Fluorotelomer sulfonates (**FTSs**)	4:2, 6:2, and 8:2 (n=3)	none	
4	N-SulfoPropyl perFluoroAlkaneSulfonAmide **(N-SP-FASA)**	C4-C6 (n=3)	none	
5	perFluoroAlkane SulfonAmide **(FASA)**	C3-C6 (n=4)	none	
6	Perfluoroalkyl sulfinate **(PFASi)**	C4-C6, C8 (n=4)	none	
7	*n*:2 tridecaFluoroAlkyl Sulfonyl(SO2) PropanoAmido-MethylPropylSulfonate ***(n*:2 FASO2PA-MePS)**	6:2, 8:2 (n=2)	none	
8	*n*:2 Fluorotelomer Sulfonamido Betaine **(N-CMAmP-*n*:2 FASA)**	C4-C6 (n=3)	none	
9	*n*:2 Fluorotelomer Sulfonamido Amine **(N-AP-*n*:2 FASA)**	C4-C6 (n=3)	none	

- Focused on PFAS related to AFFF releases
- Identified 9 major subgroups (35 compounds) for the project after screening against 150 PFAS
- Branched and linear PFAS concentrations are semi-quantitatively estimated. Branched-PFAS standards are limited to Br-PFOS and Br-PFHxS

Branched vs Linear Isomers Relevant to Types of AFFF

1. **PFCAs (C6-C14):** ECF branched and linear or FT (fluorotelomerization) linear only
2. **PFSAs (C4, C6 and C8)**: ECF branched and linear
3. **Fluorotelomer sulfonates (4:2, 6:2, 8:2):** Linear only, biodegradation product of FT-based AFFF active ingredient
4. **N-SulfoPropyl perFluoroAlkaneSulfonAmide (N-SP-FASA)(C4-C6)**: ECF branched and linear
5. **perFluoroAlkane SulfonAmide (FASA) (C3-C6):** ECF branched and linear
6. **Perfluoroalkyl sulfinate (PFASi) (C4-C6, C8):** ECF branched and linear, maybe indicator of anaerobic conditions
7. ***n*:2 tridecaFluoroAlkyl Sulfonyl(SO2) PropanoAmido-MethylPropylSulfonate *(n*:2 FASO2PA-MePS)(6:2, 8:2):** Telomer (linear only), oxidized degradation product of FT-based AFFF active ingredient
8. ***n*:2 Fluorotelomer Sulfonamido Betaine (N-CMAmP-*n*:2 FASA)(C4-C6):** Telomer (linear only), active ingredient in FT-based AFFF
9. ***n*:2 Fluorotelomer Sulfonamido Amine (N-AP-*n*:2 FASA)(C4-C6):** Telomer (linear only), active ingredient in FT-based AFFF

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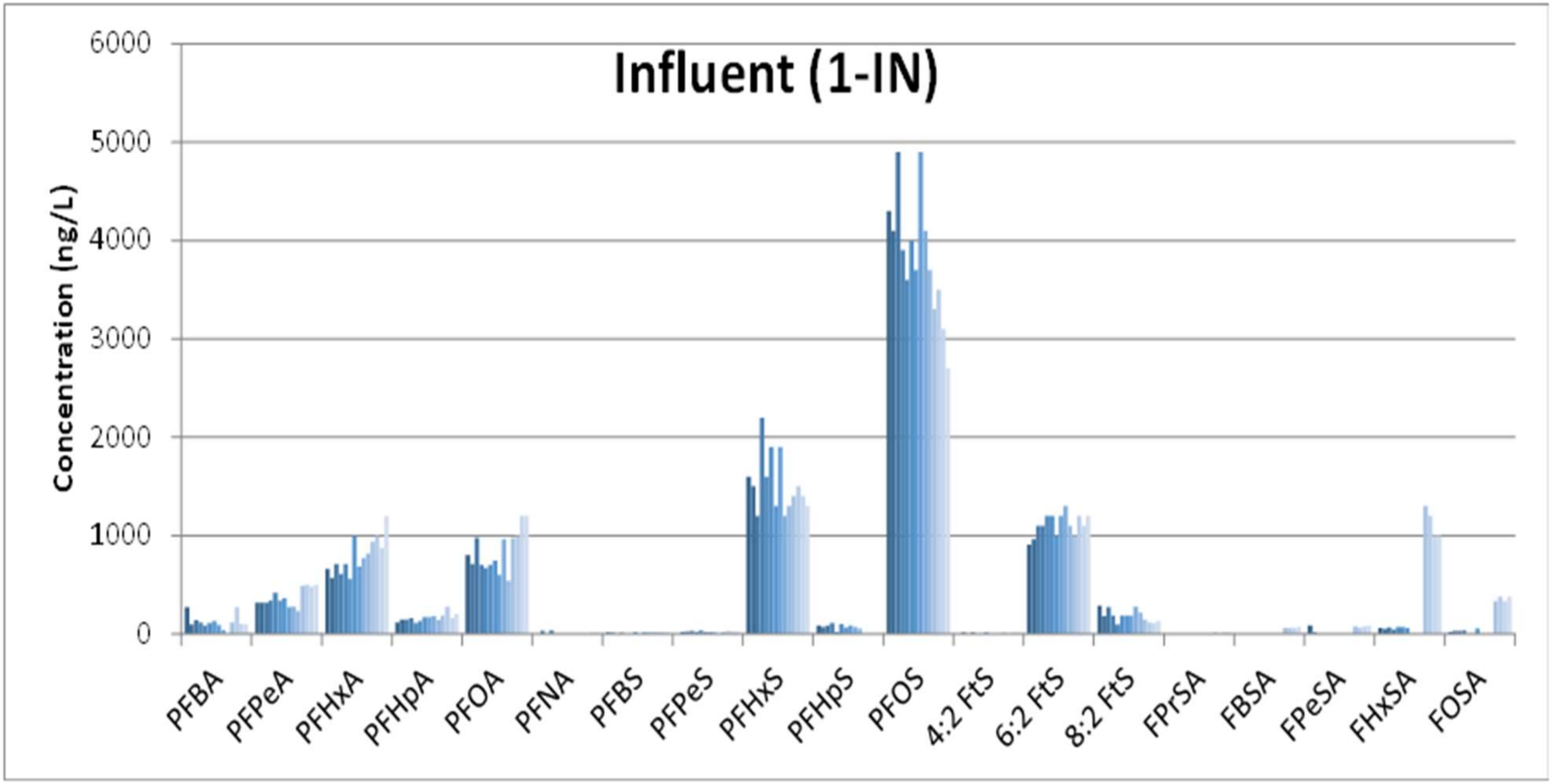
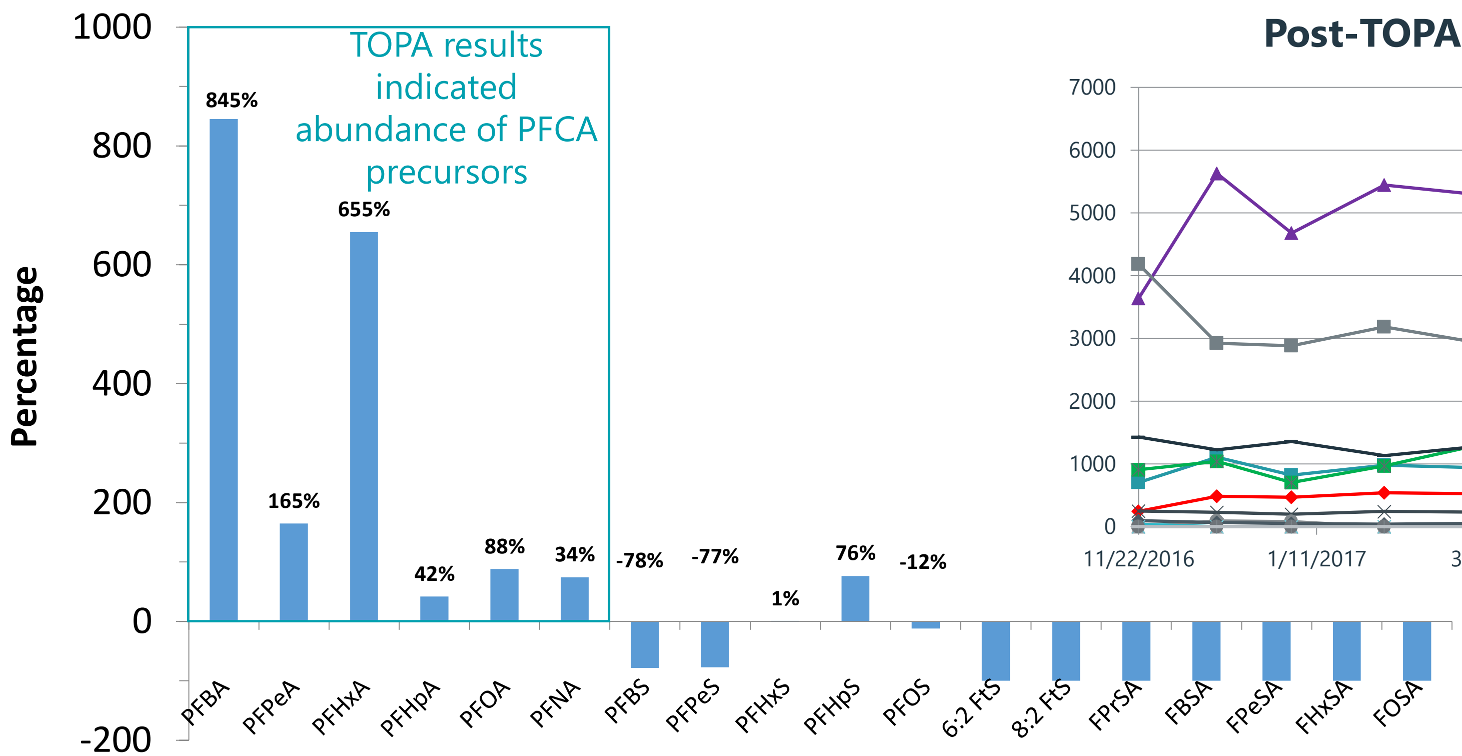
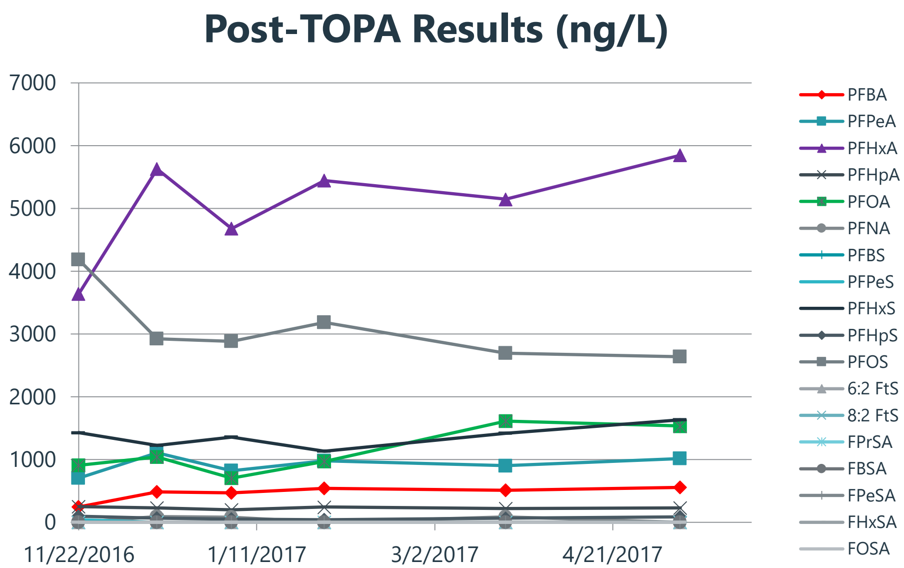
PFAS Detections in the Extracted GW

Target PFAS Analysis



Total Oxidizable Precursors in the Extracted GW





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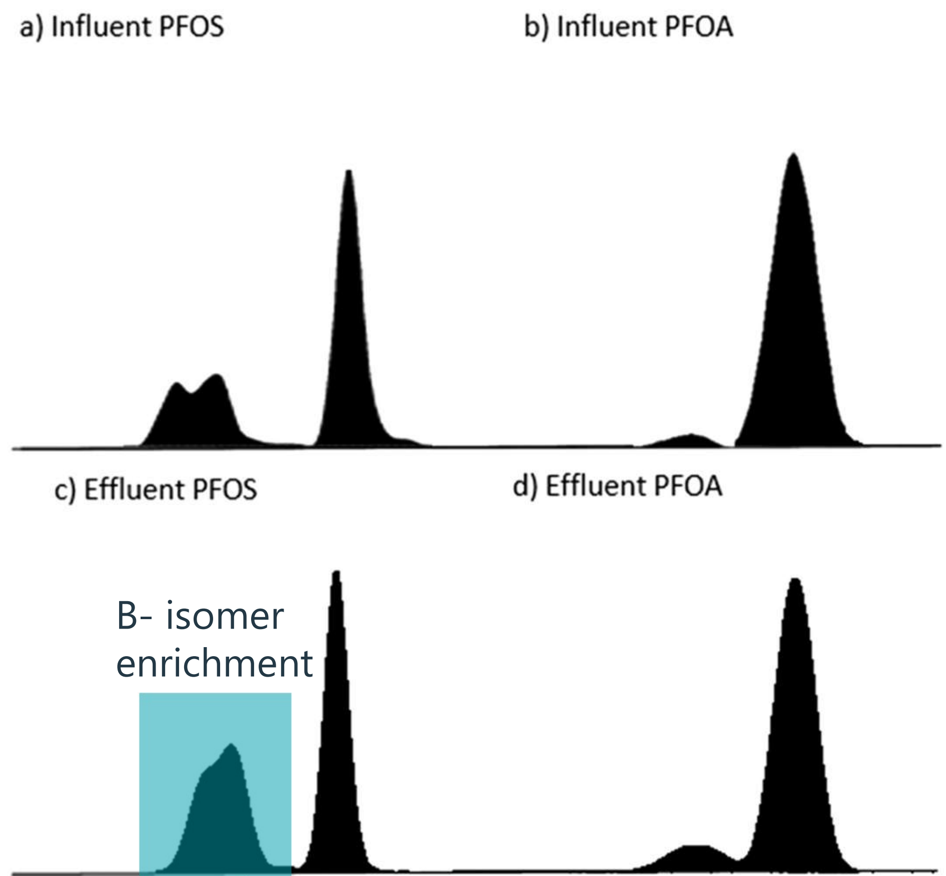
Linear vs Branched Isomers

- **Linear isomers**
  - PFAS in ECF-based AFFF are expected to have Br/L ratios close to 30/70,
  - Fluorotelomers and their transformation products (e.g., PFCAs) would be theoretically all linear (Br/L 0/100)
  - When a site used both ECF and FT-based AFFF, Br/L ratio can be less than 30/70 due to linear isomer enrichment
- **Branched isomers**
  - Branched isomers exhibit lower partition coefficients between soil and water (Kd) or soil organic matter and water (Koc)
  - Br/L can be greater than 30/70 downgradient from the source when more L isomers are retarded in the source area



Br and L isomers for a) PFOS and b) PFOA in influent and c) PFOS and d) PFOA in lead vessel effluent at 11 000 bed volumes.

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Linear vs Branched Isomers in the Extracted GW

	Average Influent Concentration (ng/L)		Branched/Linear (30/70=0.43)
PFAS	Branched	Linear	
PFBA	NA	100 ± 22	<0.43
PFPeA	19 ± 2.5	350 ± 47	0.054
PFHxA	<LOQ	740 ± 70	<0.43
PFHpA	15 ± 2.0	150 ± 20	0.1
PFOA	81 ± 7.2	820 ± 73	0.1
PFNA	<LOD	18 ± 5.7	<0.43
PFBS	<LOD	17 ± 3.0	<0.43
PFPeS	<LOD	30 ± 9.0	<0.43
PFHxS	190 ± 29	1400 ± 210	0.14
PFHpS	29 ± 5.5	62 ± 11.9	0.47
PFOS	1200 ± 110	1900 ± 170	0.63
4:2 FtS	NA	13 ± 3.0	
6:2 FtS	NA	1000 ± 76	
8:2 FtS	NA	170 ± 35	
FPeSA	<LOQ	125 ± 5.8	<0.43
FHxSA	700 ± 48	2100 ± 140	0.33
FOSA	100 ± 9.4	200 ± 19	0.5
N-TAmP FHxSA	51 ± 21	97 ± 40	0.52

Linear only, transformation products of FT based foams (4:2 FtS, 6:2 FtS, 8:2 FtS)

Transformation products of ECF foams (FPeSA, FHxSA, FOSA, N-TAmP FHxSA)

L- PFCAs were enriched (B/L<0.43) in the extracted GW

Br-PFSAs and FASAs were enriched (B/L>0.43)

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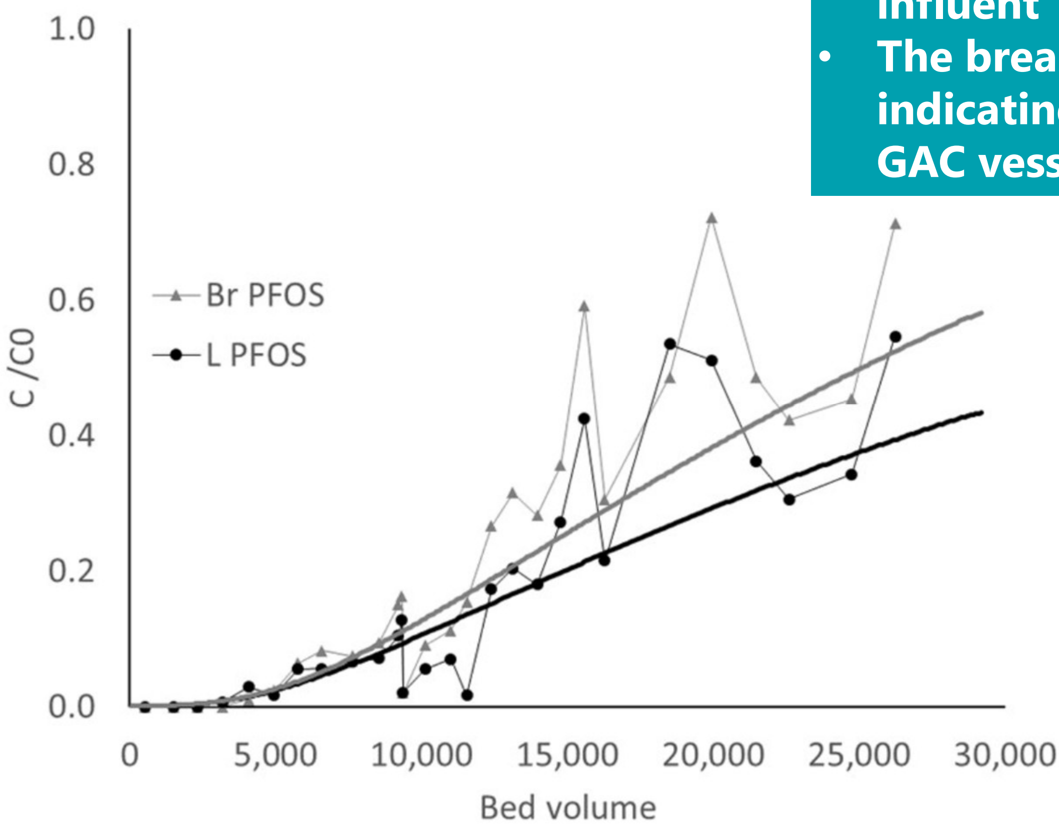
Breakthrough Curves for Br- and L-PFOS in Lag Vessel Effluent

- Average Br-PFOS/L-PFOS = 0.63 in the influent
- The breakthrough curve shows Br/L>1 indicating greater retardation of L-PFOS in GAC vessels



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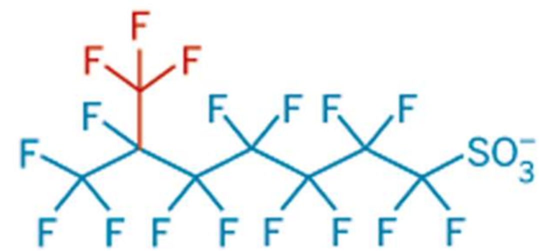
Takeaways

- Characterization of influent provides preliminary assessment of PFAS fate and transport
- Mixed uses of FT and ECT AFFF were verified at the site using multiple lines of evidence
- TOPA confirmed the abundance of PFCA precursors, but the types of PFCA precursors were not identified
- L- PFCAs were enriched (Br/L<0.43) in the extracted GW suggesting abundant uses and releases of fluorotelomers (L isomers only) that have been converted into linear PFCAs over time

PFOS Linear Isomer

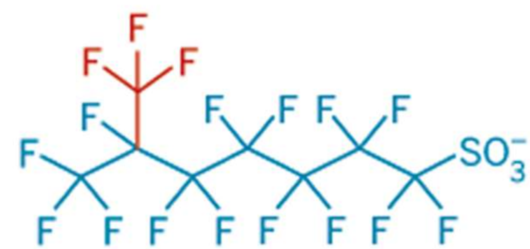


PFOS Branched Isomer (P6MHpS)

Takeaways

- GW data showed branched PFSA and FASA isomer enrichment (Br/L>0.43) in the extracted GW, 150 m downgradient from the source
- Branched isomers with lower Kd and Koc than L isomers break through GAC faster than L isomers resulting in Br isomer enrichment in the effluent
- Branched isomers would also be more leachable in the aquifer than linear isomers. This is evident by the enriched Br isomers in PFSAs and FASAs of the extracted GW

PFOS Linear Isomer



PFOS Branched Isomer (P6MHpS)

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Thank You

Shalene Thomas 11:00 am-12:30 pm | Seminar Room AFFF: Status of Use & Transition Path Forward to Fluorine-Free Foams

Usha Vedagiri 2:00 pm - 3:30 pm | Seminar Room Understanding, Managing, & Mitigating PFAS Content in Products: Terms Currently Used for PFAS Certification or Acceptability

Tony Rodolakis 4:00 pm-5:30 pm | Salon B Protecting Human Health from Consumption of PFOS in Deer Meat

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