

Exploring the Prospects and Challenges of Fluorine-Free Firefighting Foams (F3) as Alternatives to Aqueous Film-Forming Foams (AFFF): A Review

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ABSTRACT: This review provides a comparative analysis of the performance, toxicity, environmental impact, and health risks associated with fluorotelomer-based/short-chain AFFF and F3. Despite notable progress in F3 development, achieving comparable performance remains challenging in some cases. F3 formulations, while promising, are yet to be considered a direct replacement for AFFF in all Class B fire suppression scenarios due to variations in their performance across different fuel types and test conditions. Available studies indicate that commercially available F3 exhibit greater biodegradability and reduced environmental persistence compared to AFFF. However, some alternatives may still pose similar environmental impacts. Limited ecotoxicity studies suggest that some F3 may exhibit equal or even higher toxicity to aquatic species than short-chain (C6) AFFF. Toxicological assessments and risk evaluations of F3 should consider factors beyond environmental persistence, including acute and chronic ecotoxicity, potential endocrine disruption, and the full toxicological profile of foam formulations and their individual components. Further research is necessary to understand the fate, transport, bioaccumulation, and toxicity of F3 degradation products. Addressing these knowledge gaps is crucial to ensure the safe and sustainable implementation of F3 as an alternative fire suppression solution.



1. INTRODUCTION

The development of firefighting foam in the early 1900s was driven by the need to combat hydrocarbon fires resulting from the widespread use of liquid hydrocarbons and polar solvent fuels in various industries.^{1,2} Over time, the performance of firefighting foams has continuously improved along with the advancements in technology and the introduction of various foam types. The market now offers a range of firefighting foams designed to address specific fire hazards and achieve optimal suppression outcomes. Class A and Class B foams are the two prominent classes of firefighting foam. Class A foams are used to fight structural fires and wildfires, while Class B foams are designed to fight fires involving flammable liquids, gasoline, oils, jet fuel, alcohols, and oil-based paints.¹ The effectiveness of Class B foams significantly improved with the incorporation of fluorosurfactants in their composition.^{1,3} These fluorosurfactants belong to the per- and polyfluoroalkyl substances (PFAS) chemical family and have consistently served as key components in fluorine-based Class B foams for over six decades, owing to their unique surface-active properties. Although there are a number of ways to classify firefighting foams, from a PFAS standpoint, firefighting foams can be

classified into two categories: fluorinated foams containing PFAS and fluorine-free foams that do not contain PFAS.

Aqueous film-forming foam (AFFF) is a PFAS-based Class B firefighting foam that has been extensively used in firefighting activities, particularly in suppressing flammable liquid fires. The widespread use of AFFF at the fire scene, training facilities, and subsequent disposal of wastewater into the environment has led to the contamination of surface water and groundwater.^{4,5} The release of PFAS from AFFF may pose significant environmental and health risks. Fluorosurfactants in AFFF have a high environmental footprint due to their inherent chemical stability and resistance to degradation.¹ Their persistence allows PFAS-based substances to remain in the environment for decades after use.⁶ Despite the transition of foam manufacturers to modern short-chain AFFF as an

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Table 1. Terminology of Long-Chain and Short-Chain PFAS

Compound	Long-chain	Short-chain	Structure
Perfluoroalkyl sulfonic acids (PFSA)	$n \geq 6$ e.g., PFOS, PFHxS	$n < 6$ e.g., PFBS	
Perfluoroalkyl carboxylic acids (PFCA)	$n \geq 8$ e.g., PFOA, PFNA, PFDA	$n < 8$ e.g., PFHxA, PFBA, PFPeA	
PFAA Precursors	$n > 6$ e.g., 8:2 FTOH	$n \leq 6$ e.g., 6:2 FTOH, 4:2 FTOH	

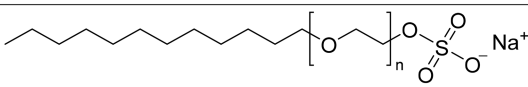
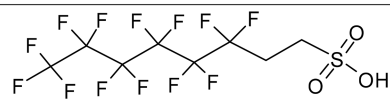
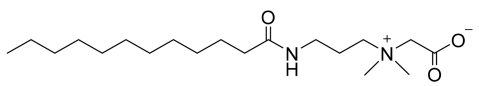
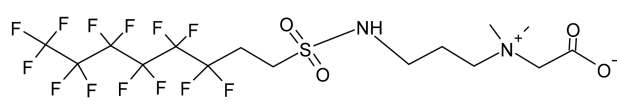
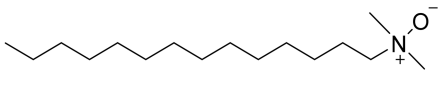
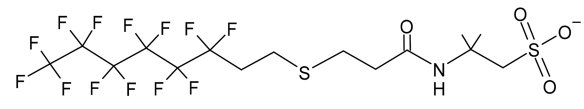
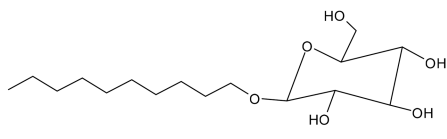
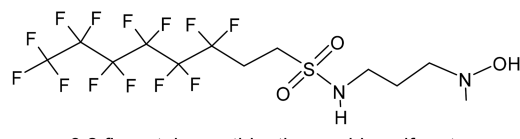
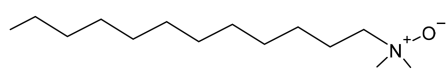
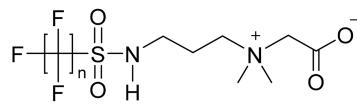
alternative to legacy PFAS-based firefighting foams, some highly persistent long-chain PFAS, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are still present in the environment. Moreover, these short-chain analogs and degradation byproducts of polyfluoroalkyl substances are similarly persistent, and highly water-soluble, allowing them to migrate beyond their intended application sites and impact nearby drinking water sources.⁷ Numerous public and private drinking water supplies have been impacted by PFAS-containing firefighting foams used at AFFF-certified civilian airports and military fire training sites.^{7–9} Elevated concentrations of PFAS have been reported in drinking water supplies near these sites.^{7,10} Individuals exposed to AFFF-contaminated drinking water have higher serum concentrations of certain PFAS than the U.S. national average.^{11–13} Multiple studies have indicated a potential association between elevated serum PFAS levels and an increased health risk.^{14–17} Exposure to PFAS, however, can vary depending on factors such as geographical location and occupation. Firefighters are the primary users of foam and can be exposed to AFFF in various ways, including during fire incidents, training exercises, handling, transportation, and disposal of foam. Exposure to AFFF may increase the risk of firefighters developing health issues.¹⁷

In response to concerns raised about the long-term environmental and health effects associated with PFAS, several

countries, and regions have taken steps to ban or restrict the use of PFAS-based AFFF. The European Chemicals Agency (ECHA) has proposed an EU-wide restriction on all PFAS in firefighting foams.¹⁸ In the United States, certain states have also taken action to limit the use of PFAS-containing foams, particularly in training exercises and non-emergency situations.^{19–21} Most recently, the U.S. Department of Defense (DoD) has published a new fluorine-free foam military specification (MILSPEC) to comply with the National Defense Authorization Act for Fiscal Year 2020, which requires the phaseout of PFAS-containing firefighting foam by October 2024.²² In this context, fluorine-free foams (F3) have emerged as an alternative to address these concerns. The development and adoption of F3 have gained attention in recent years, driven by the need for effective firefighting formulations with lower environmental and health impacts. While F3 may offer potential advantages in terms of environmental impact, their performance may differ from traditional PFAS-based foams. Additionally, in comparison to their AFFF counterparts, there is relatively limited toxicological information available for fluorine-free firefighting foams.

With the current global emphasis on promoting the use of F3, it is crucial to gather extensive data on the existing fluorine-free foams. Such data can assist stakeholders in making informed decisions in the selection and use of firefighting foams based on their specific needs and provide more direction

Table 2. Examples of Surfactants Commonly Used in AFFF and Fluorine-Free Firefighting Foams

Surfactants in F3	Surfactants in AFFF
 <p>Sodium laureth sulfate</p>	 <p>6:2 fluorotelomer sulfonate</p>
 <p>Alkyl amidobetaine</p>	 <p>6:2 fluorotelomer sulfonamide alkylbetaine</p>
 <p>N,N-Dimethyltetradecylamine N-oxide</p>	 <p>6:2 fluorotelomer thioether amido sulfonate</p>
 <p>Alkylpolyglycoside</p>	 <p>6:2 fluorotelomer thioether amido sulfonate</p>
 <p>N,N-Dimethyldodecylamine N-oxide</p>	 <p>Perfluorooctane sulfonamide betaine</p>

for future research on firefighting foam alternatives. Recognizing such a critical transition, this review paper aims to provide a thorough analysis of the performance, toxicity, and health risks associated with fluorotelomer-based AFFF and fluorine-free foams. Our goal is to provide comprehensive information on F3 for a diverse audience, including the firefighter community, policymakers, and academic researchers.

This paper begins with a brief overview of the history and classification of fluorinated and fluorine-free firefighting foams. This is followed by a discussion on the comparative analysis of AFFF and F3's performance and the challenges in transitioning to safer PFAS-free alternatives. Lastly, a summary of studies investigating the potential environmental and health risks posed by short-chain AFFF and F3 is presented. This will help in not only addressing the various challenges posed by transitioning to safer alternatives but also investigating the potential environmental and health impacts of both short-chain AFFF and F3 formulations. Terminology and background information will help policymakers and researchers understand the context and technical terms. Discussions on aquatic toxicity and the environmental impact of firefighting foams aim to inform policymakers about the regulatory and environmental considerations related to F3 use. Firefighters can also benefit from understanding the environmental implications and health risks associated with these foam uses.

2. TERMINOLOGY OF SHORT-CHAIN AND LONG-CHAIN PFAS

The PFAS family refers to a group of chemical compounds consisting of at least one perfluorinated methyl group ($-\text{CF}_3$) or a perfluorinated methylene group ($-\text{CF}_2-$) attached to

various functional groups such as carboxylic acids, sulfonic acids, and alcohols.^{23,24} Perfluoroalkyl acids (PFAA) are a subgroup of PFAS commonly used as fluorosurfactants in older AFFF formulations.²³ PFAAs are less common in newer generations of fluorotelomer-based AFFF. The two primary families within PFAA are perfluoroalkyl sulfonic acids (PFSA) and perfluoroalkyl carboxylic acids (PFCA).²⁵ There exists a clear distinction between these two families in terms of defining long-chain and short-chain compounds. In the context of PFAS, the terms "long" and "short" are used to describe the length of the carbon backbone in a molecule. In the PFSA family, long-chain compounds are defined as those with a carbon chain length of six or more, while in the PFCA family, long-chain compounds refer to those with a carbon chain length of eight or more.¹ Fluorotelomer-based surfactants present in AFFF belong to polyfluoroalkyl substances and can be transformed to form perfluorinated PFAA. Polyfluoroalkyl substances that have the potential to generate terminal perfluoroalkyl acids are known as precursors.²⁶ Long-chain precursors are referred to as polyfluoroalkyl substances with more than six carbons in length, whereas short-chain precursors consist of six carbons or less. The terminology of long-chain and short-chain PFAS is presented in Table 1.

3. FOAM INGREDIENTS AND COMPOSITION

Firefighting foam is made by diluting a foam concentrate with water. The concentrate and water form a foam solution, which is then aerated using a foam-generating device to produce the final foam product. These foam concentrates are commonly available in 1%, 3%, or 6% concentrations, each intended for specific applications.¹ The foam concentrate contains four key

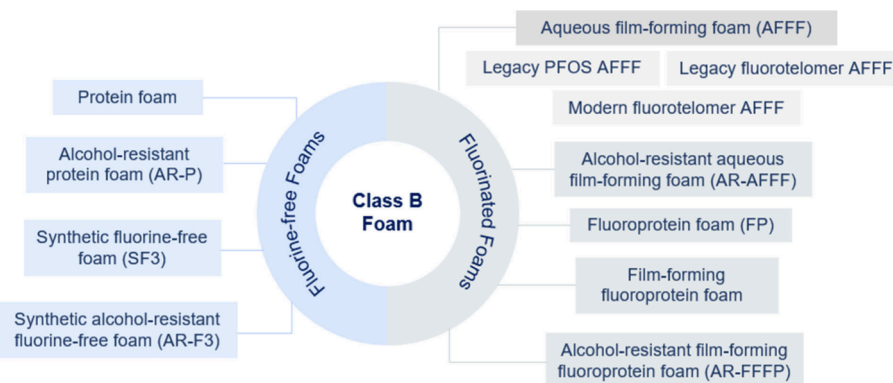


Figure 1. Types of Class B foam categorized based on the presence of PFAS (adapted from ITRC, 2022⁴⁴).

ingredients: water, surfactants, solvents, and various additives and modifiers. Water usually accounts for over 60% of the solution, while surfactants make up around 15–18%, and solvents contribute up to 20%.^{1,27} Fluorosurfactants typically comprise less than 2% of the total weight of a foam concentrate.¹ Except for F3, the surfactants commonly used in firefighting foams are typically combinations of hydrocarbon surfactants and fluorosurfactants. Both surfactant types can be classified as ionic (anionic, cationic, zwitterionic) or nonionic. Water-miscible solvents, such as isopropyl alcohol, *tert*-butyl alcohol, glycols, and glycol derivatives, are commonly used in foam concentrate.²⁸ Additives or modifiers are added to achieve the desired mechanical and chemical properties of the foam. These additives include preservatives, corrosion inhibitors, chelating agents, pH buffers, and emulsifiers.²⁸ Table 2 shows the names and structures of some surfactants commonly used in AFFF and F3 formulations.

4. FLUORINATED FOAMS CONTAINING PFAS

Legacy PFOS AFFF represents the earliest form of fluorinated foam, produced by the 3M Corporation in the US from the late 1960s until 2002 when it was voluntarily phased out.^{23,29} Marketed under the brand name Lightwater, these foams primarily contained long-chain (C8) perfluoroalkyl substances, with perfluorooctanesulfonate (PFOS) being the predominant compound.^{29,30} The PFOS in these historical AFFF formulations was synthesized using the electrochemical fluorination (ECF) process. The process involves replacing all hydrogen atoms in a straight-chain hydrocarbon with fluorine when an electric current is applied.^{31,32} In addition, these foams may have included other PFAS like PFOA, perfluorohexanesulfonate (PFHxS), and various fluorinated precursors.³³ These precursors may make up approximately one-third of the total PFAS content in 3M AFFF.³⁴

With the gradual phase-out of ECF-based AFFF formulations, manufacturers shifted to producing fluorotelomer-based surfactants using the telomerization process. Fluorotelomers are polyfluoroalkyl substances characterized by the substitution of one or more hydrogen atoms with fluorine atoms. These substances are denoted using an *n*:*x* prefix, where “*n*” indicates the number of fully fluorinated carbons and “*x*” represents the number of nonfully fluorinated carbons. The presence of reactive nonfluorinated carbons in fluorotelomers makes them more susceptible to atmospheric oxidation, potentially generating perfluoroalkyl acids (PFAA) when the bonds between perfluoroalkyl moieties and nonfluorinated groups break.²³ Legacy fluorotelomer AFFF was manufactured in the

US from the 1970s until 2016, except for the 3M Lightwater brand.⁴ This type of foam typically contains 50% to 98% short-chain (C6) fluorotelomer-based polyfluoroalkyl substances, along with long-chain PFAS.³⁵ Although not made with PFOA, these foams may still contain trace levels of PFOA and its precursors as manufacturing byproducts. Polyfluorinated precursors in fluorotelomer AFFF can break down to form PFOA and other perfluorocarboxylic acids (PFCA).^{26,35}

In response to the USEPA 2015 voluntary PFOA Stewardship Program, most foam manufacturers have now transitioned to producing modern fluorotelomer AFFF. These new foams exclusively contain short-chain (C6) fluorotelomers or short-chain fluorinated compounds. Unlike their predecessors, these short-chain fluorotelomers do not break down to produce harmful PFOA or PFOS. However, trace amounts of PFOS and PFOA may still be unintentionally present as small impurities from the telomere process. Additionally, these C6 foams can serve as PFCA precursors. When they undergo biotransformation in the environment, it can result in the formation of PFHxA, perfluoropentanoic acid (PFPeA), and 5:3 fluorotelomer carboxylic acid.^{36–38}

Another type of high-performance fluorinated foam concentrate is Alcohol-Resistant Aqueous Film-Forming Foam (AR-AFFF). Its formulation includes a combination of hydrocarbon and fluorosurfactants, water-soluble polysaccharide polymers, and stabilizers.^{39,40} AR-AFFF has distinct advantages over standard AFFF, as it effectively combats both polar (alcohol) and nonpolar (hydrocarbon) solvent fires.

Foam blankets that are not alcohol-resistant tend to absorb the fuel due to alcohol’s affinity to water, which results in the destruction of the foam blanket. AR-AFFF creates a polymeric layer between the fuel and the foam, enhancing its ability to extinguish polar solvent fires efficiently.⁴⁰ High-risk facilities such as refineries, chemical plants, or airports often require the use of AR-AFFF.⁴¹ Like the legacy AFFF, all pre-2016 AR-AFFF brands could break down to PFOA.

Fluoroprotein foams (FP) are derived from protein foams and contain small amounts of fluorosurfactants similar to those used in AFFF concentrates. These foams are well-suited for high-risk situations, such as fires involving hydrocarbon storage, processing, and transportation facilities.⁴² More complex FP formulations, such as film-forming fluoroprotein foams (FFFP) and alcohol-resistant film-forming fluoroprotein foams (AR-FFFP), typically consist of hydrolyzed protein, a blend of hydrocarbon and fluorosurfactants, and various solvents and stabilizers.^{40,43} Modern formulations use C6-based fluorosurfactants; however, pre-2016 products could

break down to PFOA in the environment. The classification of Class B foam based on presence of PFAS is presented in Figure 1.

5. FLUORINE-FREE FOAMS

Firefighting foams that do not contain fluorosurfactants or PFAS are commonly referred to as fluorine-free foams (FFF or F3).⁴⁵ Class A and most training foam are historically nonfluorinated. However, some F3 products labeled as “fluorine-free” may contain fluorosurfactants or other fluorinated compounds that do not meet the existing regulatory definitions of “PFAS-free” products. The definition of F3 varies depending on the certifying organizations. For example, the GreenScreen certification of Clean Production Action defines PFAS-free firefighting foam as having no intentionally added PFAS, and PFAS contamination level must be less than 1 part per million (ppm), measured as total organic fluorine using combustion ion chromatography.^{21,44} On the other hand, according to the military specification (MIL-F-24385), F3 must not contain intentionally added PFAS in the formulation and the foam concentrate may contain a maximum of 1 part per billion (ppb) of PFAS.²¹

Protein foam is the earliest form of F3 and was developed in the late 1930s.¹ The formulation comprises naturally occurring hydrolyzed proteins, foam stabilizers, bactericides, corrosion inhibitors, and solvents.⁴⁶ In addition to natural protein-based foams, there are synthetic fluorine-free foams (SF3) and synthetic alcohol-resistant fluorine-free foams (AR-F3) available in the market. SF3 may include silicone surfactants like carbohydrate siloxane, siloxane, or carbosiloxane, along with a mixture of foam stabilizers.⁴⁷ Unlike their fluorinated counterparts, these fluorine-free foams are less persistent in the environment and readily biodegradable.⁴⁸ F3 are not designed to form a film like AFFF; their fire suppression activity relies solely on the formation of a foam blanket.

The substances identified in F3 can be grouped into four classes based on their chemical structure: hydrocarbons, detergents, siloxanes, and proteins. Information on these substances is typically obtained from safety data sheets (SDS) provided by suppliers or compounds identified in the literature. Commonly found hydrocarbons include fatty acids, xanthan gums, sugars, alcohols, polyethylene glycol, and alkanes.^{46,49} Detergents found in these foams may belong to nonionic, anionic, or zwitterionic surfactant categories, as reported in the literature. Silicone surfactants, such as carbohydrate siloxane, have been used as an alternative to fluorosurfactants. Proteins come from sources such as horn, hoof, silk, or they can be derived from hydrolyzed protein.⁵⁰

6. PERFORMANCE OF AFFF AND F3

The fire extinguishing mechanism of AFFF differs from fluorine-free foams. AFFF extinguishes liquid fire by the joint effect of a foam layer and an aqueous film layer on the fuel surface.⁴⁷ The foam layer or blanket covers the burning fuel surface, effectively separating the fuel from oxygen in the air. Liquid drains from the foam blanket to form an aqueous film, sealing the fuel surface.⁵¹ Thus, even after the foam has dissipated, the aqueous layer can still coat the surface of the liquid hydrocarbon. In addition, rapid evaporation of water in AFFF generates a cooling effect while the film layer isolates oxygen from the fuel preventing it from reigniting. On the other hand, F3 formulations do not contain any fluorosurfac-

tants or PFAS, hence, they do not form an aqueous film to extinguish fire.⁴⁷ Instead, F3 forms a blanket of bubbles above the fuel surface, adding a cooling effect to extinguish the fire rapidly.⁴⁷ Foams are prepared for different applications and, depending on the fire types, foam solutions are not always required to form films on the fuel surface.

For all foam types, performance tests of firefighting foams are carried out based on several characteristic parameters, such as knockdown, heat resistance, fuel tolerance, vapor suppression, and alcohol tolerance (see Table 3). An ideal

Table 3. Definition of Foam Characteristic Parameters (Adapted from National Foam’s “A Firefighter’s Guide to Foam” Manual⁵⁴)

Characteristic parameters	Definition
Knockdown	The time it takes for the foam blanket to spread across a fuel surface.
Heat resistance or burnback resistance	The ability of foam bubbles to withstand an elevated temperature.
Fuel tolerance	Foam’s ability to minimize fuel uptake to prevent it from getting saturated and burnt.
Vapor suppression	The ability of the foam blanket to suppress flammable vapors and prevent their release from the fuel.
Alcohol resistance	The ability of the foam blanket to create a polymeric barrier between the fuel and the foam to avoid foam destruction by fuel absorption.
Drainage rate	The time it takes for 25% of the solution to drain from the foam over a given time period. This is often referred to as 25% drainage time.
Expansion ratio	The volume of foam produced by vigorously mixing a given volume of foam solution with air.
Application rate	The rate at which foam solution is applied to the fire, measured in gallons per minute per square foot (gpm/ft ²) or liters per minute per square foot (L/min/ft ²).

firefighting foam should exhibit good heat stability, rapid spread across the fuel surface to create a vapor seal, and resistance to fuel pick-up. The effectiveness of firefighting foams is not solely determined by the chemical composition of foam concentrates. Properties like foam viscosity, bubble size and distribution, and foam expansion ratio can also influence the foam’s performance in fire suppression.⁵² The definition of foam characteristic parameters is provided in Table 3.

AFFF are generally classified as a Newtonian fluid, although some AR-AFFF variants may exhibit different behavior. The low viscosity of AFFF allows for their use in a range of foam proportioning equipment. On the other hand, many commercial F3 are non-Newtonian or viscous, which can impact their flow rate and application rate. The foam application rate is the amount of foam solution applied per minute per square foot of the fire surface, measured in L/min/m² or gpm/ft². One study found that F3 typically require 1.5 to 3 times the application rates of C6 AR-AFFF to achieve comparable performance.⁵³ To enhance the effectiveness of F3, the study suggests employing higher application rates and using aspirated discharge devices.⁵³

While the application rate is a crucial parameter in comparing the performance of F3 and AFFF firefighting foams, there are other factors influencing the fire extinguishing performance of foams. Since F3 do not form an aqueous film like AFFF, their firefighting capabilities are greatly dependent on the characteristics of the foam blankets they generate. Properties like the foam’s surface tension, the interfacial tension between the foam and the fuel, foaming ability, and

Table 4. Comparative Analysis of the Performance between AFFF and F3

Performance parameter	AFFF	F3
Knockdown	Rapid knockdown due to the formation of an aqueous film.	Effective, but generally slower than AFFF due to lack of film formation.
Heat resistance	Excellent heat stability.	Good heat stability, however, can vary based on specific formulations.
Fuel tolerance	High tolerance to hydrocarbon fuels, effective across a range of fuel types.	Effective against heptane and some hydrocarbon fuels, but performance can vary with fuel type.
Vapor suppression	Forms an aqueous film that suppresses vapors effectively.	Relies on a “wet” foam layer, which can be less effective in vapor suppression.
Foam viscosity	Typically, low viscosity behaves as a Newtonian fluid.	Often higher viscosity, behaves as non-Newtonian fluid, affecting flow and application rates.
Foam spread rate	Rapid spreading due to low viscosity and high surface activity. Low surface tension enhances spread and vapor suppression.	Slower spread rate. The spread rate can be affected by higher viscosity. Higher surface and interfacial tension can limit effectiveness in certain scenarios.
Foam stability	High stability, with stable foam blankets enhancing burn-back resistance.	Stability varies, modern formulations show improved performance but are still generally inferior to AFFF.
Application rate	Lower application rates are required due to high effectiveness.	Typically requires 1.5 to 3 times the application rates of AFFF for comparable performance.
Compatibility with equipment	Versatile, and works well with existing foam proportioning equipment.	May require modifications to equipment due to different viscosity and flow characteristics.
Foam lifetime and degradation rate	Longer foam lifetime and slower degradation, providing sustained protection.	Shorter foam lifetime and faster degradation, particularly in hydrocarbon fires.
Environmental impact	Persistent in the environment, bioaccumulative, and toxic.	Generally lower environmental persistence, but potential aquatic toxicity remains a concern.

foam spreading property may influence the performance of foams in fighting fire.⁵⁵ F3 have been found to lack the ability to form an aqueous film on the fuel surface, even with a positive spreading coefficient.⁵⁵ However, they can still effectively extinguish heptane fires by forming a “wet” foam layer that covers the fuel surface.⁴⁷ Some studies reported that the foam-spreading performance of F3 was inferior to that of commercial AFFF.^{47,55} The high surface activity and low viscosity of foams are critical for achieving good foam spreading properties.⁴⁷ The absence of fluorosurfactant in the formulation and the foam’s high viscosity could affect F3’s spreading ability. Foam stability is also correlated with F3’s fire-extinguishing and burn-back performance, as stable foams on the fuel surface typically lead to better extinguishing results.^{47,55} The stability of F3 may vary depending on the type of surfactant and stabilizer mixture used in the foam concentrate. For example, commercial F3 containing silicone surfactant, in combination with hydrocarbon surfactants and xanthan gum stabilizer, exhibited better foam stability than AFFF.⁴⁷ Modern F3 formulations containing polysaccharides assist in retaining water within the foam matrix, thereby increasing foam drainage time.¹

In addition, foam dynamics, including the thickness of the foam layer, foam spread rate, foam lifetime, and fuel and vapor transport rate through the foam, play a critical role in extinguishing the fire.³ The foam lifetime and degradation rate are influenced by the fuel and vapor transported through the foam.⁵⁶ In the presence of a hydrocarbon fire, RF6, a commercial F3, has demonstrated a faster degradation rate compared to fluorinated AFFF.⁵⁶ This shorter foam lifetime and faster degradation may be attributed to F3’s inferior fire suppression performance relative to AFFF.⁵⁶ A slow fuel transport rate through the foam layer is desired for an extended foam lifetime. The surface property of surfactants influences fuel transport through the foam. Strongly oleophobic fluorosurfactants exhibit a low fuel solubility and an increased repulsion toward fuel. In contrast, hydrocarbon surfactants show higher fuel solubility in the foam solution, increasing permeation rates of fuel transport through the foam and

causing rapid breakdown of the firefighting foam.^{45,56} Schaefer (2008) in his study found that increasing the foam thickness, in general, enhances sealability and vapor suppression performance for both fluorinated and fluorine-free foams.⁵⁷ However, the study concluded that to achieve similar fire protection with the same thickness (e.g., 1 cm thick foam layer), F3 requires a higher application rate than high-performance AFFF.⁵⁷

Moreover, various test parameters, such as the fuel type (polar or nonpolar),^{45,53,56} water type (freshwater or synthetic seawater),⁵⁸ fuel temperature, foam quality/aspiration, and foam generation techniques (aspirated foams or compressed air foams)⁴⁵ may also affect the properties and performance of firefighting foams. Studies have found that F3’s performance varies with the types of fuel used in the test performance.⁴⁵ While commercial F3 can efficiently extinguish heptane fires,^{47,53} they may demonstrate poor performance against fuels with low flash points, such as gasoline and E10 gasoline, especially when the foam application rate is low.⁵³ Therefore, the use of heptane may not be a good representative of all hydrocarbon-based fuels for fire test performance.⁵³ Aspiration level and foam quality (i.e., expansion ratio and 25% drainage time of foam blanket) directly affect the fire suppression performance of the finished foam.⁵³ However, these parameters are influenced by the temperature and the surrounding test environment. They may not be reliable predictors of the foam’s firefighting performance under real-life fire conditions, except under ambient conditions.⁴⁵ The type of foam-generating devices used also plays a role in foam performance. Devices that produce smaller foam bubbles with adequate uniform size distribution contribute to improved drainage properties, resulting in a slower drainage rate and a more stable firefighting foam.^{45,52} Additionally, foam properties such as foam viscosity, bubble size and distribution, and foam expansion ratio can influence the overall performance of the foam in fighting fires.⁵²

In summary, commercial AFFF have demonstrated consistent fire extinguishing performance compared to many commercial F3 across a wide range of test standards. However,

modern generation F3 have shown notable improvements in performance over the past few years. With a better design of foam application devices to achieve uniform foam distribution and higher application rates, F3 have the potential to perform effectively as an AFFF alternative. Nevertheless, as of now, F3 may not be a direct replacement for AFFF in every type of Class B fire suppression scenario. Instead, the selection of firefighting foams depends on the particular needs and risks at each fire scene, emphasizing the significance of customizing the chemistry, formulation, training, and application toward individual circumstances for achieving the best fire safety results. Table 4 provides a summary of the comparative analysis of the performance between AFFF and F3.

7. CHALLENGES IN TRANSITION FROM FLUORINE-BASED AFFF TO FLUORINE FREE FOAMS

Due to emerging environmental and health concerns, regulations in the US and other countries continue to limit the use and distribution of PFAS-based AFFF. Consequently, there is a growing need for alternative firefighting foams to balance fire safety and environmental considerations. The unique hydro- and oleo-phobic characteristics, and chemically and thermally stable fluorocarbon structure have made PFAS-based AFFF excellent at extinguishing fire. However, the chemical stability that makes them effective in firefighting also contributes to their environmental persistence, bioaccumulation, and toxicity. To be considered a viable alternative, fluorine-free foams must perform with similar efficacy to that of AFFF in fire suppression scenarios.

Two approaches have been applied to reduce the use of fluorosurfactants in firefighting foams. The first involves replacing long-chain fluorosurfactants with short-chain alternatives, reducing the carbon atom count from C8–C10 (long chain) to C4–C6 (short chain).⁵⁹ The second approach is the development of fluorine-free firefighting foams. Regarding thermal stability and surface properties, C6 foams are better substitutes for long-chain C8 foams. However, eliminating carbon atoms from the surfactant's structure may impact certain foam properties, such as film-forming ability, stability, and spreading properties.⁴⁷ Due to this elimination, the surface area of C6 fluorosurfactants becomes smaller than their C8 counterparts, affecting their surface activity.⁶⁰ These changes make short-chain fluorosurfactants less effective, which is often compensated by increasing their concentration in the foam formulation. Increasing the fluorosurfactant concentration or foam thickness has been shown to significantly enhance the performance of C6 foams.⁵⁷ Moreover, the presence of the –CH₂–CH₂– linkage in fluorotelomer-based surfactants makes them less stable and potential precursors to some PFAS.⁶¹

Commercial AFFF formulations consist of proprietary mixtures of multiple chemical agents, each serving specific purposes related to fire suppression. However, the precise mechanistic roles of these ingredients in fire extinction have not been thoroughly documented in the literature. Understanding the role of surfactants in Class B fire suppression is critical as it will enable the development of fluorine-free surfactants that mimic the surface-active properties of fluorosurfactants. In addition, the fire-extinguishing performance of firefighting foams is not solely dependent on their chemical constituents. It is equally important to comprehend how foam properties (e.g., viscosity) and foam dynamics (e.g.,

fuel transport rate) influence the foam's ability to protect against fire. Identifying optimal foam properties is also essential in developing high-performing alternatives to AFFF.

Fluorine-free foam products have been on the market for decades and are used for both Class A and Class B fire suppression. Research and development have been underway for several years to develop high performance Class B F3 as a possible replacement for AFFF. Many modern generation foams have shown to meet performance specifications of standards like EN 1568-3:2018, LASTFIRE, ICAO Level B, UL162, and IMO-MS-C.1/Circ.1312, suggesting these products can achieve satisfactory fire protection against hydrocarbon fuel fires.⁵ In contrast, there are also reports that many commercial PFAS-free foams did not meet the fire test performance criteria for some of these rigorous standards.⁴⁵ Unlike AFFF, effectiveness of F3 depends on many factors and complexities, causing variability in the performance. The performance of F3 varies depending on foam characteristics, foam application rate, application techniques, the type of discharge device used, and the type of fuel they can extinguish.^{45,53,56}

The feasibility of F3 as an AFFF replacement product has remained a matter of debate, partly due to inconsistency in the literature regarding their fire suppression performance and partly due to a lack of understanding of how an effective transition can be made from a logistics standpoint. The replacement of AFFF with F3 represents multiple challenges. For transitioning to F3 options, fire departments need to make considerations like disposal of old AFFF, decontamination of old equipment, and the need for new training and equipment.⁶² The foam transition process at fire stations typically involves draining out the old foam and rinsing firefighting equipment multiple times with water, which often generates large volumes of PFAS-containing liquid wastes.⁶² Onsite treatment and disposal of AFFF-related waste can be a costly process. To ensure a successful and cost-effective transition, well-planned and site-specific foam transition protocols are essential, but currently lacking. Developing comprehensive guidelines and strategies for a smooth and efficient transition from AFFF to F3 is crucial for the widespread adoption of fluorine-free foams in firefighting practices.

8. CURRENT USE PRACTICES OF F3

In the US, AFFF is commonly used in several areas including chemical plants, fire departments, flammable liquid storage and processing facilities, oil refineries, military facilities, and aviation operations.⁴⁴ In Europe, the main applications of AFFF are the chemical and petrochemical industry, municipal fire departments, marine applications, airports, and the military.⁴⁶ Currently, F3 is mainly used in municipal and airport settings, with some applications in the chemical/petrochemical sectors.⁴⁶ Although the transition to F3 has encountered challenges, such as equipment modifications and training requirements, successful implementation has been achieved in many cases. For instance, in Europe and Australia, F3 has been successfully used as a replacement for AFFF in aviation, the petrochemical sector, and marine applications.⁴⁶ Germany, Sweden, and The Netherlands have implemented F3 in various fire suppression applications.^{5,46} Many Australian airports have transitioned to F3, and other major hub airports worldwide have increasingly transitioned to using F3 replacements.⁶³ At present, there is no federal mandate requiring airports in the US to transition to F3. However, there is a

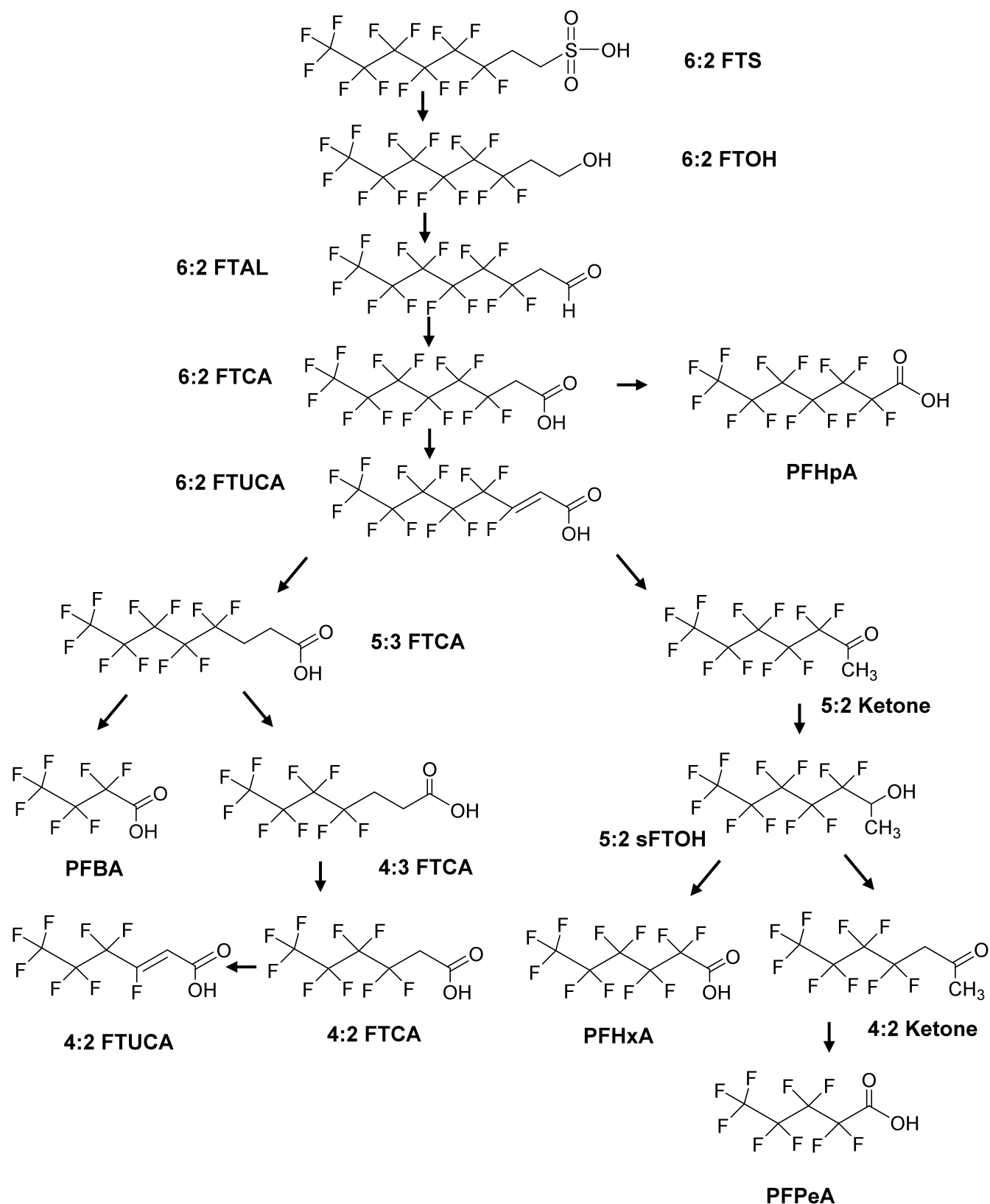


Figure 2. Proposed aerobic biotransformation pathways of 6:2 FTS (adapted from Shaw et al., 2019³⁷). Copyright 2024 Elsevier.

national transition plan outlined in the Federal Aviation Administration (FAA) Reauthorization Act to support US airports in adopting F3.⁶⁴

The military sector has not fully embraced alternatives to the same extent as other sectors. Testing, certifying F3 for military

use, and obtaining the necessary approvals for all firefighting systems will be a time-consuming and costly process. However, like applications in airports and municipal fires, F3 can be utilized in military sectors following equipment testing and adjustments. Recently, the DoD and the FAA approved two F3

Table 5. Adverse Health Impacts of Commonly Found Fluorosurfactants in AFFF and Their Metabolites

Compound	Potential source	Toxic effect	Reference
6:2 FTS	Used as surfactants in AFFF	Low aquatic toxicity. Increased liver weight, induce inflammation and necrosis in adult male mice. Sublethal effects in amphibians.	Hoke et al., 2012 ⁸⁶ Sheng et al., 2017 ¹⁰¹ Abercrombie et al., 2021 ⁸⁷
PFHxA	Degradation product of 6:2 FTS	Reduced growth and development in rats, increased hepatocellular hypertrophy in adult rats. Induce systemic toxicity, liver damage, and immunological disruption. Impact thyroid hormones and reduction in epididymal sperm counts. Increased liver weight and decreased serum cholesterol levels.	Loveless et al., 2009 ⁸⁸ Weatherly et al., 2023 ⁷⁹ NTP, 2019 ⁷⁷ Kirkpatrick, 2005 ⁷⁸
6:2 FTCA	Metabolite of 6:2 FTOH	Developmental toxicity observed in zebrafish embryos.	Shi et al., 2017 ⁸¹
5:3 FTCA	Metabolite of 6:2 FTOH	Potential bioaccumulation in both plasma and tissues upon repeated exposure to 6:2 FTOH.	Rice et al., 2020 ⁸⁰
PFBA	Metabolite of 6:2 FTOH	Reduction in thyroid hormone levels in mice and rats. Increased liver enzyme activities. Developmental and reproductive effects in female mice.	Feng et al., 2017; NTP, 2022 ^{89,90} NTP, 2022 ⁹⁰ Feng et al., 2017 ⁸⁹
PFHpA	Metabolite of 6:2 FTOH	Liver dysfunction in rodent model.	Weatherly et al., 2023 ⁷⁹

in the US that meet military performance specifications, paving the way for increased use of F3 in military applications.⁶⁵ The transition to F3 in petrochemical processing and large storage tank farms is still in progress due to challenges like foam compatibility with different liquids.⁴⁶ While challenges remain, the successful transition to PFAS-free foams in various sectors demonstrates its feasibility as an alternative to AFFF. Nevertheless, issues like decontamination and disposal of AFFF-contaminated equipment, as well as the cost of acquiring new equipment, need to be addressed to ensure a safe and smooth transition.

9. ENVIRONMENTAL AND HUMAN IMPACTS OF FIREFIGHTING FOAMS

9.1. Fluorotelomer-Based Foam. Since 2001, fluorotelomer-based AFFF has become the predominant type of Class B foam after the discontinuation of legacy AFFF production. However, this replacement occurred without conducting thorough research on their potential effects on the environment and human health. Consequently, this approach has given rise to similar concerns, as fluorotelomers can undergo a transformation in the environment or metabolize by organisms, resulting in the formation of short-chain PFAA which are highly persistent and mobile in the environment.⁵ Short-chain PFAS compounds are assumed to be safer than legacy PFAS due to their shorter estimated half-lives in humans. However, research has demonstrated that many short-chain PFAS can persist in the environment for long periods, despite having a shorter half-life in humans.⁶⁶

9.1.1. Transformation and Degradation. Fluorotelomer-based AFFF are problematic as they have been shown to transform and degrade under certain environmental conditions (e.g., aerobic soils and activated sludge).⁷⁰ This degradation process is of particular concern because many fluorotelomers are known precursor compounds for PFAAs. These precursor compounds can persist as a continual source of PFAAs in the environment, even long after the final application of AFFF, further contributing to the complexity of PFAS fate and transport. Observations at AFFF discharge sites provide evidence of the transformation of these fluorotelomers, as indicated by the detection of PFCAs that were not initially part of the original AFFF formulations.³³ PFAS derived from AFFF are diverse and exist in different forms. Polyfluorinated compounds present in fluorotelomer-based AFFF can trans-

formed into specific PFAAs as well as semistable polyfluorinated intermediates.^{67–69} Commonly identified PFAS at AFFF-impacted sites are PFCA, PFSA, and x:2 fluorotelomer sulfonates (FTS) (where, x = 4, 6, and 8).^{70,71}

The fluorinated surfactants used in fluorotelomer-based AFFF, derived from fluorotelomer thiol and sulfonyl, which eventually degrade into fluorotelomer sulfonates.⁷² These fluorosurfactants serve as fluorotelomer precursors that quickly degrade to 6:2 fluorotelomer sulfonate (6:2 FTS), a major degradation product of current AFFF.^{38,73} 6:2 FTS further slowly degrades to several degradation intermediates and terminal, short-chain PCFA products (e.g., PFBA, PFPeA, PFHxA, PFHpA).^{72–74} Transformations can proceed both chemically and biologically.^{68–70} However, biotransformation rates and pathways of these precursors may vary depending on their resistance to biotransformation.³⁷

Studies have shown aerobic transformation of fluorotelomer surfactants such as 6:2 fluorotelomer sulfonamide alkylamine (FTAA) and 6:2 fluorotelomer sulfonamide alkylbetaine (FTAB) produces 6:2 fluorotelomer alcohol (FTOH), 6:2 fluorotelomer carboxylic acid (FTCA), 6:2 fluorotelomer unsaturated carboxylic acid (FTUCA), 5:3 FTCA, and short-chain PFCA.⁷⁰ Likewise, the anaerobic transformation of certain fluorotelomer sulfonates can produce PFCA end products.⁷⁵ Some studies have proposed biotransformation pathways for these precursors, although the complete path is yet to be fully understood. The biotransformation of 6:2 FTS is presented in Figure 2.

9.1.2. Health Impact. 6:2 FTS is one of the frequently detected precursors in AFFF-impacted sites. It exhibits lower acute mammalian and aquatic toxicity than long-chain fluorotelomers (Table 5). However, 6:2 FTS still poses a risk due to its degradation products, such as PFHxA, which is a potential source of PFCA in the environment.⁷² Animal toxicity studies have reported adverse health effects of PFHxA via oral exposure, particularly affecting development, reproduction, immune function, and the liver of organisms.⁷⁶ Oral exposure to PFHxA has been shown to impact thyroid hormones and reduce epididymal sperm counts, while the ammonium salt form of PFHxA was found to cause slight developmental effects in Sprague–Dawley rats.⁷⁷ Additionally, the toxicity effect of PFHxA appears to be similar to that of legacy PFAS compounds, as evidenced by elevated liver weight and decreased serum cholesterol levels observed in rats

following oral exposure to PFHxA.⁷⁸ Limited research has been conducted on the effects of dermal exposure to PFHxA; however, a study on a murine model suggests that PFHxA has the potential to be absorbed through the skin, leading to systemic toxicity, liver damage, and immunological disruption.⁷⁹ Human epidemiological studies have limitations in establishing conclusive links between PFHxA exposure and various health outcomes due to low confidence, a scarcity of studies per health outcome, and sometimes a lack of a quantifiable measure of exposure.⁷⁶ However, existing evidence suggests that PFHxA likely causes hepatic and developmental effects in humans.⁷⁶

The practice of using PFHxA as a model for assessing the health effects of 6:2 FTS or 6:2 FTOH may underestimate the human health risk associated with fluorotelomer-based AFFF. It is essential to consider the potential impacts of 6:2 FTOH and its other metabolites, as they could significantly influence the risk assessment. Moreover, the existing studies have focused exclusively on noncancer effects, and there is currently no research evaluating the potential cancer effects of metabolites. A recent comparative study demonstrated that 6:2 FTOH is significantly more toxic than PFHxA.⁸⁰ Upon oral exposure, 6:2 FTOH is rapidly absorbed and metabolized in the liver to various metabolites, including 5:3 FTCA, 4:3 FTCA, PFHxA, PFPeA, PFBA, and PFHpA.⁸⁰ 6:2 FTCA, a common metabolite for 6:2 FTOH, has shown developmental toxicity in zebrafish embryos and demonstrated greater toxicity compared to PFCA themselves.⁸¹ Repeated exposure to 6:2 FTOH can potentially increase the bioaccumulation of the metabolite 5:3 FTCA in both plasma and tissues.⁸⁰ Similarly, PFPeA, PFBA, and PFHpA are well-known PFCA with an estimated short half-life in humans, exhibiting potential toxicity. Both toxicological and epidemiological studies suggest that PFBA exposure is likely to cause developmental, thyroid, and liver effects in humans.⁸² No toxicology study on oral exposure to PFHpA and PFPeA was identified. However, a dermal exposure study on a rodent model found that PFHpA and PFPeA can lead to liver dysfunction by altering liver gene expression.⁷⁹ The toxicological effects of commonly found fluorosurfactants in AFFF and their metabolites are listed in Table 5.

The primary sources of PFAS exposure for the general population are drinking water and dietary intake.⁸³ Firefighters can additionally be exposed to PFAS through AFFF during fire incidents and routine training activities. The exposure pathways include dermal uptake, incidental ingestion of foam, and inhalation.⁸⁴ The occurrence of PFAS inside fire stations can be high due to multiple potential sources of exposure such as products containing PFAS that are stored at the station (e.g., AFFF, turnout gear, and consumer items) and residual PFAS contamination that firefighters may bring back to the station after firefighting activities (e.g., from smoke, gear, and AFFF use).⁸⁵ Firefighters spend a significant portion of their on-duty hours at the fire station. They only wear turn-out gear and self-contained breathing apparatus (SCBA) to respond to fire scenes. However, when they are not wearing these personal protective equipment (PPE), there remains a potential risk of PFAS exposure through inhalation and dermal absorption. AFFF has historically been a significant source of firefighter exposure to PFAS.¹⁷ Firefighters with a history of using AFFF have higher serum concentrations of long-chain PFAS such as PFOA, PFOS, and PFHxS.^{91,92}

9.2. F3. The primary goal of transitioning to nonfluorinated foam options is to mitigate the potential adverse effects of fluorinated foams. Therefore, gathering extensive toxicological data on these F3 is essential to prevent similar incidents observed with fluorotelomer-based foams. Research on the environmental impact of F3 is still in its early stages, with limited toxicity studies available. Existing ecotoxicity studies have examined the effects of F3 on various organisms, including soil invertebrates,⁹³ birds,⁹⁴ plants,⁹⁵ and aquatic species.⁹⁶ The findings from these studies suggest that most commercially available F3 are either equally or more toxic compared to C6 AFFF, particularly for aquatic species.⁹⁶ In addition, F3 have shown adverse impacts on reproduction in worms⁹³ and have exhibited higher phytotoxicity than the short-chain AFFF.⁹⁵ These findings highlight potential environmental risks associated with F3 and emphasize the need for further research to understand their ecological implications. Available studies also suggest that the toxicological profiles of these nonfluorinated foams may vary among different organisms. The ecotoxicity assessment of F3 can be greatly influenced by various factors, including the test species, exposure duration, and the exposure medium (water or soil).⁹⁵ F3 have shown higher aquatic toxicity compared to mammalian toxicity in short-term exposure. For example, a recent study conducted on a mouse model found that PFAS-free foams either decreased or did not affect liver weights, unlike PFAS-containing foam, which increased liver weight.⁹⁷ However, in aquatic exposure scenarios, PFAS-free foams showed higher acute toxicity than AFFF in aquatic species.⁹⁶ There is a major research gap regarding the effect of chronic exposure to PFAS-free foams on human and wildlife health.⁹³ When considering replacement products, conducting toxicological assessments across species is crucial to carefully interpret results and evaluate potential risks to human health and ecosystems.

Similar to AFFF, F3 formulations contain hydrocarbon surfactants, and some of these surfactants have shown stronger acute lethal toxicity to aquatic species.⁹⁸ Notably, non-fluorinated anionic surfactant, sodium tetradecyl sulfate has been reported to exhibit higher toxicity in zebrafish.⁹⁸ Diethylene glycol monobutyl ether, a common ingredient of F3 formulations, has been identified as a potential contributor to increased phytotoxicity.⁹⁵ The presence of zwitterionic amine oxides, anionic alkyl sulfates, betaines, and nonionic organosilicone surfactants have been detected in F3 formulations.⁹⁵ However, the toxicity of many of these compounds remains unknown due to the lack of available data. The complex chemical compositions of these foam formulations pose significant challenges in studying their environmental behaviors and impacts. It is important to have a comprehensive understanding of the toxicological effect of foam formulations and their individual components. While manufacturer safety data sheets (SDS) may provide information on the acute toxicity of many individual components in F3, there is limited knowledge about their chronic, reproductive, and developmental toxicity.²¹

Commercial F3 often have high BOD (Biochemical Oxygen Demand) values (~330,000 mg/L) due to the presence of degradable organics such as solvents, detergents, carbohydrates, proteins, and saccharides, which can contribute to their high aquatic toxicity.⁵ However, newer generations of F3 have been developed to have lower COD (Chemical Oxygen Demand) and BOD values. During firefighting operations,

Table 6. Hazard Comparison Dashboard (HCD) for Chemicals Disclosed in the Safety Data Sheet (SDS) of Some F3 and Degradation Products of AFFF

Foam Type	Component Name/Degradation Product	CAS	Human Health Effects														Ecotoxicity		Fate			
			Acute Mammalian Toxicity			Carcinogenicity	Genotoxicity/Mutagenicity	Endocrine Disruption	Reproductive	Developmental	Neurotoxicity		Systemic Toxicity		Skin Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation	Exposure
			Oral	Inhalation	Dermal						Repeat Exposure	Single Exposure	Repeat Exposure	Single Exposure								
F3	Lauramidopropyl betaine	4292-10-8	M	I	I	I	VH	L	I	L	I	I	I	I	I	I	I	H	H	M	L	H
	Sodium dodecyl sulfate	151-21-3	M	I	VH	I	L	N/A	M	I	N/A	H	M	M	L	H	VH	H	H	M	L	VH
	2-(2-Butoxyethoxy) ethanol	112-34-5	M	I	L	I	L	H	L	L	N/A	N/A	H	N/A	I	M	H	L	N/A	L	L	VH
	N,N-Dimethyl-1-tetradecanamine N-oxide	3332-27-2	M	I	L	I	L	L	H	L	I	I	I	I	I	I	VH	VH	VH	M	L	H
	N,N-Dimethyl dodecylamine -N-oxide	1643-20-5	M	I	L	I	L	L	M	L	I	I	L	I	L	VH	VH	H	VH	M	L	H
	1-Tetradecanol	112-72-1	L	I	L	I	L	N/A	L	I	I	I	I	I	L	H	M	H	VH	M	L	H
	Disodium isodecyl sulfosuccinate	37294-49-8	N/A	N/A	N/A	N/A	VH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	H	H	L	N/A	M	L	M
	1-Dodecanol	112-53-8	L	L	M	I	L	H	L	L	I	N/A	I	H	L	L	M	H	VH	M	L	H
	Decyl beta-D-glucopyranoside	58846-77-8	L	N/A	N/A	N/A	VH	L	N/A	L	N/A	N/A	N/A	N/A	N/A	N/A	H	M	L	L	L	M
C6 AFFF	Perfluorohexanoic acid	307-24-4	M	N/A	N/A	N/A	VH	H	N/A	I	L	N/A	N/A	N/A	N/A	N/A	N/A	M	M	VH	M	M
	2-(Perfluorohexyl) ethanol	647-42-7	M	I	L	N/A	L	I	H	I	N/A	N/A	H	N/A	N/A	N/A	N/A	H	H	VH	H	L

Toxicity level: VH-Very High | H-High | M - Medium | L - Low | I - Inconclusive | N/A-No Data Available

firewater runoff can potentially enter the environment, leading to contamination of surface and groundwater sources. Although most F3 are considered readily biodegradable, little is known about their fate and transport in the environment. Currently, there is no data on any potential hazard from the combustion products of foams. There is still limited understanding of their environmental persistence and mobility. Given the anticipated increase in F3 usage and its potential release into the environment, further research is necessary to investigate the biodegradation products of these foams. In this case, nontarget analysis and suspect screening can provide valuable insights for analyzing F3-impacted sites. Furthermore, to prevent PFAS contamination, it is essential to ensure that foam containers are not made from or coated with materials containing PFAS. Additionally, more information is needed on various aspects of F3, such as their behavior during wastewater treatment, fate in drinking water, and potential formation of disinfection byproducts.²¹

Given that F3 can pose risks to aquatic environments, measures should be taken to limit environmental exposure to these foams. Although it may not always be feasible to collect runoff at an actual fire scene due to varying site conditions, some engineering controls can help improve runoff management. For example, in addition to foam extinguishing tools, facilities should install firewater runoff collection equipment to capture the runoff water and direct it to a contained area or tank for subsequent treatment.⁹⁹ On-site spill and containment equipment should be employed both during fire training exercises and actual firefighting operations.⁹⁹ Implementing

engineered containment systems, such as portable bunds, barriers, and retention ponds, can provide temporary storage for firewater runoff during firefighting operations. Additionally, fire training facilities can install permanent drainage systems that direct runoff into designated containment areas or treatment facilities.⁹⁹

9.2.1. Health Risks Associated with F3. To gain insight into the potential hazards associated with the use of these fluorine-free firefighting foams, a Hazard Comparison Dashboard (HCD) was formulated and is presented in Table 6. This table provides an overview of HCD results for some components of F3 and known degradation products of AFFF. HCD was created using the United States Environmental Protection Agency's (US EPA) Cheminformatics analysis modules, accessible at Cheminformatics.¹⁰⁰ Table 6 highlights that fluorosurfactants in AFFF and their degradation products are very persistent, with a high potential for long-range transport and environmental accumulation. The alternatives, in general, are not identified as persistent or having bioaccumulative potential. However, certain silicone-based surfactants and their degradation products, especially cyclic ones, could persist in the environment and pose risks as potential endocrine disruptors.⁵ Many commonly identified constituents in F3 formulation have been classified as toxic or very toxic to aquatic life. These key components exhibit high levels of both acute and chronic ecotoxicity. For instance, commonly used surfactants in F3, such as sodium dodecyl sulfate, N,N-dimethyl-1-tetradecanamine N-oxide, N,N-dimethyl dodecylamine-N-oxide demonstrate high acute aquatic toxicity with a

significant potential for high exposure. Solvents such as 1-dodecanol and 1-tetradecanol have low associated human health effects yet raise environmental concerns due to their very high level of ecotoxicity. Major components like sodium dodecyl sulfate, disodium isodecyl sulfosuccinate, and 2-(2-butoxyethoxy) ethanol exhibit varying levels of human health effects, ranging from low to very high toxicity in different categories such as acute mammalian toxicity and skin irritation. While certain components in the foam formulation pose minimal human health risks, others raise significant concerns. Specifically, lauramidopropyl betaine, disodium isodecyl sulfosuccinate, and decyl beta-D glucopyranoside show a very high risk of genotoxicity (Table 6).

The environmental risk and toxicity of many hydrocarbon-based surfactants are well established. However, not all human health or environmental hazard end points for each component have been evaluated. Inconclusive data in areas like neurotoxicity and systemic toxicity for many of these compounds reflects the ongoing need for comprehensive toxicological research. The lack of information on the full list of chemical substances in foam formulation due to proprietary concerns makes it challenging to draw definitive conclusions about the potential risks associated with the use of F3. In addition, variations in formulations may exist between different manufacturers, further complicating the risk assessment process. It is reasonable to conduct risk assessments of F3 as an alternative to fluorinated foam based on environmental persistence given the high environmental footprints of fluorosurfactants. However, the available data suggests that, in addition to environmental persistence, other factors such as acute and chronic ecotoxicity, potential endocrine disruption, and the full toxicological profile of all individual components should be considered for comprehensive toxicological assessments and risk evaluations. Extensive data on next-generation F3 containing novel surfactants, focusing on the environmental impact and toxicity of their degradation products, needs to be collected.²¹ Real-world exposure involves the entire formulation, not just isolated compounds. In addition to assessing the toxicity of individual compounds, a thorough evaluation of the complete foam formulation is essential, especially in the case of occupational exposure scenarios.

10. CONSIDERATIONS FOR F3 TRANSITION

While the environmental impact of firefighting foam is a major concern, firefighters are frequent users of foam and are likely to experience the highest exposure and potential health effects from its use. The risk of F3 alternatives as occupational exposure needs to be assessed including both acute and chronic health effects. As the review suggests, F3 has different properties and application rates compared to AFFF, firefighters may experience challenges while using these alternatives. Although well-established practices exist for AFFF use, the transition to F3 requires firefighters to learn new application techniques and handling procedures. Training manuals and instructional videos should be updated addressing the distinct properties and handling requirements of these new firefighting foams. Some training programs have started to incorporate information on F3. However, there is still a need for comprehensive and specialized training focusing on these alternatives. Additionally, guidelines and standards for using F3 in firefighting operations need to be established to ensure consistent and effective application. Moreover, the transition comes with a high cost of equipment modifications, training

requirements, decontamination, and disposal of AFFF-contaminated equipment. Federal policies should reflect the increased financial needs for purchasing F3, new equipment, and training and make favorable adjustments to support fire stations nationwide. Furthermore, continuous engagement with stakeholders, including firefighters, emergency responders, and community members, is necessary to gather feedback and insights for improvement of F3 use.

11. CONCLUSIONS

The current fluorine-free foams (F3) are not yet able to match the fire suppression effectiveness of AFFF in every type of application. Therefore, further research is needed to develop alternative chemicals that can provide firefighting performance comparable to the fluorosurfactants in AFFF. Studies characterizing chemical properties of the foams such as viscosity and surface tension would be beneficial in identifying the optimal combinations of foams and additives. Ultimately, these analyses can help develop PFAS-free foam formulations capable of meeting standards set by AFFF. Although progress has been made in some countries, issues such as decontamination and disposal of AFFF-contaminated equipment and the cost of acquiring new equipment need to be addressed for a safe and smooth transition. While recent findings suggest that commercially available F3 exhibits greater biodegradability and reduced environmental persistence compared to PFAS, it is important to consider that some proposed alternatives may still pose similar environmental impacts. It is essential to investigate the potential risks associated with their use, storage, and disposal. A comprehensive understanding of the environmental impacts and toxicological profiles of foam formulations is critical for achieving the ultimate goal of transitioning to fluorine-free alternatives. Knowledge of the toxicological effects of foam formulations and their components will allow us to identify the key ingredients responsible for the observed toxic effects, enabling targeted risk assessment and potential mitigation strategies. Studies should encompass a wide range of organisms and exposure scenarios to account for potential variations in effects across species and environmental conditions. As research and technology continue to evolve, there would be further improvements in F3 formulations and applications, which could expand their range of suitability for various fire suppression scenarios. Nonetheless, careful consideration of the foam's performance, compatibility with existing systems, and environmental impact remains essential in selecting the most appropriate firefighting foam for each situation.

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Notes

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REFERENCES

- (1) Korzenioswski, S. H.; et al. Fluorosurfactants in Firefighting Foams: Past and Present (Chapter 1). *Perfluoroalkyl Substances in the Environment*; CRC Press: 2019.
- (2) Ratzer, A. History and development of foam as a fire extinguishing medium. *Industrial & Engineering Chemistry* **1956**, *48* (11), 2013–2016.
- (3) Hinnant, K.; et al. Characterizing the role of fluorocarbon and hydrocarbon surfactants in firefighting-foam formulations for fire-suppression. *Fire Technol.* **2020**, *56*, 1413–1441.
- (4) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. *Environ. Sci. Technol.* **2004**, *38* (6), 1828–1835.
- (5) Allcorn, M.; et al. Fluorine-free firefighting foams (3F)–Viable alternatives to fluorinated aqueous film-forming foams (AFFF). Independent Expert Panel Convened by IPEN, 2018.
- (6) Langenbach, B.; Wilson, M. Per-and polyfluoroalkyl substances (PFAS): significance and considerations within the regulatory framework of the USA. *International Journal of Environmental Research and Public Health* **2021**, *18* (21), 11142.
- (7) Hu, X. C.; et al. Detection of poly-and perfluoroalkyl substances (PFASs) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants. *Environmental science & technology letters* **2016**, *3* (10), 344–350.
- (8) Ahrens, L.; et al. Stockholm Arlanda Airport as a source of per-and polyfluoroalkyl substances to water, sediment and fish. *Chemosphere* **2015**, *129*, 33–38.
- (9) García, R. A.; et al. Suspect screening of hydrocarbon surfactants in AFFFs and AFFF-contaminated groundwater by high-resolution mass spectrometry. *Environ. Sci. Technol.* **2019**, *53* (14), 8068–8077.
- (10) McDonough, C. A.; et al. Unsaturated PFOS and other PFASs in human serum and drinking water from an AFFF-impacted community. *Environ. Sci. Technol.* **2021**, *55* (12), 8139–8148.
- (11) Barton, K. E.; et al. Sociodemographic and behavioral determinants of serum concentrations of per-and polyfluoroalkyl substances in a community highly exposed to aqueous film-forming foam contaminants in drinking water. *International journal of hygiene and environmental health* **2020**, *223* (1), 256–266.
- (12) Daly, E. R.; et al. Per-and polyfluoroalkyl substance (PFAS) exposure assessment in a community exposed to contaminated drinking water, New Hampshire, 2015. *International journal of hygiene and environmental health* **2018**, *221* (3), 569–577.
- (13) Hurley, S.; et al. Preliminary associations between the detection of perfluoroalkyl acids (PFAAs) in drinking water and serum concentrations in a sample of California women. *Environmental science & technology letters* **2016**, *3* (7), 264–269.
- (14) Shearer, J. J.; et al. Serum concentrations of per-and polyfluoroalkyl substances and risk of renal cell carcinoma. *JNCI: Journal of the National Cancer Institute* **2021**, *113* (5), 580–587.
- (15) Bartell, S. M.; Vieira, V. M. Critical review on PFOA, kidney cancer, and testicular cancer. *J. Air Waste Manage. Assoc.* **2021**, *71* (6), 663–679.
- (16) Pelch, K. E.; et al. The PFAS-Tox Database: A systematic evidence map of health studies on 29 per-and polyfluoroalkyl substances. *Environ. Int.* **2022**, *167*, 107408.
- (17) Mazumder, N.-U.-S.; et al. Firefighters' exposure to per-and polyfluoroalkyl substances (PFAS) as an occupational hazard: A review. *Frontiers in materials* **2023**, *10*, 1143411.
- (18) Cousins, I. T.; et al. Strategies for grouping per-and polyfluoroalkyl substances (PFAS) to protect human and environmental health. *Environmental Science: Processes & Impacts* **2020**, *22* (7), 1444–1460.
- (19) Kempisty, D. M.; Racz, L. *Forever chemicals: environmental, economic, and social equity concerns with pfas in the environment*; CRC Press: 2021.
- (20) Grant, C.; Hawthorne, E.; Back, J. Firefighting Foams: Transition Roadmap for the Fire Service. In *2022 NFPA Conference & Expo*; NFPA: 2022.
- (21) Ateia, M. Sunrise of PFAS Replacements: A Perspective on Fluorine-Free Foams. *ACS Sustainable Chem. Eng.* **2023**, *11*, 7986.
- (22) Jacobson, R.; Ferraro, M. F. Environmental Deconfliction 2020: The National Defense Authorization Act for FY 2020. *Envtl. L. Rep.* **2020**, *50*, 10983.
- (23) Buck, R. C.; et al. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integrated environmental assessment and management* **2011**, *7* (4), 513–541.
- (24) Glüge, J.; et al. An overview of the uses of per-and polyfluoroalkyl substances (PFAS). *Environmental Science: Processes & Impacts* **2020**, *22* (12), 2345–2373.
- (25) Zhu, W.; et al. Vermont-wide assessment of anthropogenic background concentrations of perfluoroalkyl substances in surface soils. *Journal of Hazardous Materials* **2022**, *438*, 129479.
- (26) Yi, S.; et al. Biotransformation of 6:2 fluorotelomer thioether amido sulfonate in aqueous film-forming foams under nitrate-reducing conditions. *Environ. Sci. Technol.* **2022**, *56* (15), 10646–10655.
- (27) Ruyle, B. J.; et al. Isolating the AFFF signature in coastal watersheds using oxidizable PFAS precursors and unexplained organofluorine. *Environ. Sci. Technol.* **2021**, *55* (6), 3686–3695.
- (28) Libal, J. P.; Siem, M. A. Use of an indicator as a marker in foam concentrates; Google Patents, 2020.
- (29) Nilsson, S.; et al. Biomonitoring of per-and polyfluoroalkyl substances (PFAS) exposure in firefighters: Study design and lessons learned from stakeholder and participant engagement. *International Journal of Hygiene and Environmental Health* **2022**, *242*, 113966.
- (30) Darwin, R. L. Estimated Quantities of Aqueous Film Forming Foam (AFFF) in the United States, 2004. 2018 [cited 2023 10/02]; Available from: <https://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC13FU-SUBM-PFOA-FFFF-2-20180112.En.pdf>.
- (31) Barzen-Hanson, K. A.; et al. Discovery of 40 classes of per-and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater. *Environ. Sci. Technol.* **2017**, *51* (4), 2047–2057.
- (32) Lindstrom, A. B.; Strynar, M. J.; Libelo, E. L. Polyfluorinated compounds: past, present, and future. *Environ. Sci. Technol.* **2011**, *45* (19), 7954–7961.
- (33) Backe, W. J.; Day, T. C.; Field, J. A. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from US military bases by nonaqueous

large-volume injection HPLC-MS/MS. *Environ. Sci. Technol.* **2013**, *47* (10), 5226–5234.

(34) Ruyle, B. J.; et al. Nitrifying microorganisms linked to biotransformation of perfluoroalkyl sulfonamido precursors from legacy aqueous film-forming foams. *Environ. Sci. Technol.* **2023**, *57* (14), 5592–5602.

(35) Weiner, B.; et al. Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6:2 fluorotelomermercaptoalkylamido sulfonate (6:2 FTSAS). *Environmental Chemistry* **2013**, *10* (6), 486–493.

(36) Harding-Marjanovic, K. C.; et al. Aerobic biotransformation of fluorotelomer thioether amido sulfonate (Lodyne) in AFFF-amended microcosms. *Environ. Sci. Technol.* **2015**, *49* (13), 7666–7674.

(37) Shaw, D. M.; et al. Degradation and defluorination of 6:2 fluorotelomer sulfonamidoalkyl betaine and 6:2 fluorotelomer sulfonate by *Gordonia* sp. strain NB4–1Y under sulfur-limiting conditions. *Sci. Total Environ.* **2019**, *647*, 690–698.

(38) Zhang, S.; et al. Biotransformation potential of 6:2 fluorotelomer sulfonate (6:2 FTSA) in aerobic and anaerobic sediment. *Chemosphere* **2016**, *154*, 224–230.

(39) Martin, T. J. Fire-fighting foam technology. *Foam engineering: Fundamentals and applications* **2012**, 411–457.

(40) Król, B.; Prochaska, K.; Chrzanowski, L. Biodegradability of firefighting foams. *Fire technology* **2012**, *48*, 173–181.

(41) Kaller, M.; et al. An Evaluation of the Firefighting Performance of Alcohol-Resistant Aqueous Film Forming Foams (AFFF-AR) and Alcohol-Resistant Fluorine-Free Foams (FFF-AR) in the Past Two Decades. *Fire Technol.* **2023**, *59* (2), 429–452.

(42) General Foam Information [cited 2023 10/3]; Available from: <https://www.chemguard.com/pdf/General-Foam-Information.pdf>.

(43) Garcia, G.; Durual, P. Alcohol resistant film-forming fluoroprotein foam concentrates; Google Patents, 1998.

(44) Interstate Technology & Regulatory Council (ITRC). PFAS Technical and Regulatory Guidance Document and Fact Sheets PFAS-1. 2022 [cited 2023 10/5]; Available from: <https://pfas-1.itrcweb.org/>.

(45) Dahlbom, S.; Mallin, T.; Bobert, M. Fire test performance of eleven PFAS-free class B firefighting foams varying fuels, admixture, water types and foam generation techniques. *Fire Technol.* **2022**, *58* (3), 1639–1665.

(46) Nicol, L.; et al. *The use of PFAS and fluorine-free alternatives in fire-fighting foams*; Wood Environment & Infrastructure Solutions UK, 2020.

(47) Sheng, Y.; et al. Environmentally friendly firefighting foams used to fight flammable liquid fire. *Fire Technol.* **2021**, *57*, 2079–2096.

(48) Gharehveran, M. M.; et al. Per- and polyfluoroalkyl substances (PFAS)-free aqueous film forming foam formulations: Chemical composition and biodegradation in an aerobic environment. *Journal of Environmental Chemical Engineering* **2022**, *10* (6), 108953.

(49) Goodwin, J. *Colloids and interfaces with surfactants and polymers*; John Wiley & Sons: 2009.

(50) Kang, W.; et al. Experimental study on fire-extinguishing efficiency of protein foam in diesel pool fire. *Case Studies in Thermal Engineering* **2019**, *16*, 100557.

(51) Xu, Z.; et al. Fire-extinguishing performance and mechanism of aqueous film-forming foam in diesel pool fire. *Case studies in thermal engineering* **2020**, *17*, 100578.

(52) Laundess, A. J.; et al. Small-scale test protocol for firefighting foams DEF (AUST) 5706: effect of bubble size distribution and expansion ratio. *Fire technology* **2011**, *47*, 149–162.

(53) Back, G. G. An evaluation of the firefighting effectiveness of fluorine-free foams. *Fire Technol.* **2023**, *59*, 3107.

(54) National Foam. *A Firefighter's Guide to Foam*; National Foam, Inc.

(55) Sheng, Y.; et al. Study of environmental-friendly firefighting foam based on the mixture of hydrocarbon and silicone surfactants. *Fire Technol.* **2020**, *56*, 1059–1075.

(56) Hinnant, K. M.; Conroy, M. W.; Ananth, R. Influence of fuel on foam degradation for fluorinated and fluorine-free foams. *Colloids Surf., A* **2017**, *522*, 1–17.

(57) Schaefer, T. H.; Dlugogorski, B. Z.; Kennedy, E. M. Sealability properties of fluorine-free fire-fighting foams (FfreeF). *Fire Technol.* **2008**, *44*, 297–309.

(58) Dlugogorski, B. Z.; Schaefer, T. H. Compatibility of aqueous film-forming foams (AFFF) with sea water. *Fire Safety Journal* **2021**, *120*, 103288.

(59) Giesy, J. P.; Kannan, K. Peer reviewed: perfluorochemical surfactants in the environment. *Environ. Sci. Technol.* **2002**, *36* (7), 146A–152A.

(60) Peshoria, S.; et al. Short-chain and long-chain fluorosurfactants in firefighting foam: a review. *Environmental Chemistry Letters* **2020**, *18*, 1277–1300.

(61) Winchell, L. J.; et al. Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review. *Water Environment Research* **2021**, *93* (6), 826–843.

(62) Horst, J.; et al. *Transitioning Per- and Polyfluoroalkyl Substance Containing Fire Fighting Foams to New Alternatives: Evolving Methods and Best Practices to Protect the Environment*; Wiley Online Library: 2021; pp 19–26.

(63) Bluteau, T.; et al. The global PFAS problem: Fluorine-free alternatives as solutions firefighting foams and other sources—Going fluorine-free. White Paper prepared for IPEN by members of the IPEN Expert Panel and associates. In *Meeting of the Stockholm Convention Conference of the Parties (COP9)*, Geneva, Switzerland, 2019.

(64) Gutierrez, M. G. M.; Mina, S. FAA Issues Plan for Transition to Fluorine-Free Firefighting Foam. 2023 [cited 2024 4/3]; Available from: <https://andersonkreiger.com/faa-issues-plan-for-transition-to-fluorine-free-firefighting-foam/>.

(65) Heron, G. Transition to fluorine-free foam: Now or later? 2024 [cited 2024 4/3]; Available from: <https://www.thermalrs.com/2024/03/14/transition-to-fluorine-free-foam-now-or-later/>.

(66) Cousins, I. T.; et al. The precautionary principle and chemicals management: The example of perfluoroalkyl acids in groundwater. *Environ. Int.* **2016**, *94*, 331–340.

(67) Mejia-Avendaño, S.; et al. Generation of perfluoroalkyl acids from aerobic biotransformation of quaternary ammonium polyfluoroalkyl surfactants. *Environ. Sci. Technol.* **2016**, *50* (18), 9923–9932.

(68) Chen, H.; et al. Fast generation of perfluoroalkyl acids from polyfluoroalkyl amine oxides in aerobic soils. *Environmental Science & Technology Letters* **2020**, *7* (10), 714–720.

(69) Liu, M.; et al. Stability of nitrogen-containing polyfluoroalkyl substances in aerobic soils. *Environ. Sci. Technol.* **2021**, *55* (8), 4698–4708.

(70) D'Agostino, L. A.; Mabury, S. A. Aerobic biodegradation of 2 fluorotelomer sulfonamide-based aqueous film-forming foam components produces perfluoroalkyl carboxylates. *Environmental toxicology and chemistry* **2017**, *36* (8), 2012–2021.

(71) Baduel, C.; Paxman, C. J.; Mueller, J. F. Perfluoroalkyl substances in a firefighting training ground (FTG), distribution and potential future release. *Journal of hazardous materials* **2015**, *296*, 46–53.

(72) Wang, N.; et al. 6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants. *Chemosphere* **2011**, *82* (6), 853–858.

(73) Méndez, V.; et al. Aerobic biotransformation of 6:2 fluorotelomer sulfonate by *Dietzia aurantiaca* J3 under sulfur-limiting conditions. *Science of The Total Environment* **2022**, *829*, 154587.

(74) Gonzalez, D.; et al. Assessment of PFAS fate, transport, and treatment inhibition associated with a simulated AFFF release within a WASTEWATER treatment plant. *Chemosphere* **2021**, *262*, 127900.

(75) Li, F.; et al. Anaerobic biodegradation of 8:2 fluorotelomer alcohol in anaerobic activated sludge: Metabolic products and pathways. *Chemosphere* **2018**, *200*, 124–132.

(76) Environmental Protection Agency. IRIS Toxicological Review of Perfluorohexanoic Acid [PFHxA, CASRN 307-24-4] and Related

Salts. Integrated Risk Information System, Center for Public Health and Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency: Washington, DC, 2023.

(77) National Toxicology Program. Toxicity studies of perfluoroalkyl carboxylates administered by gavage to Sprague Dawley (Hsd: Sprague Dawley SD) Rats. Toxicity Report Series, 2019 (97).

(78) Kirkpatrick, J. A combined 28-day repeated dose oral toxicity study with the reproduction/developmental toxicity screening test of per-fluorohexanoic acid and 1H, 1H, 2H, 2H-tridecafluoro-1-octanol in rats, with recovery: Final Report. WIL-534001. *WIL Research Laboratories, LLC* 2005, 1, 1–75.

(79) Weatherly, L. M.; et al. Systemic toxicity induced by topical application of perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), and perfluoropentanoic acid (PFPeA) in a murine model. *Food Chem. Toxicol.* 2023, 171, 113515.

(80) Rice, P. A.; et al. Comparative analysis of the toxicological databases for 6:2 fluorotelomer alcohol (6:2 FTOH) and perfluorohexanoic acid (PFHxA). *Food Chem. Toxicol.* 2020, 138, 111210.

(81) Shi, G.; et al. 6:2 fluorotelomer carboxylic acid (6:2 FTCA) exposure induces developmental toxicity and inhibits the formation of erythrocytes during zebrafish embryogenesis. *Aquatic Toxicology* 2017, 190, 53–61.

(82) Environmental Protection Agency. Human Health Toxicity Values for Perfluorobutane Sulfonic Acid (CASRN 375-73-5) and Related Compound Potassium Perfluorobutane Sulfonate (CASRN 29420-49-3); US Environmental Protection Agency Office of Research and Development, 2018.

(83) Domingo, J. L.; Nadal, M. Human exposure to per-and polyfluoroalkyl substances (PFAS) through drinking water: A review of the recent scientific literature. *Environmental research* 2019, 177, 108648.

(84) Rosenfeld, P. E.; et al. Perfluoroalkyl substances exposure in firefighters: Sources and implications. *Environmental Research* 2023, 220, 115164.

(85) Young, A. S.; et al. Per-and polyfluoroalkyl substances (PFAS) and total fluorine in fire station dust. *Journal of exposure science & environmental epidemiology* 2021, 31 (5), 930–942.

(86) Hoke, R. A.; et al. Comparative acute freshwater hazard assessment and preliminary PNEC development for eight fluorinated acids. *Chemosphere* 2012, 87 (7), 725–733.

(87) Abercrombie, S. A.; et al. Sublethal effects of dermal exposure to poly-and perfluoroalkyl substances on postmetamorphic amphibians. *Environ. Toxicol. Chem.* 2021, 40 (3), 717–726.

(88) Loveless, S. E.; et al. Toxicological evaluation of sodium perfluorohexanoate. *Toxicology* 2009, 264 (1–2), 32–44.

(89) Feng, X.; et al. Exposure of pregnant mice to perfluorobutanesulfonate causes hypothyroxinemia and developmental abnormalities in female offspring. *Toxicol. Sci.* 2017, 155 (2), 409–419.

(90) National Toxicology Program. NTP Technical Report on the Toxicity Studies of Perfluoroalkyl Carboxylates (Perfluorohexanoic Acid, Perfluorooctanoic Acid, Perfluorononanoic Acid, and Perfluorodecanoic Acid) Administered by Gavage to Sprague Dawley (Hsd: Sprague Dawley SD) Rats (Revised), 2022.

(91) Rotander, A.; et al. Elevated levels of PFOS and PFHxS in firefighters exposed to aqueous film forming foam (AFFF). *Environ. Int.* 2015, 82, 28–34.

(92) Dobraca, D.; et al. Biomonitoring in California firefighters: metals and perfluorinated chemicals. *Journal of occupational and environmental medicine* 2015, 57 (1), 88–97.

(93) Yu, X.; Ceja-Navarro, J. A.; Wu, X. Sublethal toxicity of fluorine-free firefighting foams in soil invertebrate *Caenorhabditis elegans*. *Environmental Science & Technology Letters* 2022, 9 (6), 561–566.

(94) Hossain, F.; et al. Acute Oral Toxicity of Nonfluorinated Fire-Fighting Foams to Northern Bobwhite Quail (*Colinus virginianus*). *Environ. Toxicol. Chem.* 2022, 41 (8), 2003–2007.

(95) Wu, X.; et al. Chronic toxicity of PFAS-free AFFF alternatives in terrestrial plant *Brassica rapa*. *Science of The Total Environment* 2022, 850, 158100.

(96) Jones, D. K.; et al. Acute toxicity of eight aqueous film-forming foams to 14 aquatic species. *Environ. Sci. Technol.* 2022, 56 (10), 6078–6090.

(97) East, A. Comparative toxicity of seven aqueous film forming foams (AFFFs) to in vitro systems and *Mus*. *Environmental Toxicology and Chemistry* 2023, 42, 2364–2374.

(98) Annunziato, K. M.; et al. Chemical characterization of a legacy aqueous film-forming foam sample and developmental toxicity in zebrafish (*Danio rerio*). *Environ. Health Perspect.* 2020, 128 (9), 097006.

(99) Fire Fighting Foam Coalition. Best Practice Guidance for Use of Class B Firefighting Foams; 2016.

(100) Cheminformatics [cited 2023 11/15]; Available from: <https://www.epa.gov/comptox-tools/cheminformatics>.

(101) Sheng, N.; et al. Comparative hepatotoxicity of 6:2 fluorotelomer carboxylic acid and 6:2 fluorotelomer sulfonic acid, two fluorinated alternatives to long-chain perfluoroalkyl acids, on adult male mice. *Arch. Toxicol.* 2017, 91, 2909–2919.