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Fluorotelomer Carboxylic Acid Degradation: Implications for Septic Systems

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Fluorotelomer Carboxylic Acid Degradation: Implications for Septic Systems

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Honors Thesis

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1. Abstract

Per- and polyfluoroalkyl substances, or PFAS, are a group of manmade organic chemicals that have been widely used since the 1940's due to their resistance to heat, water, and oil. These compounds are associated with negative health outcomes including poor thyroid function, reproductive toxicity, and carcinogenicity. Because products with PFAS are widely used in residential settings, and because many PFAS do not completely degrade during wastewater treatment/handling, septic systems may be an important non-point source of PFAS to groundwater. Many homes that have septic systems, which discharge wastewater effluent to the subsurface, also use groundwater as a drinking water source; therefore, understanding what types of PFAS are found in septic systems as well as how they transform is important for protecting rural drinking water supplies. The goals of this project were to: (1) map the transformation pathways of six PFAS known as fluorotelomer carboxylic acids (FTCAs) using chemical transformation prediction software; (2) delineate how FTCAs may degrade in septic system environments; and (3) more broadly identify biotransformation trends for FTCAs relevant to other natural and engineered systems. Research on how PFAS transform in septic systems remains limited, therefore the findings of this research will support a growing body of knowledge that serves to help predict the types of compounds that are being discharged from these systems to the subsurface. The results of this study suggest that some FTCAs follow a distinct breakdown pathway despite the number of carbon fluorine bonds they have, and the environmental conditions of individual septic systems control the extent to which transformation pathways occur.

2. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large family of synthetic compounds that have been used in commercial and industrial settings since the 1940’s (FDA, 2024). These substances are commonly found in commercial products including detergents, waterproof clothing, nonstick cookware, and floor wax due to their thermal stability and ability to repel water and oil (Zhang et al., 2020). Many PFAS are being phased out or banned because they exhibit toxicity effects including immunotoxicity, genotoxicity, reproductive toxicity, neurotoxicity, and carcinogenicity (Bright, 2023). They have also been shown to interfere with thyroid function in humans (Zhang et al., 2020). PFAS are difficult to treat and remove because they do not completely break down in the environment; rather, they only partially degrade to other PFAS, termed “terminal” products. There are over 5,000 types of these compounds, and they have been detected in even the most remote environments in the world, such as the high Arctic (Rhoads et al., 2008). These pollutants are also found in the blood of 99% of Americans (Environmental Working Group, 2018).

Understanding how PFAS break down and transform in the environment is critical for gaining a better understanding of the types of PFAS humans and animals are exposed to, the types of PFAS that should be tested for during water quality analyses, and the environmental conditions that give rise to different metabolites. The goals of this research project were to (1) map the transformation pathways of six PFAS known as fluorotelomer carboxylic acids (FTCAs) using chemical transformation prediction software; (2)

delineate how FTCAs may degrade in septic system environments; and (3) more broadly identify biotransformation trends for FTCAs relevant to other natural and engineered systems.

3. Literature Review

PFAS are released into the environment from point sources such as landfills, wastewater treatment facilities, and firefighting training sites (Utah DEQ, 2023). It is easier to identify sources of pollution and to implement mitigation strategies when PFAS are being released from discrete locations. Non-point sources of pollution, on the other hand, such as runoff and septic system discharge, are much more difficult to address. The prevalence of PFAS containing products in residential settings has led to the detection of PFAS in septic systems (Schaider et al., 2016). Septic systems are commonly used in rural communities where groundwater is also used as a drinking water source. In New Hampshire, approximately 60% of homes rely on septic systems for the treatment of wastewater (NHDES, 2019). Nearly half rely on private wells for drinking water (NHDES, n.d.). The extent to which PFAS are treated and removed during septic system treatment is still being studied. However, if septic systems are not removing PFAS and then discharging effluent containing these chemicals to the subsurface, there is great potential for the contamination of groundwater drinking water supplies (see Figure 1).

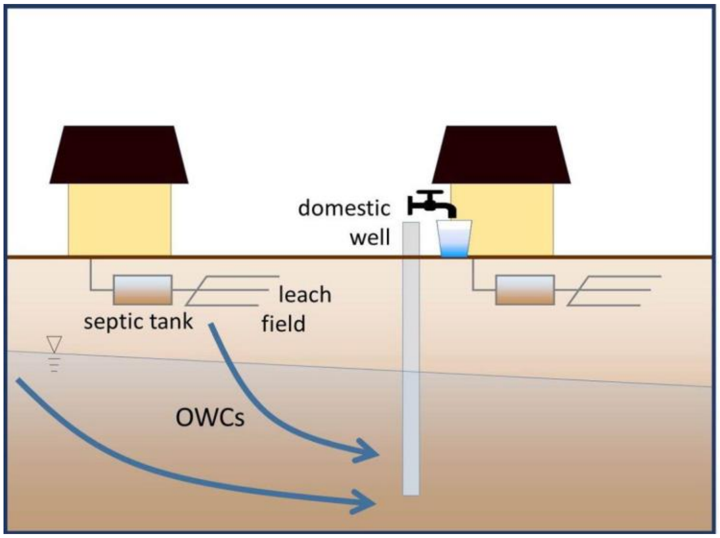


Figure 1: Organic wastewater contaminants (OWCs) such as PFAS released to the subsurface by septic systems have the capacity to contaminate groundwater (Schaider et al., 2016).

A study of 20 homes in areas of Cape Cod served exclusively by onsite wastewater treatment systems and private wells found four types of PFAS in more than 50% of wells sampled; detection of these compounds was linked to septic system discharge (Schaider et al., 2019). Another study of 450 homes in Wisconsin with shallow private wells found at least one type of PFAS in 71% of samples. According to the study, "...most of the samples in this region have no nearby waste land application, leaving septic system effluent as a likely source for most of these samples" (Silver et al., 2023).

In order to protect humans from PFAS in drinking water, it is necessary to understand how PFAS entering these septic systems transform and break down. The types of metabolites generated during septic treatment are different from those generated in other environments due to the unique set of environmental conditions within these systems. Onsite wastewater treatment systems are typically suboxic or anaerobic, meaning oxygen is generally depleted due to the high chemical oxygen demand of the wastewater. Optimal temperatures for these systems range from 25°C to 35°C, and pH should be between 6 and 9 (EcoCare, 2021). Septic systems function with the help of bacteria, algae, protozoa, fungi, rotifers, and nematodes. These microbes metabolize organic material and inorganic ions in order to grow (Maine CDC, 2013). Septic system treatment occurs in two stages; first, solids separation and anaerobic digestion occur. Then, the effluent from the septic tank is further treated both physically and biologically in the leach field. Figure 2 shows a typical onsite wastewater treatment system.

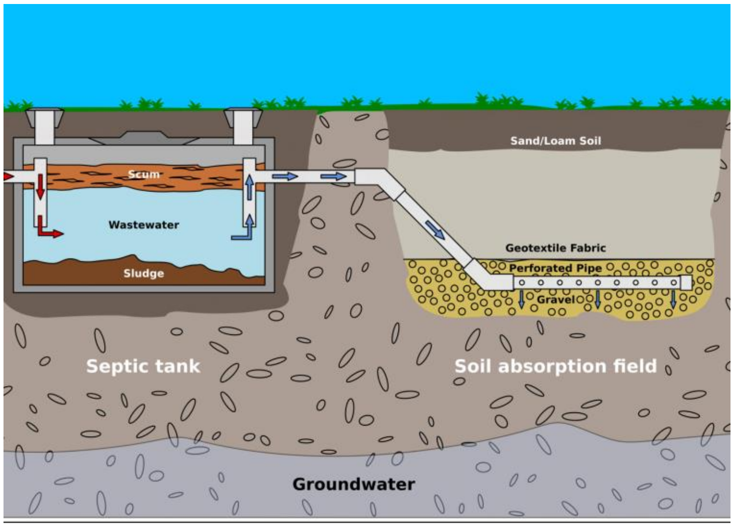


Figure 2: A basic septic system design includes a septic tank in which solids are separated and digested followed by a soil absorption field/leach field where further physical and biological treatment occurs.

The transformation of PFAS precursors into other metabolites is facilitated by the microorganisms already present in septic systems. Being able to predict the types of compounds generated from biotransformation enables us to understand what types of

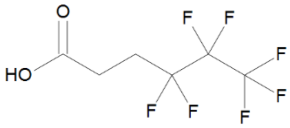
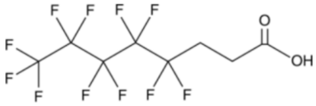
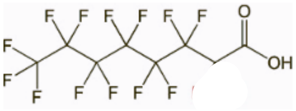
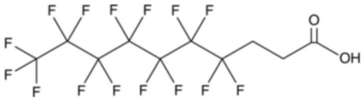
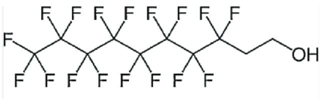
PFAS are found in treated effluent and nearby private wells. In 2021, the Environmental Protection Agency (EPA) created a new tool for predicting transformation pathways and physicochemical properties of organic chemicals called the Chemical Transformation Simulator (CTS). This modeling tool was recently expanded to include PFAS transformation pathways in environmental and metabolic settings. The reaction schemes in the CTS are based on peer-reviewed literature and regulatory reports (Weber et al., 2022). The tool includes proposed transformation products (PTPs) in order to rationalize the formation of experimentally verified transformation products (TPs) (Weber et al., 2022). Reaction systems used to generate pathways include aquatic systems, aerobic activated sludge, anaerobic digester sludge, aerobic and anaerobic soil, marine sediment, landfill leachate, and bacterial cultures. Types of reactions documented in the PFAS environmental reaction libraries include oxidation, reduction, hydrolysis, hydroxylation, decarboxylation, hydrodefluorination, desulfonation, *N*-deacetylation, and *N*-dealkylation (Weber et al., 2022).

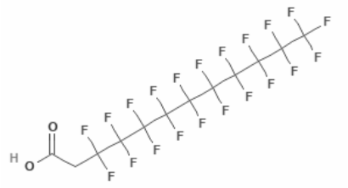
For this project, the CTS was used to determine potential reaction pathways for a selected group of PFAS known as fluorotelomer carboxylic acids (FTCAs). FTCAs are intermediates in the degradation of fluorotelomer alcohols (FTOHs) to perfluorinated carboxylic acids (PFCAs) (Shi et al., 2017). FTCAs have been detected in precipitation, septic systems, wildlife, and surface waters (Shi et al., 2017). Research has shown that PFCAs, transformation products of FTCAs "...are associated with developmental and hormonal effects, immunotoxicity, and promote tumor growth in rodents through their role as PPARα agonists” (Rand et al., 2017). Another study of the impact of 6:2 FTCA on zebrafish embryos found that “6:2 FTCA exposure decreased the hatching and survival percentages, reduced the heart rate, and increased the malformation of zebrafish embryos" (Shi et al., 2017). It is very likely that these compounds and their transformation products also negatively impact human health, increasing the importance of understanding how they break down in septic system environments.

4. Methods

Table 1 shows the six compounds that were mapped using the CTS. The compounds to be mapped were determined using data provided by Dr. Jennifer Harfmann of the New Hampshire Department of Environmental Services (NHDES) (Harfmann, n.d.). The NHDES has begun testing residential community septic systems for PFAS in an effort to understand possible discharges to ambient groundwater, which serves as a drinking water source in many New Hampshire communities. NHDES data sampled from septic systems indicated the following six FTCAs were commonly present, making them an appropriate choice for this study.

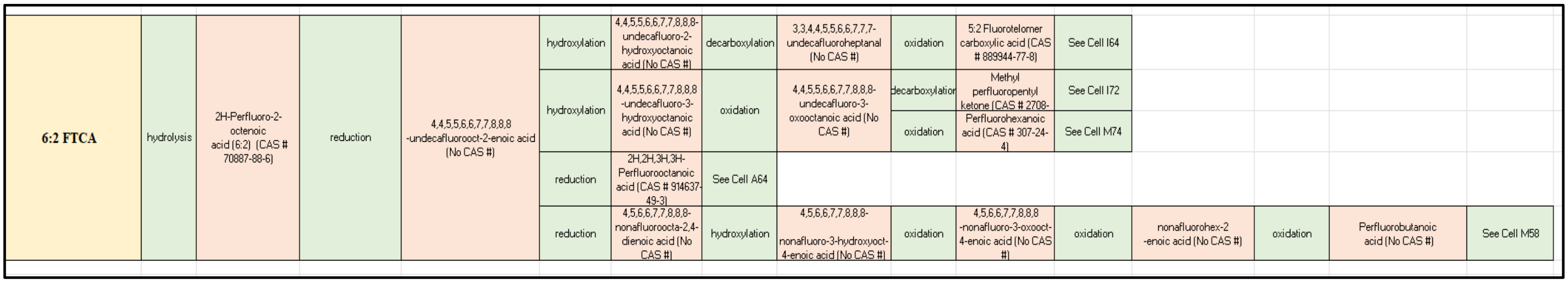
Table 1: Selected Compounds and Their Structures

Compound Name	Molecular Structure
3:3 FTCA	
5:3 FTCA	
6:2 FTCA	
7:3 FTCA	
8:2 FTCA	

10:2 FTCA	

To map these compounds in the CTS, each canonical SMILES code, or “Simplified Molecular Input Line Entry System” code was input into the transformation product workflow. The CTS identifies the entered compound and populates the screen with the compound’s structure, preferred name, CAS (Chemical Abstracts Service) number, and average mass. Then, the “user-selected” PFAS Environmental reaction library is selected. The first-generation transformation product is shown along with its physicochemical properties, the type of reaction that takes place, and the atomic mass. Then, the transformation products for the first-generation product can be determined using the same process until terminal metabolites are reached.

The pathway information was extracted from CTS and mapped in this thesis using Microsoft Excel. A branching format was used in which the breakdown products and required reactions stemmed from the precursor’s assigned cell. The types of reactions were shown in green and generated compounds were marked in orange cells. The method of mapping used is illustrated in the pathway for 6:2 FTCA (Figure 3). Some cells reference other cells on the transformation spreadsheet in order to repeat having to map the same pathway multiple times. CAS numbers were noted along with each compound’s preferred name.



6:2 FTCA	hydrolysis	2H-Perfluoro-2-octenoic acid (6:2) (CAS # 70887-88-6)	reduction	4,4,5,5,6,6,7,7,8,8,8 -undecafluorooct-2-enoic acid (No CAS #)	hydroxylation	4,4,5,5,6,6,7,7,8,8,8-undecafluoro-2-hydroxyoctanoic acid (No CAS #)	decarboxylation	3,3,4,4,5,5,6,6,7,7,7-undecafluoroheptanal (No CAS #)	oxidation	5:2 Fluorotelomer carboxylic acid (CAS # 889944-77-8)	See Cell I64				
					hydroxylation	4,4,5,5,6,6,7,7,8,8,8 -undecafluoro-3-hydroxyoctanoic acid (No CAS #)	oxidation	4,4,5,5,6,6,7,7,8,8,8-undecafluoro-3-oxooctanoic acid (No CAS #)	decarboxylation	Methyl perfluoropentyl ketone (CAS # 2708-	See Cell I72				
									oxidation	Perfluorohexanoic acid (CAS # 307-24-4)	See Cell M74				
					reduction	2H,2H,3H,3H-Perfluorooctanoic acid (CAS # 914637-49-3)	See Cell A64								
					reduction	4,5,6,6,7,7,8,8,8-nonafluoroocta-2,4-dienoic acid (No CAS #)	hydroxylation	4,5,6,6,7,7,8,8,8-nonafluoro-3-hydroxyoct-4-enoic acid (No CAS #)	oxidation	4,5,6,6,7,7,8,8,8 -nonafluoro-3-oxooct-4-enoic acid (No CAS #)	oxidation	nonafluorohex-2 -enoic acid (No CAS #)	oxidation	Perfluorobutanoic acid (No CAS #)	See Cell M58

Figure 3: The transformation pathway of 6:2 FTCA illustrates the mapping process used for this thesis.

For the individualized mapping of these precursors to regulated or common end products, the structure output from the CTS was used to illustrate changes in molecular structure. The National Library of Medicine’s “PubChem” database was also used to determine the nicknames for the generated chemicals when possible (U.S. National Library of Medicine, n.d.).

5. Results

The first project deliverable was a spreadsheet containing the full transformation pathways for the six chosen FTCAs. The full spreadsheet can be found in the appendix. From this data, it was determined that there were a total of 6 possible reactions involved in the transformation of these products. The processes and their definitions are shown in Table 2.

Table 2: Types of Reactions Involved in the Transformation of FTCAs

Type of Reaction	**Definition**
Oxidation	The loss of electrons during a reaction.
Reduction	The gain of electrons during a reaction.
Hydroxylation	A chemical process in which a hydroxyl (-OH) group is introduced into an organic compound.
Decarboxylation	A chemical reaction that removes a carboxyl group (COOH) and releases CO2 during a reaction.
Hydrolysis	The addition of water to a large molecule to break it into multiple smaller molecules.
Hydrodefluorination	A reaction in which a substrate of a carbon–fluorine bond is replaced by a carbon–hydrogen bond.

Following the identification of the reactions involved in the transformation of FTCAs, the terminal breakdown products for each of the selected compounds were determined. These results are summarized in Table 3. The bolded compounds are regulated in the state of New Hampshire and, as of April 2024, they are also regulated by the EPA.

Table 3: Terminal Breakdown Products of the Chosen FTCAs

Compound	**Terminal Breakdown Products**

3:3 FTCA	- TFA-d: trifluoroacetic acid-d
	  - (CAS # 599-00-8)
	- PFPrA: perfluoropropionic acid
	  - (CAS # 422-64-0)
	- Heptafluorobutyric acid (also called heptafluorobutanoic acid)
	  - (CAS # 62765-25-7)
	- 4,5,5-trifluoro-3-hydroxypent-4-enoic acid
	  - (No CAS #)
	- TFPA: 2,3,3,3-Tetrafluoropropanoic Acid
	  - (CAS # 359-49-9)
	- 4,4,4-trifluoro-3-hydroxybutanoic acid
	  - (CAS # 400-35-1)
	- 3,3,3-Trifluoropropionic acid
	  - (CAS # 2516-99-6)
	- PFPA: pentafluoropropanoic acid
	  - (CAS #422-64-0)
	- 2,3,4,4,4-hexafluorobutanoic acid
	  - (CAS # 62765-25-7)
	- HFBA: heptafluorobutanoic acid
	  - (CAS # 375-22-4)

5:3 FTCA	**Precursor to 4,4,5,5,6,6,6-Heptafluoro-2-hexenoic acid (CAS # 356-03-6) which is the first product of 3:3 FTCA after it is oxidized, therefore all of the 3:3 FTCA products are also 5:3 FTCA products.*
	- 2H-Perfluoropentanoic acid
	  - (No CAS #)
	- PFPeA: Perfluoropentanoic acid
	  - (CAS # 2706-90-3)
	- PFHxA: Perfluorohexanoic acid
	  - (CAS # 307-24-4)
	- PFBA: Perfluorobutanoic acid
	  - (CAS # 375-22-4)
	- 2H-Perfluorohexanoic acid
	  - (No CAS #)

6:2 FTCA	**Precursor to 5:3 FTCA therefore all of the 5:3 FTCA metabolites are also metabolites of 6:2 FTCA.* *Precursor to 4,4,5,5,6,6,6-Heptafluoro-2-hexenoic acid (CAS # 356-03-6) which is the first product of 3:3 FTCA after it is oxidized, therefore all of the 3:3 FTCA products are also 6:2 FTCA products.*
	**Precursor to 6:2 FTCA, therefore, it has the same transformation products as 6:2*

7:3 FTCA	*FTCA.*
	- PFHpA: Perfluoroheptanoic acid
	  - (CAS # 375-85-9)
	- 2H-Perfluoroheptanoic acid
	  - (No CAS #)
	- 2H-Perfluorooctanoic acid
	  - (CAS # 142821-03-2)
	- **PFOA: Perfluorooctanoic acid**
	  - (CAS # 335-67-1)

8:2 FTCA	**8:2 FTCA, like 7:3 FTCA, is a precursor to 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10 -Pentadecafluorodec-2-enoic acid (CAS # 755-03-3). Since this is the first transformation product of 7:3 FTCA (oxidation), 8:2 FTCA has the same transformation products as 7:3 FTCA.*

10:2 FTCA	**Precursor to 8:2 FTCA, therefore it has the same transformation products of 8:2 FTCA.*
	- **PFNA: Perfluorononanoic acid**
	  - (CAS # 375-95-1)
	- 2H-Perfluorononanoic acid
	  - (No CAS #)
	- PFDA: Perfluorodecanoic acid
	  - (CAS # 335-76-2)
	- 2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-octadecafluorodecanoic acid
	  - (No CAS #)

The data in Table 3 suggests a relationship in the way larger FTCA molecules break down into smaller FTCA molecules. This relationship, which is shown in Figure 4, was interpreted using the generated spreadsheet and verified by the literature (Kolanczyk et al., 2023). The pathway shows that FTCAs give rise to fluorotelomer unsaturated carboxylic acids (FTUCAs) before giving rise to FTCAs with fewer carbon fluorine bonds. Some of the reactions shown are reversible; for example, 3:3 FTCA is oxidized to form 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid, but 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid can also be reduced to reform 3:3 FTCA. There are likely missing compounds within this pathway; however, due to the lack of verified CAS numbers and nicknames for each of the compounds produced by the CTS, only the following compounds could be identified.

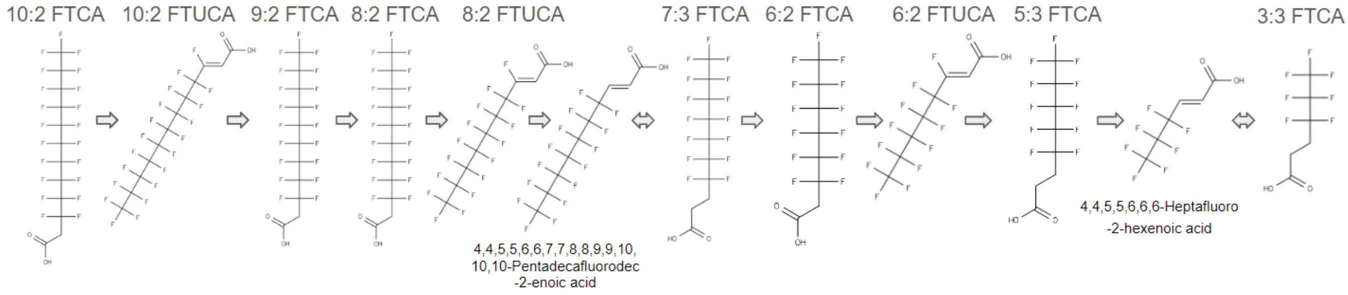


Figure 4: FTCAs transform to FTUCAs before giving rise to FTCAs with fewer carbon fluorine bonds.

The next phase of the research was to determine patterns in the transformation of FTCAs to regulated or common terminal products. Two of the six compounds that were mapped were chosen (5:3 FTCA and 7:3 FTCA). These two compounds were chosen because they produce terminal products that are either well studied or commonly found in wastewater at high concentrations (Kurwadkar et al., 2022). Structure transformation diagrams were generated for the specific parts of these compounds’ pathways that generate PFHxA for 5:3 FTCA and PFOA for 7:3 FTCA. The two ways in which 5:3 FTCA can produce PFHxA are shown in Figures 5 and 6, and the two ways in which 7:3 FTCA can produce PFOA are shown in Figures 7 and 8.

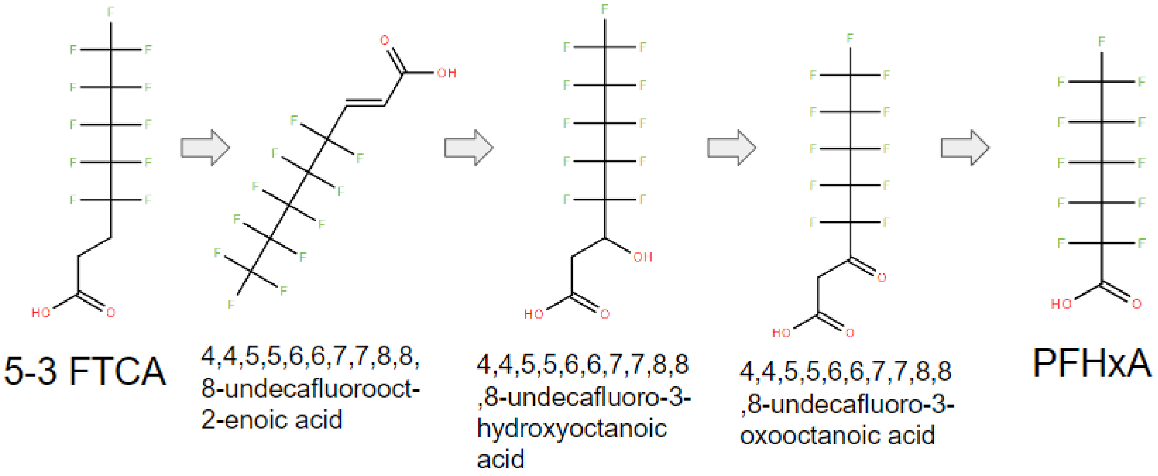


Figure 5: Pathway 1 for the transformation of 5:3 FTCA to PFHxA is illustrated.

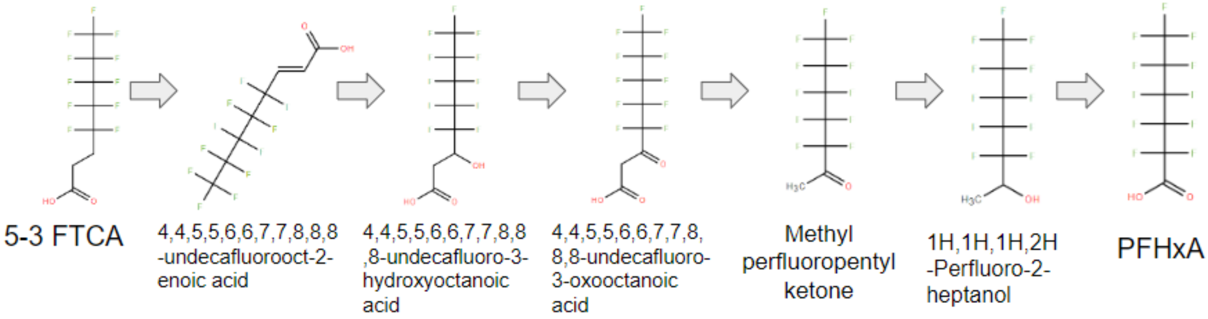


Figure 6: Pathway 2 for the transformation of 5:3 FTCA to PFHxA is illustrated.

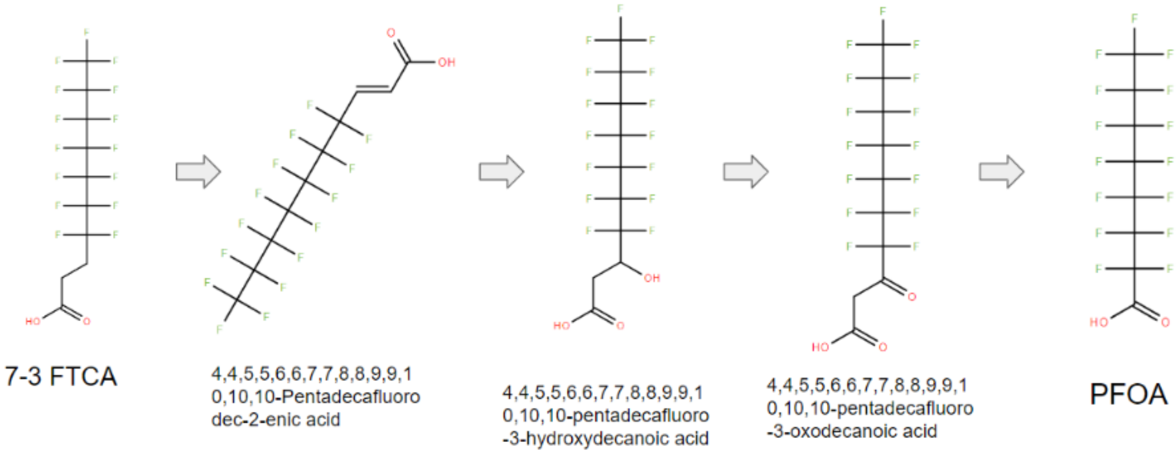


Figure 7: Pathway 1 for the transformation of 7:3 FTCA to PFOA is illustrated.

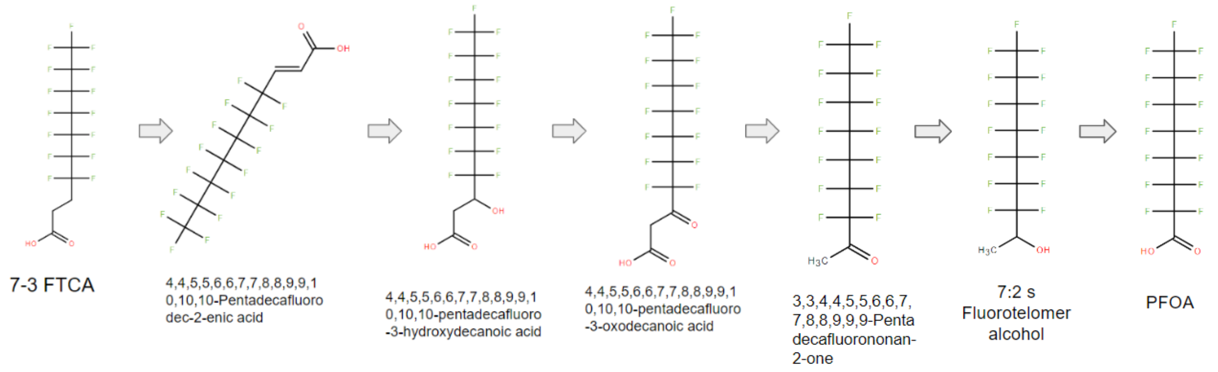


Figure 8: Pathway 2 for the transformation of 7:3 FTCA to PFOA is illustrated.

The branched pathways for 5:3 FTCA and 7:3 FTCA that include both of these pathways as well as the reaction types are shown in Figure 9 and Figure 10.

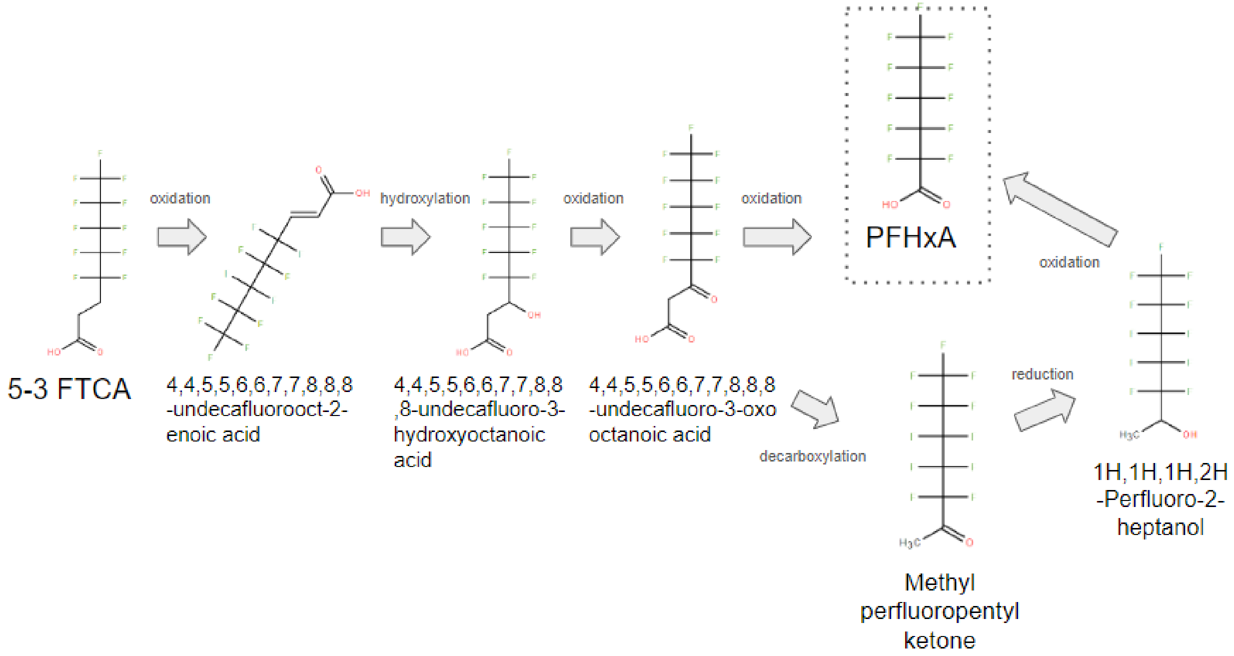


Figure 9: The 5:3 FTCA pathways and reactions are illustrated.

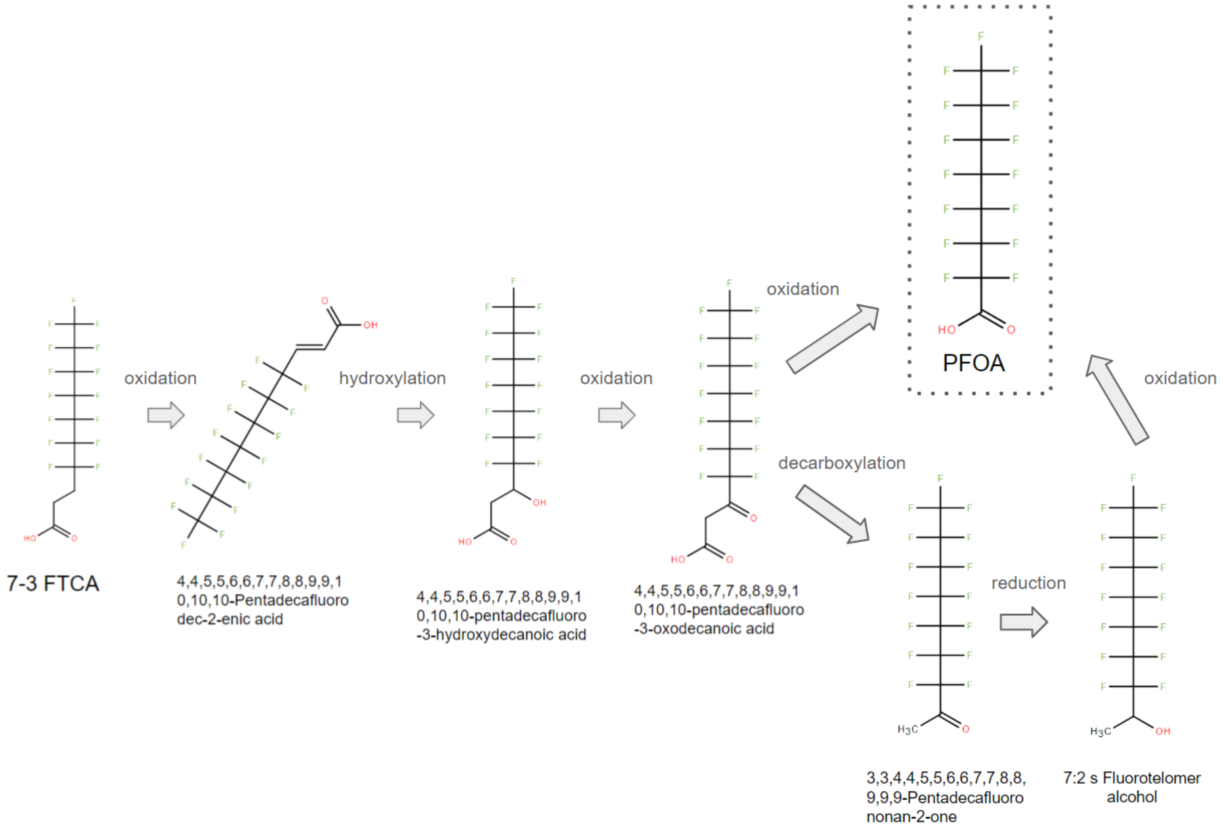


Figure 10: The 7:3 FTCA pathways and reactions are illustrated.

6. Analysis

As shown in Table 2, the types of reactions that might be involved in FTCA transformation include oxidation, reduction, hydroxylation, decarboxylation, hydrolysis, and hydrodefluorination. The likelihood of each type of reaction in septic system environments is highly dependent on environmental factors. For example, if the septic systems are aerated, then oxidation will likely occur; however, most septic systems have reducing conditions, meaning reduction is more likely to occur (Humphrey et al., 2024).

In regard to the terminal breakdown products of the six compounds, it was found that PFOA, one of the most well studied and regulated PFAS compounds, was a possible product from 7:3 FTCA, 8:2 FTCA, and 10:2 FTCA. In addition, 10:2 FTCA also produces PFNA, another PFAS regulated in drinking water. Smaller chain molecules including 6:2 FTCA, 5:3 FTCA, and 3:3 FTCA are not predicted to produce PFOA or PFNA because both terminal products require more carbon fluorine chains than these molecules have.

Relationships were also identified between the different FTCAs studied. 5:3 FTCA degrades to 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid which is the first product of 3:3 FTCA after it is oxidized, meaning all of the transformation products of 3:3 FTCA are also transformation products of 5:3 FTCA. 5:3 FTCA is also a transformation product of 6:2 FTCA, meaning the transformation products of 5:3 FTCA are also transformation products of 6:2 FTCA. Likewise, 6:2 FTCA is a transformation product of 7:3 FTCA. 8:2 FTCA gives rise to 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodec-2-enoic acid which is the first transformation product of 7:3 FTCA (oxidation); therefore, 8:2 FTCA has the same transformation products as 7:3 FTCA. 8:2 FTCA is also a transformation product of 10:2 FTCA. Figure 4 depicts the relationship between these compounds as well as some intermediate products that are created during the transformation products. The CTS output suggests that FTCAs transform to FTUCAs (fluorotelomer unsaturated carboxylic acids) before transforming to FTCAs with fewer carbon fluorine bonds. There are gaps present in this figure due to the lack of CAS numbers and nicknames associated with these intermediate products; for example, 9:2 FTCA likely gives rise to 9:2 FTUCA before 8:2 FTCA is produced. However, this compound could not be distinguished in the generated pathway because it is difficult to distinguish compound nicknames from their IUPAC names.

In order to identify more patterns in how FTCAs transform, two of the six selected compounds were chosen for further examination. The goal of this process was to identify the steps involved in the formation of two terminal products that are common in wastewater systems as well as the likelihood of these processes. The transformation of 5:3 FTCA to PFHxA was first examined. According to the EPA, “PFHxA is a breakdown product of other PFAS that are used in stain-resistant fabrics, paper food packaging, and carpets; it is also used for manufacturing photographic film, and it is used as a substitute for longer chain perfluoroalkyl carboxylic acids (PFCAs) in consumer products. PFHxA has been found to accumulate in agricultural crops and has been detected in household dust, soils, food products, and surface, ground, and drinking water” (EPA, 2023). PFHxA is a common transformation product of short-chain fluorotelomers that contain six carbons or less (Anderson et al., 2019). To delineate trends, the 5:3 FTCA pathway was examined in the Excel spreadsheet. It was determined that there are two ways in which 5:3 FTCA can produce PFHxA. Both of these pathways are depicted separately in Figures 5 and 6, and the branched pathway is shown in Figure 9. The pathways both involve the oxidation of 5:3 FTCA to 4,4,5,5,6,6,7,7,8,8,8-undecafluorooct-2-enoic acid, the hydroxylation of 4,4,5,5,6,6,7,7-,8,8,8-undecafluorooct-2-enoic acid to 4,4,5,5,6,6,7,7,8,8,8- undecafluoro-3-hydroxyoctanoic acid, and the oxidation of 4,4,5,5,6,6,7,7,8,8,8-undecafluoro-3-hydroxyoctanoic acid to 4,4,5,5,6,6,7,7,8,8,8-undecafluoro-3-oxooctanoic acid. The pathways then become different; in the first pathway, 4,4,5,5,6,6,7,7,8,8,8-undecafluoro-3-oxooctanoic acid is oxidized to PFHxA directly. In the second pathway, 4,4,5,5,6,6,7,7,8,8,8-undecafluoro-3-oxooctanoic acid is decarboxylized to methyl perfluoropentyl ketone, which is reduced to 1H,1H,1H,2H-Perfluoro-2-heptanol which is then oxidized to PFHxA. Like 5:3 FTCA, there are also two ways in which 7:3 FTCA can produce PFOA, one of the most well studied and regulated types of PFAS. Both pathways involve the oxidation of 7:3 FTCA to 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodec-2-enic acid, the hydroxylation of 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodec-2-enic acid to 4,4,5,5,6,6,7,7,8, 8,9,9,10,10,10-pentadecafluoro-3-hydroxydecanoic acid, and the oxidation of 4,4,5,5,6, 6,7,7,8,8,9,9,10,10,10- pentadecafluoro-3-hydroxydecanoic acid to 4,4,5,5,6, 6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-oxodecanoic acid. Then, the pathway splits; in pathway one, 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-oxodecanoic acid is immediately oxidized to PFOA. In the second pathway, 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-oxodecanoic acid is decarboxylized to 3,3,4,4,5,5,6,6,7,7, 8,8,9,9,9-pentadecafluorononan-2-one which is reduced to 7:2 FTOH which is then oxidized to PFOA. Through this mapping process, it was determined that the exact same transformation steps occur for 5:3 and 7:3 FTCA to produce the selected terminal products. Pathway one for both involves oxidation, hydroxylation, oxidation, and oxidation again. Pathway two for both involves oxidation, hydroxylation, oxidation, decarboxylation, reduction, and oxidation again. All changes to the functional end of each molecule are the same with each step (i.e. if a double bond is added to 5:3 FTCA in the first transformation step, the same is true for 7:3 FTCA). This indicates that the breakdown pathways for these two molecules are the same, with the only difference being the number of carbons present in the molecules. The variation in transformation product naming between 5:3 FTCA and 7:3 FTCA can be attributed to the different number of carbons present.

The next step of the research process was to determine if the formation of PFHxA by 5:3 FTCA or PFOA by 7:3 FTCA via either of the two pathways is likely to occur in a septic environment. Based on the generated pathways, it is clear that the only structural changes that are occurring during transformation are related to the functional groups rather than the carbon-fluorine backbone or “tail.” Since the carbon fluorine bonds in PFAS are so difficult to break and since these reactions are only changing the functional group structure rather than the tail structure, they are likely to occur in septic environments, as significantly less energy is required by the microorganisms to make changes to the functional ends. This theory is supported by the literature: “...one study indicated that PFOA was biologically inert, while others showed significant transformation of the functional head groups of perfluorinated compounds produced by electrochemical fluorination (ECF) and polyfluorinated compounds produced from the fluorotelomerization process (FT) leading to the idea that only transformation of the functional group, and not the fluorinated tail, was likely” (LaFond, 2023). Other researchers have found that the defluorination process is extremely slow (Wackett, 2021). Even though this evidence points to the fact that these transformation pathways could happen, the individual types of reactions and the environmental conditions that enable them are what truly dictate the extent of the transformation process. In wastewater systems, oxidation occurs as a function of coupled redox between oxygen and organic matter. In wastewater treatment plants, blowers add oxygen to wastewater; oxygen itself is a highly efficient terminal electron acceptor, meaning it provides microbes with a lot of energy to oxidize organic matter. Nitrate is also a compound that can give microbes the energy to oxidize organic matter; however, when these electron acceptors are used up, different reactions begin to take place. Most septic systems are anaerobic and, therefore, favor reduction over oxidation. As a result, most of the oxidation reactions occurring during FTCA transformation likely occur very slowly while reduction reactions occur more quickly. I concluded that the transformation of 5:3 and 7:3 FTCA to PFHxA and PFOA is possible in septic system environments, but since oxidation is the predominant reaction taking place, degradation likely occurs very slowly. Oxidation could occur in other parts of the system (i.e. while waste moves from the house to the tank or when the treated septage enters the leach field and moves into the subsurface).

7. Conclusions and Recommendations

As the public gains awareness about the impacts of PFAS on human and environmental health, industrial manufacturing processes, commercial goods, drinking water, and wastewater will become highly regulated. The EPA just recently announced the final National Primary Drinking Water Regulation (NPDWR) for PFOA, PFOS, PFNA, GenX chemicals, PFHxS, and mixtures of PFAS in drinking water (EPA, 2024). However, these new rules only apply to public water systems, leaving individuals relying on private wells as a drinking water source and septic systems for wastewater treatment especially vulnerable because they are not subject to routine monitoring. Ensuring that rural communities have access to safe drinking water will not only require the monitoring of groundwater supplies but also effective treatment of their wastewater by septic systems. In order to ensure that septic systems have the capacity to remove and sequester PFAS, we first need to understand what types of PFAS are entering these onsite systems, what reactions are occurring in the subsurface, and how these reactions influence contaminant concentrations in leach fields.

This research study identified a class of PFAS compounds that are commonly found in septic systems and investigated how these chemicals may be transforming in septic systems. Not only was it was found that large FTCA molecules have the capacity to produce PFOA and PFNA, but this research also suggests that FTCA compounds may follow a distinct pathway to produce a subset of terminal end products with carboxyl functional groups regardless of the length of the carbon-fluorine backbone. These pathways are possible in septic system environments, but whether these reactions are rate limited in septic systems remains to be seen. The findings of this study will help environmental engineers and scientists characterize the types of transformation pathways that occur in septic systems. Understanding what reactions are occurring in septic systems will inform our understanding of the types of PFAS that are being discharged to leach fields where they have the capacity to contaminate drinking water supplies. In the future, pilot tests in which influent and effluent samples are taken should be conducted so the extent to which FTCAs transform in septic systems can be monitored in real time. In addition, the CTS could be significantly improved if additional parameters such as pH, dissolved oxygen content, etc. could be input into the simulator; this would allow for more robust conclusions regarding PFAS transformation in unique environments like septic systems.

8. References

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9. Appendix

The full spreadsheet can be found at the following link: PFAS Transformation.xlsx. Use the password “PFAS” to gain viewing access.