Transformation of ECF-based PFAS in AFFF-Impacted Soil

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Background

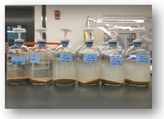
- More than 700 military sites with known or suspected PFAS discharges from aqueous film-forming foam (AFFF) application(s)[1]
- 3M AFFF containing electrochemical fluorination (ECF)-based PFAS account for 75% AFFF stockpiled on military bases[2]
- Biotransformation (BTF) of a few AFFF-derived ECF-based PFAS has been studied[3-5]

OBJECTIVE

Evaluate the environmental fate and transformation of the AFFF-derived ECF-based precursors and unravel the associated transformation products and pathways.

Methods

Field sample collection
at AFFF -impacted site
Loring AFB (Aroostook County, ME)



308-day Microcosm experiment
Abiotic/Biotic Transformation

Group	Components			
	Soil	Spiked AFFF[a]	e-donor	Other
Live treatment	Loring soil	Yes	DGBE[b]	N/A
Abiotic control		Yes		N/A
Live control		N/A		1 g/L NaN_3

a.0.1% v/v 3M Light Water™ AFFF concentrate (FC-203CF)
b.DGBE: diethylene glycol butyl ether

LC-HRMS

Non-targeted Analysis (NTA) and Targeted Analysis

- Identify/tentatively identify PFAS present in the microcosms over 308 days

- Categorize PFAS into **AFFF components** and **transformation products** based on area counts over time and difference between treatment groups
- Compare the environmental stability (i.e., transformation or formation extent) of AFFF components by comparing **log2-fold changes (LFCs)** in peak area counts between day 308 and day 0

Results

- **15 classes of PFAS in a historical 3M AFFF formulation were identified/tentatively identified** including 9 classes categorized as AFFF components (shaded in yellow), 8 classes categorized as transformation products (shaded in blue), and 2 classes as both AFFF components and transformation products (shaded in green).

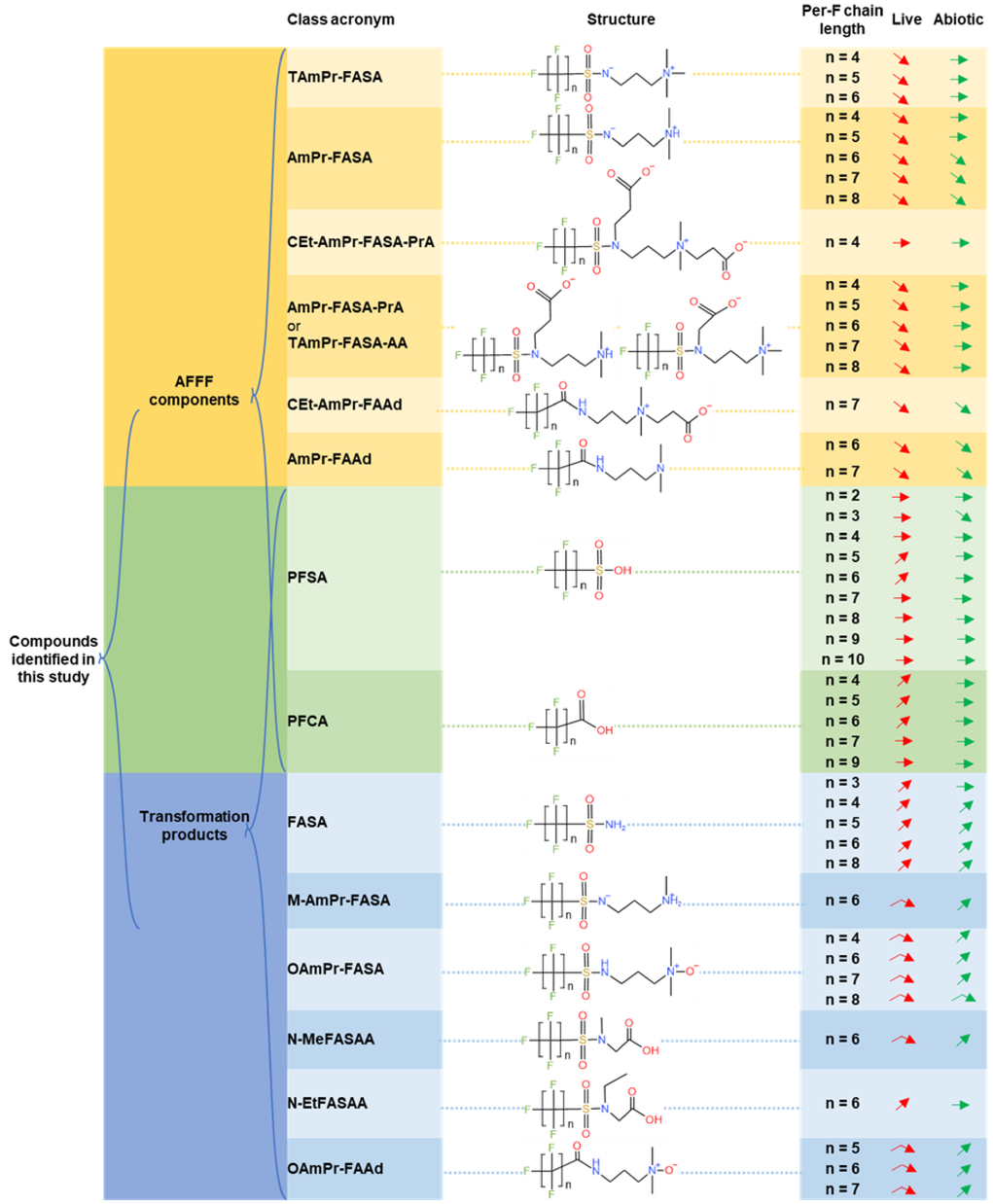


Figure 1. The chemical structures of the PFAS classes, and general trends of peak area in live treatment and abiotic control over the 308-day incubation of each homologue within each class were illustrated.

- **Structurally relevant factors impact PFAS stability**

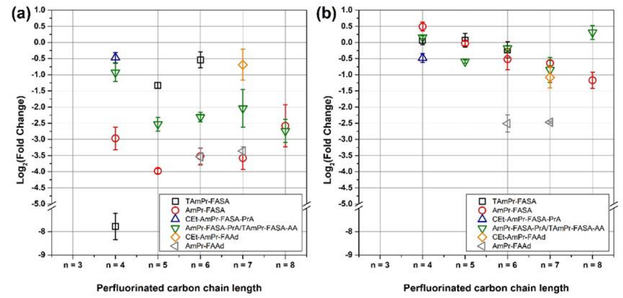
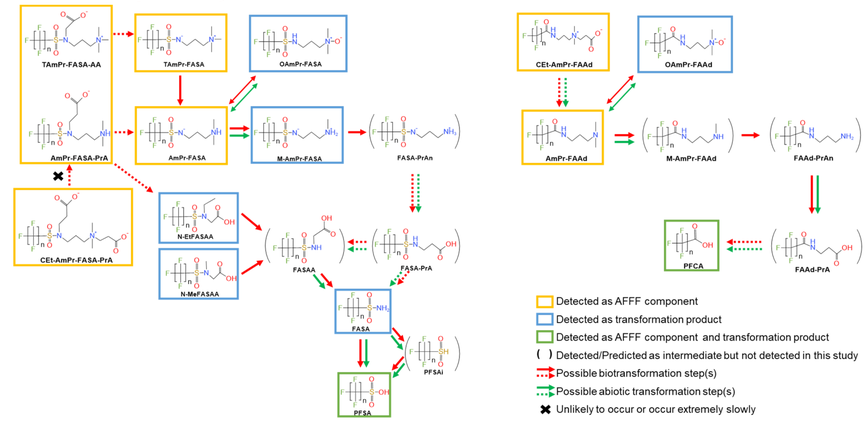


Figure 2. Log_2-fold changes (LFCs) in peak areas of PFAS classes categorized as AFFF components between day 308 and day 0 in (a) live treatment and (b) abiotic control, respectively.

- **Carbon chain length of perfluorinated moiety**
  TAmPr-FASA, AmPr-FASA, AmPr-FASA-PrA/TAmPr-FASA-AA
- **Sulfonamide vs Carboximide**
  AmPr-FASA vs AmPr-FAAd
- **Functional groups on 2nd N atom**
  Methyl group (TAmPr-FASA vs AmPr-FASA)
  Carboxyalkyl group (CEt-AmPr-FAAd vs AmPr-FAAd)
- **Functional group on 1st N atom**
  CEt-AmPr-FASA-PrA

- **Transformation pathways of sulfonamide/carboxamide-based PFAS**



Key Takeaways

- Multiple classes of PFAS identified/tentatively identified in this study are susceptible to abiotic/biotic transformation.
- Environmental stability of ECF-based precursors in the AFFF formulation is dependent on their structural characteristics. Longer carbon chain of the perfluorinated moiety and additional functional groups in the nonfluorinated moiety are likely to be more resistance to biotransformation.

Implications and Future work

- AFFF release into soils leads to long-term PFAS contamination in the source zone and adjacent areas.
- This study provided a broader view on the environmental stability of different classes of PFAA precursors.
  - Guidance for PFAS manufacturers to produce biodegradable substitution.
  - Optimize resource allocation for site cleanup.
- To better predict fate of different PFAS, evaluation of individual PFAS biotransformation and development of quantitative structure–BTF relationship models are needed.

References

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[5] Liu, M.; Munoz, G.; et al. *Environ. Sci. Technol.* **2021**, 55(8), 4698–4708.

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