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3 Firefighting Foams

The PFAS Team developed an Aqueous Film-Forming Foam training video with content related to this section.

The purpose of this section is to assist aqueous film-forming foam (AFFF) users (first responders, regulators, environmental managers, and environmental professionals) who manage AFFF releases. The section includes information about the applications, environmental impacts, and regulations associated with firefighting foams.

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It should be noted that the priority of firefighters and first responders is to protect life and property. The information provided supports decision-making about firefighting using AFFF so that potential impacts to the environment can be minimized and mitigated once the fire emergency is ended, or at such time that sufficient resources are deployed to the scene to both handle the fire emergency and mitigate the environmental risks posed by AFFF use. Fluorine-free foam (F3) alternatives are also discussed; these foams are not "film-forming" and are mechanistically different than AFFF in how they work to extinguish a fire. Figure 3-1 illustrates the life cycle considerations of AFFF. The considerations are discussed in subsequent sections.



Figure 3-1. Life cycle considerations for Class B Foams.

Source: S. Thomas, Battelle. Used with permission.

3.1 Foam Formulations

There are two major classes of firefighting foam, Class A and Class B foams. Class A foams are not considered in this document as they are intended for use on Class A or wood fuels. They are made from hydrocarbon-based surfactants, do not contain intentionally added PFAS, and are appropriate to use for their intended purpose. They are covered under NFPA 1150 (Standard on Foam Chemicals for Fires in Class A Fuels) (NFPA 2022).

Class B firefighting foams are commercial surfactant solutions that are designed and used to combat Class B flammable fuel fires. PFAS (fluorinated surfactants) are the active ingredient in Class B fluorinated foams. When mixed with water and discharged, the fluorinated foam forms an aqueous film that quickly cuts off the oxygen to the fire, cools it, extinguishes the fire, and prevents the fire from relighting. Class B foams have been (and continue to be) stored and used for fire suppression, fire training, and flammable vapor suppression at military installations and civilian facilities and airports (<u>Hu et al. 2016</u>), as well as at petroleum refineries and bulk storage facilities and chemical manufacturing plants (<u>CONCAWE 2016</u>). Additionally, local community fire departments have used and may maintain quantities of firefighting foam in their inventories for use in training and emergency response. Facilities that manufactured fluorinated firefighting foams and landfills that received firefighting waste are also potential sources of PFAS in the environment.

All Class B foams are not the same in composition and mechanism used to extinguish fire. Although not usually categorized this way from a fire protection viewpoint, they can be divided into two broad categories from a PFAS composition perspective: fluorinated foams that contain PFAS and F3 that do not contain PFAS. Figure 3-2 highlights the two broad categories of Class B foams and their subcategories.

Figure 3-2. Types of Class B foams

Source: S. Thomas, Battelle. Used with permission.

All Class B foams have the potential to create an adverse environmental impact if released uncontrolled to the environment, particularly if the foam reaches drinking water sources, groundwater, surface water, or other natural waters. For all Class B foams, including F3, there is a potential for acute aquatic toxicity and excessive biological and chemical oxygen demand, as well as nutrient loading, depending on where the discharge occurs (see Section <u>3.11.1.3</u>).

This section is focused on AFFF because of its long-term and widespread use and associated impacts to human health and the environment. AFFF is of particular concern because it contains PFAS.

As discussed elsewhere in this document, many PFAS are highly persistent and mobile in the environment and are not removed by traditional drinking water treatment methods typically used by public water suppliers.

The fluorosurfactants in AFFF formulations can be produced either using the electrochemical fluorination (ECF) process or the fluorotelomerization (FT) process. Both ECF-derived and telomer-derived AFFF contain diverse mixtures of PFAS (Barzen-Hanson et al. 2017). The ECF process results in a PFAS mixture dominated by perfluoroalkyl acids (PFAAs)—both perfluoroalkane sulfonate (PFSA) and perfluoroalkyl carboxylate (PFCA) homologues, while the fluorotelomerization process exclusively produces AFFF formulations consisting of polyfluorinated compounds (Houtz et al. 2013). ECFbased AFFF formulations were voluntarily phased out of production in the United States in approximately 2002 (Section 2.4.1). Despite the phaseout, however, ongoing permitted use of legacy AFFF can still result in long-chain PFAA contamination. Several organizations (for example, U.S. Department of Defense) commenced systematic replacement of legacy PFOS AFFF with modern fluorotelomer AFFF as early as 2018, but some legacy AFFF remains in service or stockpiled at other facilities (<u>Section 3.11.1</u>).

Other foams such as alcohol-resistant foams (AR-AFFF), filmforming fluoroprotein foams (FFFP), alcohol-resistant filmforming fluoroprotein foams (AR-FFFP), fluoroprotein foam (FP), and alcohol-resistant fluoroprotein foam (FPAR), as illustrated in Figure 3-2, also contain PFAS and similar precautions and considerations should be taken.

Fluorotelomer foams have been in use since the 1970s and became the predominant foam after 2001, when the major manufacturer (3M) of long-chain ECF-based foams (legacy PFOS foam) discontinued production (Leeson et al. 2021). Fluorotelomerization-derived AFFF is still manufactured and used in the United States but has been reformulated to limit, if not eliminate, long-chain PFAS; these foams are now referred to as modern fluorotelomer foams. Studies show ECF-based AFFF is a primary source of PFAS at AFFF-impacted sites, likely due to the longer period of ECF-based AFFF use and the relative coincidence of implementation of engineering controls for releases with increased use of telomer-based AFFF (<u>CONCAWE 2016; Anderson et al. 2016</u>).

To further classify AFFF products in terms of current usage and environmental considerations, they can be divided into three categories, including legacy PFOS AFFF, legacy fluorotelomer AFFF, and modern fluorotelomer AFFF (as shown in Figure 3-2).

- Legacy PFOS AFFFs were created in the 1960s by 3M and manufactured in the United States from the late 1960s until 2002 exclusively by 3M and sold under the brand name "Light Water" (USDOD 2014). 3M was the sole supplier from the mid-1960s until 1973. 3M did license some companies overseas to use their products and formulations. Legacy PFOS AFFFs contain PFOS and PFSAs such as perfluorohexane sulfonate (PFHxS) (Backe, Day, and Field 2013). Although phased out of production in 2002, legacy PFOS AFFFs are the dominant source of PFAS at AFFF-impacted sites (CONCAWE 2016). Furthermore, because of its long shelf life, stock of legacy PFOS AFFF could exist at any given fire department today.
- Legacy fluorotelomer AFFF were manufactured and sold in the United States from the 1970s until 2016 and

encompass all other brands of AFFF besides 3M Light Water or their licensed products (<u>Schultz et al. 2006</u>). Specifically from 1973 onward, several manufacturers created fluorotelomer-based AFFFs that met the Mil-Spec criteria. Although they are not made with PFOA, they contain polyfluorinated precursors (<u>Backe, Day, and Field</u> 2013; <u>Place and Field 2012</u>) that are known to transform to PFCAs, including PFOA (<u>Weiner et al. 2013</u>; <u>Harding-Marjanovic et al. 2015</u>).

Modern fluorotelomer AFFF was developed in response to the USEPA 2010/2015 voluntary PFOA Stewardship Program (<u>USEPA 2018</u>). Most foam manufacturers have now transitioned to the production of only short-chain (C6) fluorotelomerbased fluorosurfactants. These modern fluorotelomer AFFFs, or "C6 foams," do not contain or break down in the environment to PFOS or PFOA and are currently considered to be less toxic and have reduced bioaccumulative potential compared to long-chain (C8) fluorosurfactants. But under particular environmental conditions, breakdown products of C6 foams can include PFHxA, PFPeA, and 5:3 FTCA (<u>Kempisty, Xing, and Racz 2018</u>). Modern fluorotelomer AFFF may contain smaller levels of PFOA as an unintended manufacturing impurity or byproduct.

Fluorotelomer foams, short-chain fluorotelomer foams, and C6 foams are analogous and will be referred to as "modern fluorotelomer foams." When discussing legacy PFOS or C8 foams, the term "legacy foams" will include both legacy PFOS AFFF and legacy fluorotelomer AFFF.

Legacy foams were first introduced by the naval firefighting services in 1964 (<u>Gipe and Peterson 1972</u>). The U.S. Naval Research Laboratory (NRL) began research on the development of firefighting foams in the 1960s. This led to advancements in fire suppression performance and increased firefighting safety (<u>US Naval Research Laboratory 2017</u>). In 1969, the U.S. Department of Defense (USDOD) issued military specification MIL-F-24385, which dictates the performance of all AFFF (with performance standards referred to as "Mil-Spec"). AFFFs shown to perform to MIL-F-24385 requirements are listed on the U.S. military's AFFF Qualified Product Listing (QPL). The first date AFFF was placed on this list was May 15, 1970 (MIL-F-24385 QPL/QPD History of Type 6 AFFF). DOD maintains the online qualified products database (QPD) that lists all AFFF agents that have been tested and qualified by the NRL to meet the Mil-Spec, currently referenced as MIL-PRF-24385, (<u>USDOD 2018</u>). On July 1, 2006, the Federal Aviation Administration (FAA) required that commercial airports certified under 14 CFR Part 139 purchase only AFFF that is Mil-Spec compliant (<u>FAA 2016</u>; 14 CFR 139.317). The FAA Reauthorization Act modified that requirement. In January 2023, the performance specification for F3 land-based, freshwater applications was released as MIL-PRF-32725. This latest specification requires manufacturers to certify that PFAS has not been intentionally added to the formulation and that the concentrate contains a maximum of 1 ppb of PFAS (<u>USDOD 2023</u>). More information can be found in <u>Section 3.12.3</u>.

Different types of AFFF were produced to meet firefighting specifications, such as Mil-Spec, rather than formulated to contain a specified mixture of PFAS. AFFFs are a complex mixture of both known and unidentified PFAS. Multiple AFFF formulations have been produced over the years, and the exact composition of any given AFFF used or manufactured in any given year is variable (<u>Backe, Day, and Field 2013</u>). However, due to the production methods, any given AFFF formulation contains complex mixtures of PFAS, many of which can be identified only by nontargeted analytical methods (<u>Barzen-Hanson et al.</u> <u>2017</u>) (see <u>Section 11</u> for information about analytical methods).

AFFF is typically formed by combining hydrocarbon surfactants, organic solvents, fluorosurfactants, polymers, and other additives (Kempisty, Xing, and Racz 2018). AFFF concentrates are commercially available in 1%, 3%, and 6%. Figure 3-3 illustrates the typical composition of a 3% AFFF concentrate; estimates are that water/diluent makes up more than 60% of the concentrate, up to 20% is solvents, and as much as 15-18% is surfactants, of which less than 2% is fluorosurfactants. When the concentrate is mixed with water, the resulting solution achieves the interfacial tension characteristics needed to produce an aqueous film that spreads across the surface of a hydrocarbon fuel to extinguish the flame or reduce the hydrocarbon vapors. This is a general estimate and composition can vary.



Figure 3-3. Typical composition of 3% AFFF concentrate.

Source: S. Thomas, Battelle. Adapted from Kempisty, Xing, and Racz 2018.

3.2 AFFF Characteristics

As sectors and industries continue to transition from fluorinated foams to F3s and investigation and remediation activities related to AFFF continue, an understanding of current and historical AFFF products is an invaluable asset to identify and delineate potential sources. This includes, where available:

- whether an AFFF product is/was considered a modern or legacy foam and if it is/was manufactured using fluorotelomerization or electrochemical fluorination
- when an AFFF product is/was approved for use and for what specific use/application and to what specific performance standard(s)
- any other pertinent and available information on the product (for example, compatibility, composition information, equipment requirements)

Table 3-1 provided as a separate Excel file, includes the above information for specific AFFF products.

Some research has been conducted to specifically characterize AFFF formulations in both legacy and modern foams. Barzen-Hanson et al. (2017) presented information about AFFF composition over time. Field et al. (2017) summarized information on the commercial formulations approved for use by the DOD in a document, "FAQs regarding PFAS associated with AFFF use at U.S. military sites." Shojaei et al. (2022) characterized PFAS composition in Buckeye Platinum Plus C6 3% MS-AFFF (i.e., Platinum Plus C6) using targeted analysis, total oxidizable precursor assay (TOP), suspect screening, and nontargeted analysis. Results show that the sum of PFAS identified during target analysis comprised only 0.2 percent of total PFAS. 6:2 FTS and PFHxA were the most abundant target PFAS among the 12 monitored target PFAS. Suspect screening identified seven PFAS in six classes, which were largely comprised of C6 FT-based precursors (>99%). The most prevalent class was n:2 FTSAPr-DiMeAn, which may be a byproduct of fluorotelomer betaine synthesis. Nontarget analysis identified ten PFAS within nine classes of n:2 fluorotelomer sulfonamides, with 6:2 FTSAPr-AmHOPrS (CASRN 76201-56-4) being the most prevalent PFAS. PFAS composition of Platinum Plus C6 is different from the older Premium 3MS reported by Han et al. (2021).

ECF-based AFFFs contained primarily C6-C8 perfluoroalkyl sulfonates, with some zwitterionic C4-C6 perfluoroalkyl sulfonamides (FASAs) containing carboxylic acid and tertiary amine functionalities. Fluorotelomer-based AFFF formulations normally contained fluorotelomer thioamidosulfonates (FtTAoS) (4:2, 6:2 and 8:2) with 6:2 FtTAoS as the dominant compound, and very low perfluoroalkyl sulfonates or carboxylates (Backe, Day and Field 2013).

Some legacy nonfluorinated foams, notably those that are protein-based, form thick, viscous foam blankets on liquid hydrocarbon fuel surfaces. These foams are typically referred to as mechanical foams. These foams extinguish fires using strong bubble structure to smother the fire as opposed to the film and bubble structure of AFFF. More recent F3s are similar to the legacy protein foams in that they rely solely on the foam blanket to contain the fuel vapors to extinguish the fire (F3s do not produce a surfactant film on the fuel surface like AFFF). As a result, air-aspirating discharge devices may be required to optimize the capabilities of these products (NFPA Research Foundation 2022).

Many of the commercially available F3s have been tested to, and or listed/approved to, the legacy foam test protocols. These protocols include but are not limited to Underwriters Laboratories (UL), Factory Mutual (FM), European Standards (abbreviated EN), and International Civil Aviation Organization (ICAO) standards (<u>NFPA Research Foundation 2022</u>).

3.3 Mechanisms for Release to the Environment

Firefighting foam is applied by mixing foam concentrate and water to make the firefighting foam solution, which typically contains less than a fraction of a percent of fluorinated surfactants once in mixture. When applied to a fire, the foam solution is aerated at the nozzle, yielding finished firefighting foam. Thousands of gallons of foam solution may be applied during a given event. Figure 3-4 illustrates the use of firefighting foam, how it may be released to the environment, and potentially affected media. Once released to the environment, AFFF can contaminate soil, surface water, sediment, and groundwater. Section 5 includes details and references for fate and transport of PFAS in the environment.



Figure 3-4. Release of firefighting foam.

Source: Adapted from figure by J. Hale, Kleinfelder. Used with permission.

Firefighting foams are released into the environment through various practices and mechanisms (<u>Anderson et al. 2016</u>; <u>Hale</u> <u>2016</u>; <u>Thalheimer et al. 2017</u>) such as:

- low-volume releases of foam concentrate during storage, transfer, or operational requirements that mandate periodic equipment calibration
- moderate-volume discharge of foam solution for apparatus testing and episodic discharge of AFFF-containing fire suppression systems within large aircraft hangars and buildings
- occasional, high-volume, broadcast discharge of foam solution for firefighting and fire suppression/prevention for emergency response
- periodic, high-volume, broadcast discharge for fire training
- accidental leaks from foam distribution piping between storage and pumping locations, and from storage tanks and railcars.

AFFF-impacted sites often are also contaminated with petroleum hydrocarbons from unburned fuel. PFAS and hydrocarbon plumes at these sites may follow the same flow paths, though the extent of contamination may be significantly different. These co-contaminants, particularly light nonaqueous phase liquids (LNAPLs), may affect the fate and transport of AFFFderived PFAS (<u>Guelfo and Higgins 2013</u>; <u>Lipson</u>, <u>Raine</u>, <u>and Webb 2013</u>; <u>McKenzie et al</u>. 2016), see <u>Section 5.2.5</u>. Certain airbased or in situ oxidation remedial activities aimed at treating co-contaminants may affect PFAS composition, fate, and transport as well (<u>McKenzie et al</u>. 2015). Additionally, the altered soil and groundwater geochemistry and redox conditions may result in oxidation of some PFAS precursor compounds, degrading them to terminal PFAAs (<u>Harding-Marjanovic et al</u>. 2016; <u>McKenzie et al</u>. 2016; <u>McGuire et al</u>. 2014). For additional detail on transformations of precursors see <u>Section 5.4</u> and <u>Section 10.4.6</u>.

The USDOD has undertaken an evaluation of potential firefighting foam contamination at its facilities nationwide (<u>Anderson</u> <u>et al. 2016</u>). Similar efforts have been undertaken by some states. For example, the Minnesota Pollution Control Agency (MPCA) conducted a statewide survey of firefighting foam use at training sites. Working with the State Fire Chiefs Association, the MPCA identified more than two dozen locations where Class B foams were likely used in firefighting training (<u>Antea Group 2011</u>).

Figure 2-21 illustrates common elements of CSMs associated with the potential AFFF release scenarios at fire training areas.

3.4 AFFF Fate and Transport

3.4.1 Physical and Chemical Characteristics

Factors that affect fate and transport of PFAS from AFFF releases, as concentrate or in mixture with water, include the chain lengths of the PFAS, their ionic states, the type of functional group(s), and the extent of fluorination. These factors strongly influence the extent of PFAS partitioning and transformation that occurs in the environment. The distribution and composition of legacy PFOS AFFF and legacy and modern fluorotelomer AFFF differ in the environment based on their different chemical constituents and physical and chemical properties (MPART 2020). It is important to consider any precursor PFAS that can transform to PFAAs over time and add to concentrations of known PFAAs in the environment, such as PFOS and PFOA. The relatively high solubilities of most PFAS in AFFF contribute to their migration rates in groundwater. Current published data and physical properties of PFAS differ and some chemical data are experimental, extrapolated, or modeled. Section 4 summarizes some of the available physical and chemical properties for PFAS. Tabulated values and references are included in Table 4-1 (provided as a separate Excel file).

3.4.2 Fate and Transport Processes

Fate and transport process information is used to address questions related to potential risk, conceptual site model (CSM), and treatment of PFAS. The mechanisms of partitioning, transport, and transformation of PFAS, which occur across different environmental media, are summarized in <u>Table 3-2</u> below. <u>Section 5</u> provides the detailed discussion and references.

Fate and Transport Process	Description	Role in Transport
Partitioning Refer to <u>Section 5.2</u>	• Competition between hydrophobic and lipophobic C-F "tail" and nonfluorinated polar and hydrophilic head groups causes partitioning to interfaces such as: soil/water water/air water/NAPL co-contaminants	 Controls distribution in environment Preference for air-water interface influences aerosol transport and deposition, and vadose zone transport (unsaturated conditions provide significant air water interfacial area)
Advection, Diffusion, Dispersion Refer to Sections 5.3, 10.4	 PFAS diffusion in groundwater is slow but greater in air and surface water Atmospheric transport, e.g., from AFFF applications, results in deposition to soil/surface water/surfaces PFAS are mobilized from soil to groundwater or to surface water through runoff and leaching 	 Facilitate transport of PFAS in and across media Increase contaminant distribution. Research on the potential impacts of diffusion on PFAS persistence in natural soils is ongoing. Adamson et al. (2020) conducted a study that estimated the relative distribution of different PFAS between high and low permeability soils at AFFF fire training area
Abiotic Transformation Refer to <u>Section</u> <u>5.4.4.1</u>	 Abiotic processes that can transform precursors under ambient environmental conditions include hydrolysis, photolysis, and oxidation 	 Results in chemicals with different physical and chemical properties May alter risk May affect treatment selection
Biotic Transformation Refer to Sections 5.4.4.2 and 5.4.4.3	 PFOA, PFOS, and other PFAAs are resistant to microbial degradation Biotransformation of various precursors has been reported 	 Results in chemicals with different physical and chemical properties May alter risk May affect treatment selection

Table 3-2. Fate and transport process considerations

3.4.3 Fate and Transport Considerations for AFFF Remediation

Knowledge of the type of AFFF and the constituents released to the environment is critical for adequate site characterization and CSM development. Physical and chemical properties and environmental processes play key roles in identifying contaminant capture and collection methods and selection of treatment technologies. The effects of co-contaminants, such as petroleum hydrocarbons, on fate and transport of AFFF constituents is addressed in <u>Section 3.3</u> and partitioning into NAPL co-contaminants is addressed in <u>Section 5.2.5</u>. Many traditional technologies, such as air stripping and soil vacuum extraction, which rely on volatilization, have been found to be ineffective for PFAS, which typically have low volatilities and are highly soluble. The stability and persistent nature of PFAS in the environment also make current bioremediation approaches ineffective.

Proven and developing treatment technologies for treatment of PFAS are presented in <u>Section 12</u>, which also includes details on the roles of physical and chemical characteristics and transport processes in technology selection. For example, water treatment technologies, such as GAC adsorption and ion exchange, have been proven to be effective because they rely on the hydrophobic and ionic properties of PFAS. Field-implemented technologies for soil include excavation and landfill disposal or mixing with sorbent for stabilization. The potential for leaching associated with disposal is reduced by stabilization. Many new technologies that rely on the unique properties of PFAS are under development.

3.5 Forensic Analysis of AFFF

Forensic analysis of AFFFs should be based on fingerprinting the composition of unknown samples and comparison with published fingerprints that are further discussed in this section. Many limitations must be considered in such investigations, including the changes in original manufactured product fingerprint due to precursor transformation in time, potential presence of impurities due to manufacturing processes and/or equipment used, and differences in original fingerprints for distinct manufactured batches. While there are tests that may be performed to help understand and overcome some of these limitations, every case should be based on site-specific data and historical information. For example, total oxidizable precursors (TOP) may be performed to evaluate the changes in original AFFF fingerprints due to precursor transformations in time and the data should be interpreted within site-specific context considering potential deviations due to site-specific conditions. AFFF products stored for long periods of time may have changed the original PFAS fingerprint even if those products were not released and exposed to environmental conditions. Therefore, when trying to identify the type and original composition of AFFF products, multiple lines of evidence should be employed, including historical information, chemical fingerprinting via targeted PFAS analysis, TOP analysis, and total organic fluoride (TOF) content. Ultimately, nontargeted PFAS analysis may also be employed for in-depth evaluations and matching of foams with suspected sources. More information on these specific tests is provided in <u>Section 10.5</u> and <u>Section 11</u>.

Although many types of PFAS are identified in the AFFF formulations, due to the lack of analytical standards, quantitative information is not available for all identified individual PFAS, whereas qualitative detections and area counts are reported (D'Agostino and Mabury 2014; Barzen-Hanson et al. 2017; D'Agostino and Mabury 2017; Ruyle et al. 2021). There is quantitative information on the composition of a series of AFFF formulations manufactured in different years by several manufacturers, including 3M, ChemGuard, Ansul, Buckeye, and National Foam (Annunziato et al. 2020; Houtz et al. 2013; Backe, Day, and Field 2013; Ruyle et al. 2021; Herzke, Posner, and Olsson 2009; KEMI, 2015). The chemistry of AFFF is complex, consisting of anionic, cationic, zwitterionic, and neutral compounds; in addition, different formulations of AFFF from the same manufacturer may also vary in chemistries (Backe, Day, and Field 2013; Houtz et al. 2013; Barzen-Hanson et al. 2017). AFFF includes many fluorinated and nonfluorinated surfactants. Total surfactants are thought to range from approximately 15 to 18 percent. Some references cite about 5-10% (w/w) are nonfluorinated surfactants have also been detected in the AFFF-impacted groundwater (García et al. 2019). For forensic analysis, evaluating the source attribution of PFAS from AFFF used for emergency response or fire training operations and understanding the manufacturing history, timing of release, potential sources, degradation products, isomer profiles, and environmental partitioning of PFAS during transport are very important (Dasu et al. 2022; Guelfo et al. 2021; Dorrance et al. 2017).

3.5.1 Manufacturing and Chemistry

PFAS are commonly produced by two manufacturing processes: electrochemical fluorination (ECF) and fluorotelomerization. For example, legacy 3M AFFF brand name Light Water was manufactured by electrochemical fluorination, and the legacy longer chain and the new replacement shorter chain (C6) fluorotelomer-based AFFFs are manufactured by the fluorotelomerization process. More detailed information on these processes is presented in <u>Section 2.2.5</u>, and more detailed information on AFFF as it relates to these processes is presented in <u>Section 3.1</u>. Despite the recorded differences and complex composition of AFFF products, several general traits have been established in the literature based for each manufacturing processes and the final products and byproducts formed by using these two processes are different.

The ECF process results in a mixture of linear and branched fluorinated molecules of various carbon chain lengths, both even and odd carbon chains (<u>Buck et al. 2011</u>). The ratio of linear and branched isomers ranges from 70 to 80% linear and 20 to 30% branched isomers (<u>Kissa 2001</u>; <u>Buck et al. 2011</u>; <u>Benskin et al. 2007</u>). The ECF process produces varying amounts of C2-C10 PFAAs (<u>Backe, Day, and Field 2013</u>). Some of the ECF chemistries are based on perfluorooctane sulfonyl fluoride (POSF), a major raw material used to manufacture surfactants (such as perfluorooctane sulfonate (PFOS)), and other raw materials such as sulfonamides, sulfonamido alcohols, and related monomers (<u>Backe, Day, and Field 2013</u>; <u>D'Agostino and</u> <u>Mabury 2014</u>; <u>Buck et al. 2011</u>).

The other important manufacturing process of PFAS is the telomerization process, which mainly produces linear isomers with an even number of carbon chains as the major products, although some odd-numbered carbon chains have also been produced (Kissa 2001). The nomenclature of PFAS manufactured by the telomerization process includes n:2 fluorotelomers (see Section 2.2.4.1), where n represents the perfluorinated carbon chain length and 2 represents the nonfluorinated ethane attached to the functional group, such as alcohols, carboxylates, sulfonates, etc. (Buck et al. 2011). Fluorotelomers (FT) are predominantly produced in 4:2-, 6:2-, 8:2-, and 10:2-carbon chain lengths, although 12:2 has been seen in FT Mil-Spec AFFF (Backe, Day, and Field 2013). Fluorotelomer alcohols or iodides are commonly used as raw materials in the telomerization process to produce fluorotelomer sidechain polymers. At many of the AFFF-impacted sites, perfluorooctanoic acid (PFOA), PFOS, and perfluorohexane sulfonic acid (PFHxS) are the most prevalent PFAS detected. The phaseout of the longer chain PFAS by global manufacturers has resulted in quantifiable increase in shorter-chain concentrations and decreased concentrations of longer chains at some of the areas investigated (Ruyle et al. 2021).

3.5.1.1 Reported PFAS Profiles in AFFFs Manufactured Via ECF vs. Telomerization.

In spite of the recorded differences and complex composition of AFFFs, several main traits may be established among AFFs manufactured by each mentioned process based on the literature-reported data (<u>Annunziato et al. 2020; Houtz et al. 2013;</u> <u>Backe, Day, and Field 2013; Ruyle et al. 2021; Herzke, Posner, and Olsson 2009; KEMI 2015</u>). These traits provide the basis for chemical fingerprinting of PFAS in AFFFs and environmental media.

AFFFs manufactured via ECF process (by 3M) are reported to contain both precursor PFAS (including: PFBSAm, PFPeS-Am, PFBS-AmA, PFPeS-AmA, and PFHxS-AmA) and PFSAs (which are typically predominant) and PFCAs. The AFFFs manufactured via fluorotelomerization process are reported to contain mostly precursor PFAS, with some PFCAs also being reported in some of these AFFFs (Ruyle et al. 2021). Upon oxidation (for example, transformation of precursor PFAS in time and due to exposure to environmental conditions), both main types of AFFFs generate PFCAs with distinct profiles described below.

- The profiles of PFCAs in ECF-manufactured AFFFs after oxidation are consistent among various manufactured batches and years and are different from the profiles reported before oxidation. The oxidized ECF-manufactured AFFFs PFCA profiles should be more representative for environmental profiles of spilled AFFFs and have the following common traits: the predominance of PFHxA (61–75%), followed by PFBA (12–26%), and PFPeA (2–25%) (Houtz et al. 2013). Smaller amounts of PFOA and PFHpA are also reported in these oxidized foams.
- The profiles of PFCAs in AFFFs manufactured by telomerization generated after AFFF oxidation have several common traits among manufacturers (for example, Chemguard, Ansul, Buckeye, National Foam), which seem to be preserved along the years. These traits include the predominance of PFPeA (25-49%), followed by PFBA (19-28%), PFHxA (13-20%), and PFHpA (3-20%), and the presence of smaller amounts of PFOA (1-9%) and PFNA (1-4%) (Houtz et al. 2013).
- The profiles of PFSAs in manufactured (nonoxidized) AFFFs are preserved among ECF-manufactured AFFFs from different years (1988, 1989, 1992, 1993, 1998, 1999, 2001), including batches from the same years, as reported by Houtz et al. (2013). The PFAS profiles of 3M-manufactured AFFFs are consistent in the strong predominance of PFOS (85-90%), followed by PFHxS (7-12%), with smaller amounts of PFHpS and PFBS also detected. Similar profiles are reported by Backe, Day, and Field (2013) and by Ruyle et al. (2021), with the addition of PFPeS detected in small amounts.
- The profiles of PFCAs in manufactured AFFFs (non-oxidized) vary more among the reported manufactured batches and years than in the case of the PFAS profiles mentioned before. Despite these variations, several traits can be observed: In some of the analyzed AFFFs manufactured by ECF (Houtz et al. 2013), PFPeA predominates, followed by PFHxA and PFOA, while in ECF-manufactured AFFFs analyzed by other authors, these proportions

change to some extent with the predominance of PFHxA and PFOA, and with smaller amounts of PFPeA, PFBA, and PFHpA also reported (for example, see data reported by <u>Backe, Day, and Field 2013</u>, <u>Annunziato et al. 2020</u>, and <u>Ruyle et al. 2021</u>).

In AFFFs manufactured by telomerization, only a few had PFCAs detected before oxidation and the profiles were quite variable, as reported by Ruyle et al. (2021), with the predominance of PFHxA and PFBA in many analyzed foams, and the predominance of PFHpA, PFOA, and PFNA in few other foams. In several different analyzed foams, <u>Herzke, Posner, and</u> <u>Olsson 2009</u> reported the predominance of PFHxA and PFPeA, followed by PFOA and PFBA, with PFDcA (at comparable amounts with PFBA) reported in one foam, while smaller amounts of PFDoA were reported in another foam.

Benotti et al. (2020) reported PFAS profiles for several FT-manufactured modern AFFFs, consistent with those described here and reported by other authors mentioned before (for example, <u>Herzke, Posner, and Olsson 2009</u>), consisting predominantly of 6:2 FTS among detected precursor PFAS and PFHxA among detected PFCAs. Additionally, the Benotti et al. (2020) study pointed out the predominance of even-numbered PFCAs (PFBA, PFHxA) over their odd-numbered homologues in AFFFs manufactured via telomerization. Notably, this study also pointed out the presence of smaller amounts of long-chain PFCAs (including PFOA, PFDA, PFDA) and PFSAs (PFHxS and PFOS) in the modern AFFFs that were analyzed. The authors attributed these findings to the manufacturing process from fractional distillation of feedstock or to cross-contamination during manufacturing and handling.

3.5.2 Factors Affecting the PFAS Fate and Fractionation

PFAS forensic analysis of environmental samples is often challenging as many of the PFAS-contaminated sites consist of comingled sources. Many of the AFFF-impacted sites often contain a mix of different formulations of AFFF, either from the same manufacturing source (ECF or telomer-based), or a mix of different sources. Many of the PFAS analytes exhibit a wide range of physical and chemical properties, and hence are transported from the source zones and redistributed downstream through environmental fractionation (Lindstrom et al. 2011; McGuire et al. 2014). Higher water solubility and mobility of short-chain PFAS contribute to the relatively high concentrations of short-chain PFAS in aqueous matrices downstream from the source areas. The isomer profiles present at the source of contamination will change and redistribute after a certain distance from the source (Adamson et al. 2020; Nickerson et al. 2021). Due to the high solid/water distribution coefficient (K_d) , longer chain PFAS have a greater affinity than shorter chain PFAS to partition to sediments, sludge, and soils (Higgins and Luthy 2006; Kwadijk, Korytár, and Koelmans 2010; Schulz, Silva, and Klaper 2020). PFAS, due to their electrostatic nature, may also adsorb onto soils due to the soils' electrostatically charged surfaces (Adamson et al. 2020). Groundwater transport of PFAAs depends on the concentration, chain length, soil characteristics, partitioning behavior, and in situ precursor biotransformation followed by the redistribution of the transformation products (Guelfo and Higgins 2013; McGuire et al. 2014; Anderson et al. 2016). Additionally, the presence of co-contaminants and/or remediation products in subsurface may also affect PFAS fate and transport (Guelfo and Higgins 2013; McKenzie et al. 2015; Brusseau 2018; Hatton et al. 2018) and should be considered in a forensic investigation.

All these factors indicate that the PFAS fingerprint at the source could be different compared to the downstream sample locations. Hence, forensic analysis of such complex AFFF-impacted comingled sources would require consideration of many factors and multiple lines of evidence to better understand the identification and delineation of sources. These include: (1) PFAS profiles, including PFCAs and PFSAs isomer profiles and chain-length ratios, which may differ from source, based on the environmental fractionation; (2) unique source-specific markers, which require a detailed understanding of known sources to identify a source related to a sample (McGuire et al. 2014; KEMI 2015; Guelfo and Adamson 2018); and (3) high-resolution mass spectrometry (HRMS) tools to help identify and characterize a broad suite of PFAS analytes to understand the sourcespecific markers (D'Agostino and Mabury 2014; Barzen-Hanson et al. 2017; D'Agostino and Mabury 2017; Newton et al. 2017; Ruyle et al. 2021). In addition to HRMS analysis, application of statistical analysis tools showed great promise in identifying sources of PFAS contamination (Zhang et al. 2016; Kibbey, Jabrzemski, and O'Carroll 2020; Nason et al. 2021). However, statistical analysis of any PFAS data sets should be done with caution, considering comparability between data sets in terms of sampling and analytical techniques used, as well as environmental transformations expected based on sample location and site-specific parameters. A forensic approach based on multiple independent lines of evidence increases certainty. Examples of lines of evidence that may be developed for PFAS forensic evaluation include chemical profiles of PFCAs and PFSAs, isomer profiles, signature PFAS (for example, via nontargeted analysis), historical document review, and fate and transport evaluation and modeling (see also Sections 4, 5, 10, and 11).

3.5.3 Summary of Forensic Analysis of AFFF

Employing a lines of evidence approach to identify what AFFF product or products have been used at a particular site is a useful first step during site assessment. The identification of products may help the practitioner to predict what PFAS compounds may be present, including likely precursors and degradation products. Understanding product use will improve site conceptual model development at the outset. Lines of evidence that may be used to identify AFFF products include interviews with site users, bills of lading or procurement records, and finally, analysis of environmental samples. Foam product groups (for example, legacy ECF-manufactured AFFFs, legacy fluorotelomer AFFFs, and modern AFFFs) differ in key ways as presented below.

The proprietary nature of source information, complex PFAS chemistry, and lack of analytical standards pose many challenges in understanding the source identification (see also <u>Section 10.5</u> and <u>Section 11.4</u>) and attribution at AFFF-impacted sites. Using only targeted PFAS analysis may be useful, since several common traits are evident in AFFFs and may help differentiate between AFFFs and other types of PFAS sources. However, differentiation between multiple AFFF sources may become more difficult based just on targeted analysis data (for example, PFCA and PFSA data), especially for comingled plumes away from the source area where environmental fractionation may play an important role. Nontargeted analysis using HRMS helps in understanding the chemistry beyond the standard targeted analysis data and shows great promise in identifying and delineating PFAS contamination; however, HRMS is still a relatively new and developing tool and its results should be interpreted carefully in the context of the specific investigation. Considering multiple lines of evidence while conducting forensic investigations helps to identify PFAS source attribution and manage AFFF-impacted sites.

A series of recent publications provide data and information relevant to AFFF source evaluation, as synthesized below:

- AFFF fingerprints seem to be preserved in fish from polluted freshwater systems and were used to differentiate AFFF versus other PFAS sources in fish, namely the paper industry and long-range atmospheric transport (Langberg et al. 2022). Specifically, a total of 454 liver samples and 581 muscle samples from 11 fish species were investigated. The fish samples from AFFF-polluted sites had a predominance of PFOS, suggestive of legacy ECF-manufactured AFFFs. High percentages of PFOS were also observed in fish samples contaminated from the paper industry, but the PFCA profiles were distinct from those in fish contaminated by AFFFs. In fact, the profiles of PFCAs were distinct between AFFFs and the other PFAS sources (paper industry and long-range atmospheric transport). The PFCAs profiles in fish from waters contaminated from the paper industry and via long-range atmospheric transport had higher percentages of long-chain PFCAs, as compared with those from fish in waters contaminated by AFFFs. Additionally, PFUnDA/PFDA and PFTrDA/PFDoDA ratios were different between the two non-AFFF sources, being higher in the case of long-term atmospheric transport.
- Dasu et al. (2022) performed a comprehensive review of PFAS concentration profiles from both main direct (fluorochemical manufacturing plants, consumer products, metal-plating operations, AFFF use) and indirect sources (landfills and wastewater treatment plants). They found that both groundwater and soil at or near AFFF-contaminated sites had higher median PFOA and PFOS concentrations as compared to those from groundwater and soils near the other main studied sources. Dasu et al. (2022) pointed out the potential for environmental transformation of many unknown PFAS present in AFFF into persistent PFAS, acting as long-term PFAS sources. From a fingerprinting perspective, the study indicates that the commonly analyzed PFAS compounds are ubiquitously detected in environments contaminated by distinct main sources, pointing out the need for high-resolution tools such as nontargeted analysis and combined methods of total fluorine and/or extractable fluorine for better source attribution of PFAS. However, Dasu et al. (2022) did not include an analysis of the relative proportions of individual PFAS compounds in media contaminated by different sources, which could have forensic relevance.
- The high precision methods used by Liu et al. (2022) in analyzing PFAS-contaminated soil and groundwater at four Canadian airports, consisting of HRMS and an improved total oxidizable precursor (TOP) assay, may be of high utility in forensic applications. Based on these analytical techniques, 93 classes of PFAS could be investigated and characterized at these Canadian airports.
- A comprehensive study of PFAS in surface water near U.S. Air Force bases (<u>East, Anderson, and Salice 2021</u>) determined that, according to the legacy AFFF composition, a four-chemical mixture composed of PFOS, PFHxS, PFHxA, and PFOA generally accounted for >80% of the sum of all routinely reported PFAS in a sample. This observation is relevant in building AFFF-representative

PFAS fingerprints.

- The predominance (90%) of 6:2 fluorotelomer sulfonate in modern AFFFs has been confirmed by Ruyle et al. (2021), who developed and applied a "novel method (Bayesian inference) for reconstructing the fluorinated chain lengths, manufacturing origin, and concentrations of oxidizable precursors obtained from the total oxidizable precursor (TOP) assay" (Ruyle et al. 2021). These authors were able to identify 14 major fluorotelomer compounds present in modern AFFF "yielding a priority list that accounts for almost all detectable PFAS in contemporary AFFF." Testing for these fluorotelomers may help differentiate between AFFF and non-AFFF sources of PFAS.
- Kibbey, Jabrzemski, and O'Carroll (2020) "explored the use of supervised machine learning classifiers for allocating the source of PFAS contamination based on patterns identified in component concentrations." "The deep neural network and Extra Trees exhibited particularly high performance at classification of samples from a range of sources, [showing that] patterns exist in PFAS water sample data that can allow forensic source allocation." While these methods are complex and evolving, they show promise for PFAS allocation at complex sites.
- Shojaei et al. (2022) provided useful data on the chemical composition of AFFFs currently certified for use by the U.S. military. These authors used several distinct analysis techniques, including targeted analysis by HRMS, TOP, and nontargeted analysis. The study identified nine novel classes of PFAS comprising 10 individual compounds that made up ~90% of total PFAS measured in the tested foam. The combination of TOP with nontargeted analysis holds great potential for PFAS source identification.

3.6 AFFF Procurement and Inventory

This section discusses procurement and inventory of AFFF, including suggestions for storing inventory to minimize the potential for accidental releases.

3.6.1 Foam Selection and Requirements

Multiple manufacturers in the United States and abroad produce AFFF concentrate in 1%, 3%, or 6% concentrations. Most AFFF sold or in stock in the United States is either 1) listed by Underwriters Laboratory (UL) based on conformance with UL Standard 162, "Foam Equipment and Liquid Concentrates," or 2) tested by NRL and granted qualification by U.S. Naval Sea Systems Command in accordance with the Mil-Spec. Only AFFF meeting the Mil-Spec has been used in military applications and at FAA-regulated airports.

Military and FAA AFFF applications subject to Mil-Spec account for more than 75% of AFFF used in the United States (Airport Cooperative Research Program <u>ACRP (2017)</u>). Hence, the production of AFFFs has historically been driven by firefighting specifications, such as Mil-Spec, which requires a specific percentage concentration of PFAS. Current Mil-Spec AFFFs contain \leq 1% (approx. 0.5–0.6%) fluorosurfactants after the concentrate is mixed with water to create the final foam solution used to extinguish or prevent high-hazard flammable liquid fires; however, the exact AFFF PFAS mixtures are highly variable. Non-Mil-Spec Class B foams can vary from fluorine-free to having concentrations of PFAS similar to Mil-Spec AFFF. Furthermore, where fire risk allows it, users who are not subject to Mil-Spec requirements are less likely to use foam formulations that contain PFAS given the environmental implications and increasing prevalence of F3. However, the knowledge of environmental implications of PFAS was historically lacking and is still not widely understood by first responders, and there are many historical examples of AFFF use by municipal fire departments during fire response activities.

3.6.2 AFFF Storage and Handling

AFFF concentrate is available from the manufacturers in containers ranging from 5-gallon buckets to 5,000-gallon tanker trucks. The most common method of shipping is in 5-gallon buckets, 55-gallon drums, or 265-gallon intermediate bulk containers. Shipping containers are typically not double walled but made of plastic, steel, or steel reinforced plastic tote construction to resist damage/puncture. Per National Fire Protection Association (NFPA) 11, Section 4.3.2.3, bulk liquid storage tanks should be fabricated from or be lined with materials compatible with the concentrate, designed to minimize evaporation of foam concentrate, and stored within the listed temperature limitations (NFPA 2016).

In fire suppression systems, the AFFF concentrate is typically stored in either an atmospheric (nonpressurized) tank or a bladder tank (pressurized). Atmospheric tanks are single- or double- walled tanks and can supply proportioning foam

concentrate pumps or venturi-based proportioners that feed the suppression system. Atmospheric tank piping arrangements may include recirculation from downstream of the pump back to the tank. The bladder tanks contain a bladder filled with foam concentrate that is squeezed by water between the shell of the tank and the bladder. As long as the bladder integrity is maintained, the foam concentrate does not mix with the shell water.

Safety data sheets are provided by all manufacturers for each specific type of AFFF. Labels on shipping containers conform to U.S. Department of Transportation (USDOT) standards. AFFF and AFFF-impacted materials (soils and absorption materials), including concentrate being disposed, rinsate, and foam supply system materials, are not currently considered to be hazardous materials under federal regulations. Some individual states have passed legislation to include PFOS, PFOA, and other PFAS on their hazardous substances list and otherwise restrict the sale and use of AFFF (for example, (Washington Senate 2018) (New York State 2017). Regulations are discussed further in Section 3.12

As with any potentially hazardous substance, the best practice for storage and handling is to ensure containment until proper disposal. AFFF materials should be labeled to clearly indicate the contents of the container. It is important that all containers are kept clean so that any signs of leakage can be easily and quickly identified during container inspections, with the labeling pointed outward for easier reading.

3.7 Foam Systems and Operations

Class B firefighting foams are employed globally to fight flammable liquids fires where risk of damage to property or human life is high. These products are particularly prevalent in airport settings. This section describes common AFFF system operations, including system testing and training. Additionally, information is provided in <u>Section 3.11</u> for organizations that want to replace legacy PFOS AFFF systems with modern fluorotelomer AFFF or F3.

3.7.1 Fixed System Testing

Fixed fire suppression systems that utilize any of the foam types and application methods are permanent designs and should incorporate the containment, collection, and runoff components in the event of system discharge into the design. Examples include flammable liquid warehouse, waste treatment facility, and aircraft hangar fire suppression systems. New systems should be designed to include foam containment and collection mechanisms such that foam releases that occur during testing or activation are not released to the environment, or the AFFF can be captured for disposal. AFFF design standards require minimum durations for foam system discharge to meet the suppression/control requirements and in some cases require specific volumes of concentrates and foam solution to be contained in on-site storage tanks. Fixed AFFF proportioning systems that are connected to city water mains should be fitted with backflow preventers to protect the city water mains from potential AFFF contamination.

Codes, standards, and authorities having jurisdiction over fixed system testing, such as NFPA Standards 16 (NFPA 2019) and 25 (NFPA 2017), can require that the equipment produce a foam/foam solution that can be tested and compared to laboratory standards. System testing generates a small amount of foam that should be contained or controlled by the design to the best extent possible for proper disposal. Foam can be wetted with fog nozzles/mist to knock down the foam and dilute it. Gentle squeegee and sweeping are required to keep the solution from aspirating during cleanup and dilution. Alternatives, such as testing with water (without foam) or testing with fluorine-free training foam or surrogate liquids having similar physical properties, may be considered to minimize disposal issues. Check applicable regulatory requirements for testing to determine frequency and type of testing required, as well as what is specifically mandated for foam type before any alternatives are considered to ensure compliance with appropriate laws.

3.7.2 Mobile Firefighting Equipment Testing

Firefighting equipment requires inspection, calibration, and testing to ensure reliability and performance to specifications. In accordance with fire protection standards (for example, NFPA Standard 412, (<u>NFPA 2020</u>) and manufacturer's recommendations, the testing of mobile firefighting equipment should be conducted routinely and documented.

Multiple pieces of equipment can be tested or inspected simultaneously. Mobile equipment, including but not limited to mobile foam extinguishers, firefighting vehicles, and marine craft, can be collected, tested, and cleaned and foam concentrate samples can be collected in a single location to minimize potential impacts. It is recommended that testing of mobile firefighting equipment is executed at purpose-built facilities specifically designed to capture and contain all generated foam and wastewater for treatment, reuse, or disposal.

Conditions during equipment testing should include secondary containment measures to ensure foam solutions can be captured and managed and environmental impact minimized. Alternatives to traditional testing methods may be considered, such as:

- using water or surrogate solutions for training
- testing equipment indoors
- spraying into drums or other containers
- testing within lined pits or spill containment equipment
- testing with closed-loop AFFF testing systems to minimize and eliminate discharge (FAA 2023).

Other controls include not testing during adverse weather conditions, not testing where the facility is not deemed fit for purpose, conducting a risk assessment of the activity, and minimizing foam wastewater volume generated whenever possible. As with fixed fire suppression systems, mobile equipment that complies with NFPA Standard 412 requires that the equipment produce a foam/foam solution that can be tested and compared to laboratory-analyzed solutions (NFPA 2020).

3.7.3 Training Exercises

Facilities should have specifically designed areas and structures to conduct training exercises involving flammable liquid fires and foam systems. The fire training areas (FTAs) should be arranged to contain/control the training site for the safety of the persons being trained. Control of training fires as well as applied foam and/or foam solutions is maintained by the facility design. The FTA should also be designed for collection/recovery of unburned fuels as well as the foam solution and fire water following the completion of training exercises. Conducting outside exercises during windy weather conditions should be avoided, as the foam solutions can be difficult to contain due to natural aspiration and windblown transport.

Past training exercises at airports and military installations employed large quantities of foam/foam solutions. To prevent further releases to groundwater, USDOD issued a policy in January 2016 requiring prevention of "uncontrolled land-based AFFF releases during maintenance, testing, and training activities. Current USDOD policies prohibit using AFFF with PFOS for testing, maintenance, or training exercises with the exception of shipboard activities.

Consider minimizing the volume of foam used to the greatest extent possible. If permitted by the applicable regulatory requirements for training, consider entirely discontinuing the practice of using expired legacy AFFF and modern fluorotelomer AFFF as training foam. Whenever possible, seek fluorine-free alternatives for training events; consider training with water or training foam where practicable, not Class B foam, and certainly not with Class B foam containing PFAS. Any wastewater or foam generated from training activities should be kept to a minimum and foam spraying should be restricted to target areas only (not sprayed over wide areas). Preplanning responses that deploy AFFF can identify weaknesses in both AFFF use strategies and in fuel and fire water runoff and containment. This can also identify the need for calling mutual aid early to assist with containment tactics.

Training protocols with F3s must be established. While F3 foam does not contain PFAS, some F3 foams may contain other additives or chemicals that could be harmful to the environment or human health. As such, any training involving F3s should also consider the mitigation measures established for AFFF.

3.8 Emergency Firefighting Operations

Fire response planning in advance can identify various options for firefighting and contingency planning for fire wastewater capture. Where possible and as setup allows, consider containing and recovering AFFF used for emergencies for disposal. Use mutual aid resources to assist with containing the fuel and fire water runoff should your department not have the resources available to fight the fire emergency and contain the runoff (Section 3.7). Although federal law currently does not prohibit the use of existing stocks of legacy AFFF, any discharge of foam containing PFAS to public waters can be considered a release of a "pollutant or contaminant" under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 42 U.S. Code § 9601, and therefore may be subject to remediation requirements.

Emergency scenarios vary case by case. Industrial plant fire brigades and responding emergency crews utilize portable foam generators or monitor nozzles to apply foam to pooled flammable liquids (potential fires) or existing fires. In cases where the fire involves a fixed

Consideration should be given to parts of facilities not protected by the fixed foam system that could be subject to AFFF application in the event of an emergency incident and opportunity for containment of foam. system, it is critical that an arrangement for containment/control of runoff is included in the design. The following are examples of how preplanning can better inform the use and containment of AFFF at an industrial facility:

- Industrial processes have many components, and only portions of the process are protected by the fixed foam systems. For example, a scrubber, or filter found within industrial smokestacks, may be part of the process that is not protected by the foam system and may be outside the discharge area where design considerations have been made for containment/control. Emergency response units may be required to apply foam/water to the location of the scrubber, outside the planning boundaries, in the event the fire that originated in the process was conveyed to the scrubber unit.
- At oil refineries, F3 may be used for small incidents and fluorinated foam reserved for the large tank fires. Fluorine-free and new generation C6 foams have been tested in large-scale tests (involving up to 40 m foam travel requirements) and could be considered suitable for application to fires involving some tank sizes and the associated dike area fires. But firefighting foam use is rapidly evolving, and as such, those responsible for tank application foam selection should refer to the latest test results from any recognized independent source (for example, LASTFIRE) to determine whether F3 could meet the performance requirements.
- On some remote industrial sites, where no immediate threat to life or property exists, and given the additional resources necessary to manage the wastewater produced, the best response may be to let the fire burn instead of applying AFFF.

3.8.1 Best Management Practices (BMPs)

BMPs are key to the use of AFFF in the most environmentally responsible manner with the goal of minimizing risk from their use. It is important to establish BMPs prior to use in an emergency so that BMP equipment, procedures, and training are already in place. Although firefighting personnel may be aware that the foams they are using contain chemicals, they may not be aware of the potential environmental effects of AFFF use. Training of firefighting personnel is important to ensure BMPs are discussed and employed consistently and effectively.

Example BMPs, adapted from the Fire Fighting Foam Coalition (FFFC 2016) are summarized in Table 3-3. Table 3-3 also includes some information from Angus Fire (2017). Users should follow BMPs to protect themselves, others, and the environment when using AFFF and other foams. Further BMP guidance can be found in other documents, such as the Best Practice Guidance developed by the Fire Fighting Foam Coalition (FFFC 2016), and the US National Fire Protection Association's NFPA 11 NFPA (2016)[692]. Users at DOD facilities have other BMPs to follow. Other industry associations such as American Petroleum Institute (API) have also issued BMPs (API 2020).

Other foams such as alcohol-resistant foams (AR-AFFF), filmforming fluoroprotein foams (FFFP), alcohol-resistant filmforming fluoroprotein foams (AR-FFFP), fluoroprotein foam (FP), and alcohol-resistant fluoroprotein foam (FPAR), as illustrated in Figure 3-2, also contain PFAS and similar precautions and considerations should be taken.

Section 3 provides supporting information for the BMPs presented in Table 3-3, as follows:

- Foam selection and storage are discussed in <u>Section 3.6</u> (AFFF Procurement and Inventory).
- Use is detailed in <u>Section 3.7</u> (Foam Systems and Operations).
- Planning and mitigation are covered in Sections <u>3.8</u> (Emergency Firefighting Operations) and <u>3.9</u> (Immediate Investigative and Cleanup Actions).
- Disposal is addressed in <u>Section 3.10</u> (AFFF Disposal).

<u>Table 3-3</u> addresses current operating procedures for selection, storage, use, planning and mitigation. For complete changeout and transition from AFFF to fluorine-free across an entire system, detailed consideration should be made regarding performance, compatibility, decontamination, treatment, and disposal.

Table 3-3. BMPs for AFFF (and Other Foams) Selection, Storage, Use, Planning and Mitigation, and Disposal (adapted from FFFC 2016)

Life Cycle	ВМР
Foam Selection	 Public safety first. Use AFFF and other fluorinated Class B foams only in the following situations: Class B liquid fires and/or spills with significant risks to public safety or of property loss, where specific extinguishing rates and burnback times are necessary Facilities where AFFF is required until F3 replacement that meets Mil-Spec has been approved
	2. Evaluate whether Class B foam is needed for a specific hazard, or if an alternative product, such as an F3 can provide the needed level of protection. The proper agent to use for your hazard "must be evaluated well in advance of an emergency situation" (FFFC 2016).
	1. Develop a foam inventory and stock tracking system documenting foam composition, date of purchase, lot number, brand, and manufacturer.
	2. "Obtain and follow manufacturers' recommendations for foam concentrate and equipment" (FFFC 2016). The amount of foam in the system should be at least enough for the group of hazards that simultaneously need to be protected against.
	3. Designate transfer areas and store Class B foam concentrate (all foam, not only AFFF) in a covered area with secondary containment.
	 Design storage tanks to minimize evaporation of concentrate. Label containers clearly to identify the type of concentrate and its intended concentration in solution. Keep foam within the temperature limitations provided by the manufacturer.
Storage	5. Properly maintain foam systems to prevent accidental discharges. Conduct regular inspections of tanks, storage containers, and any associated piping and machinery. Any leaks of foam concentrate should be addressed immediately to minimize environmental impacts. Maintain records of accidental releases, including date, volume, and foam type. Be cognizant of state and local reporting requirements for releases.
	6. Corrosion is reported by some to generally not be an issue with foam concentrates, but exceptions exist. Check safety data sheets to evaluate corrosivity of your product. Manufacturers recommend stainless steel, high-density polyethylene (HDPE), or polypropylene containers for AFFF storage. Avoid using aluminum, galvanized metal, and zinc in storage tanks, piping, and handling equipment for foam concentrates (Angus Fire 2017).
	7. Ensure compatibility of foams per manufacturer specifications before change-outs. Do not mix different types or brands of foam concentrates unless all the foams are compatible. As an example, all foams that meet Mil-Spec 24385 are considered compatible.

Life Cycle	ВМР					
	1. Consider the firefighter and public safety first.					
	2. Eliminate the use of AFFF and other fluorinated "Class B foams for training and testing of foam systems and equipment" whenever possible. Instead, use specially designed nonfluorinated, PFAS-free "training foams available from most foam manufacturers." (FFFC 2016).Be aware that such training foams result in longer extinguishments and less burnback protection.					
	3. If the authority having jurisdiction requires testing of equipment or training of firefighters using AFFF, training foams that do not contain fluorinated compounds are preferred and, in many cases, required. All foams, regardless of type, should be captured during training and testing.					
	4. Evaluate firefighting strategy to determine if Class B foam is needed or if a Class A foam or just water can succeed in fighting the fire.					
Use	5. Provide containment, treatment, and proper disposal of foam solution. Avoid direct release to the environment to the greatest extent possible.					
	6. Collect, treat, and properly dispose of runoff/wastewater from training events or live fire events to the greatest extent possible. Prevent discharge to storm drains and surface water to the greatest extent practicable.					
	7. Use appropriate personal protective equipment (PPE) when handling and using AFFF and identify how to decontaminate and or dispose of PPE materials and gear that come into contact with foam.					
	8. "Follow applicable industry standards for design, installation, maintenance, and testing of foam systems" (FFFC 2016).					
	9. Keep records of when and where foam is used to respond to incidents, including foam type, manufacturer, brand, and amount used.					
	10. Make note of any sensitive receptors (for example, streams, lakes, homes, wells) identified in the vicinity of foam use and report to environmental agencies as required.					
Planning and Mitigation	1. Develop and communicate documented processes for a facility or installation with the stakeholders and regulatory agencies before a release occurs. Stakeholders may include local fire department, elected officials, landowners, interested parties, and local environmental groups.					
	2. Prepare runoff collection plans, equipment, and training processes for all foam and those specific to fluorinated Class B foam use.					
	3. Create mitigation plans for uncontrolled releases of foam concentrate or foam solution to minimize environmental impacts (<u>FFFC 2016</u>).					
	4. Quickly and thoroughly clean up any contaminated environmental media after foam release following established mitigation plans.					
	5. Design new firefighting systems to accommodate F3s. Consider their different properties, modes of action, and effectiveness.					
	6. Prioritize education, training, and preplanning to ensure the safest and most efficient use of foam and equipment during an incident.					

Life Cycle	ВМР
Disposal	1. Proper disposal of foam is imperative. See <u>Section 3.10</u> . When available, consider disposal of AFFF inventory to state collection and disposal programs. Refer to Interim Guidance on Destroying and Disposing of Certain PFAS and PFAS-Containing Materials That Are Not Consumer Products (<u>USEPA 2020</u>).
	2. Terminate any donation programs for expired or unused AFFF concentrate (for example, donation to fire training school). Instead, as stated above, encourage collection/proper storage/disposal of expired or unused AFFF.
	3. Monitor developments in new treatment and disposal technologies.

3.8.2 Personal Protective Equipment

The use of personal protective equipment (PPE) is highly recommended when exposure to AFFF, as well as other firefighting foams, is anticipated. A critical aspect of PPE is ensuring the proper use of the equipment. The equipment should be used correctly, maintained, and decontaminated routinely (<u>Queensland Government 2021</u>).

During the application or immediate cleanup of AFFF foam, the use of a self-contained breathing apparatus or positive pressure-supplied air respirator is recommended to avoid respiratory exposure. Dermal exposure should also be avoided, as skin contact can result in irritation and dryness. When responding to fires, first responders should wear appropriate turnout gear, or proximity gear per their specific department requirements.

PPE cleanup after using AFFF (as well as other foams) is discussed in the next section.

3.8.2.1 Decontamination

Although PPE will prevent initial exposure to AFFF, contamination of the PPE itself can present health risks. Decontamination of the PPE and personal hygiene are crucial preventative measures in reducing or avoiding exposure to AFFF, as well as in avoiding cross-contamination. Since there is little PFAS-specific guidance on PPE decontamination, general PPE use and decontamination approaches should be used, as discussed below.

When handling AFFF concentrate or foam, it is imperative to avoid hand-to-mouth contact. After the use or cleanup of AFFF, responders should wash hands and use other decontamination procedures to remove any residual AFFF from the skin. Responders should remove contaminated clothing and launder before reuse.

PPE should be placed in a bag and container after exposure to AFFF as well as other foams. In 2014, NFPA released its latest edition of NFPA 1851: Selection, Care and Maintenance of Protective Ensembles for Structural Firefighting and Proximity Firefighting. This standard provides guidance for proper care of firefighting protective gear as well as health hazards associated with improper maintenance or contamination of protective equipment (NFPA 2014). The standard outlines different decontamination measures for turnout gear as well as proximity gear.

Turnout gear is the general PPE for firefighting. It should be machine washed in warm water in the normal cycle. Turnout gear should be spot treated with warm water, a soft brush, and mild detergent prior to being machine washed. When hand washing and spot treating PPE, wear protective gloves—either latex or PVC— to avoid skin contact with any residual AFFF. No fabric softener or bleach should be used. The turnout gear should never be washed in home washing machines, as this practice has the potential to contaminate personal clothing. Advanced cleaning is suggested at least on a yearly basis (Avsec 2015).

Although PPE decontamination prior to reuse is important, it is equally important to recognize when decontamination is not possible. In this case, the gear should be discarded in accordance with local, state, and federal regulations.

When decontaminating or laundering PPE, the disposition of the waste stream should be considered. The potential for environmental impacts due to laundering in washing machines is not well defined, but the potential does exist. Regulatory agencies should consider including decontamination procedures when working with firefighters, refinery safety personnel, and other potential first responders to develop BMPs.

3.8.3 Initial Mitigation Efforts for Firefighting Foam

Initial mitigation efforts following a release of firefighting foam include source control, containment tactics, and recovery tactics. Each is further described in this section.

Discharges of AFFF can occur during firefighting operations, system testing, equipment malfunctions, or incidental releases. In addition to foam, a large amount of water is often applied when attempting to suppress a fire. Due to the highly miscible nature of AFFF, the main objective of the initial mitigation efforts should be to reduce the footprint of contamination by limiting the spread of foam and fire water. This is often done through various containment and recovery tactics while making sure that the release has been abated and response personnel are safe.

Specific department or facility fire wastewater management considerations may be outlined in a fire response plan, which should include information such as resources available within the facility or department fire protection jurisdiction to contain and recover fire water, protect sensitive areas (for example, public and private water systems, storm drains, surface water, critical wildlife habitat), and address safety considerations when conducting water management tactics. By using the fire response plan, first responders familiar with the content can increase the potential for a successful response while reducing or eliminating any imminent or substantial threat to human health, safety, welfare, or the environment.

3.8.3.1 Source Control

In addition to AFFF application for emergency response, accidental discharge of AFFF can occur from faulty or malfunctioning equipment such as hard-lined fire suppression systems in aircraft hangars or equipment used to apply or contain foam (for example, fire engines or storage tanks). The first step in any response is to stop the accidental discharge or release at the source by disabling or shutting off the system, if possible, and then temporarily or permanently repairing the malfunctioning equipment. By controlling the source, the impact to the environment is minimized.

3.8.3.2 Containment Tactics

Due to AFFF's miscible nature, as well as the large amount of water often applied in combination with the foam, containment tactics that prevent or minimize surface water runoff are critical during and after emergency response activities. Proper containment tactics may also reduce the footprint of the affected area to make the containment and cleanup easier. Depending on resources available to response personnel and conditions of the release, tactics such as ditching, berming, diking, damming, and blocking storm drains, culverts, or other surface inlets can help to contain runoff. When using these tactics, it is important to ensure that any digging activity will not result in breaking through a confining layer that would allow contaminated water to move more quickly into the subsurface and specifically to groundwater. Several response organizations have tactics manuals available online for review, including the Spill Tactics for Alaska Responders (STAR) Manual (AK DEC 2014) and Alaska Clean Seas Tactics Manual (Alaska Clean Seas 2017). Most manuals are targeted at tactics proposed to be conducted after a release of oil or other petroleum products, but most of these tactics will also apply to AFFF releases. General guidance, similar to this section, on containment tactics to be conducted after a foam discharge has been provided by several other organizations, including the Firefighting Foam Coalition (FFFC 2016, 2018) and the Queensland Department of Environment and Science (Queensland Government 2021).

As stated previously in this section, preplanning can greatly assist with prioritizing sensitive areas or locations that need protection during the mitigation or response effort after an AFFF discharge, as well as the resources necessary to succeed with this strategy. The containment tactics used and resources required will differ among sites. Preparedness can be increased by identifying potentially sensitive areas. Also, designing infrastructure such as aircraft hangars with foam-applying fire suppression systems so that the discharged foam is automatically directed to storage tanks or containment structures can minimize the need for any cleanup. The DOD has provided guidance via Engineer Technical Letters (USACE 2018) that address containment/disposal system design for AFFF discharges from open systems (such as nozzle and deluge sprinkler systems) and closed systems (in which individual sprinkler heads are activated only by heat of a fire).

Because no single set of containment tactics is going to be applicable to all facilities or departments where a foam discharge occurs, it is important for each user to conduct preplanning to identify solutions that fit its facilities, objectives, and specific response scenarios.

3.8.3.3 Initial Recovery Tactics

Recovery tactics can differ depending on the amount of AFFF released, as well as whether the AFFF is discharged during firefighting operations or accidentally (for example, from malfunctioning equipment). Collection of large volumes of AFFF concentrate or the 1%, 3%, or 6% AFFF mixture combined with water could require the use of mechanical devices such as pumps or vacuum trucks, while absorbent material might suffice to clean up after a smaller release. The AFFF and water

mixture has a low flammability and a high flash point, so there is no need to use intrinsically safe pumps or mechanical devices unless other, more flammable compounds are present in the fire water being recovered.

It may be beneficial to remove affected AFFF saturated materials such as soil and vegetation to reduce or eliminate surface or subsurface migration of potential contaminants. Removal of contaminated media may reduce or eliminate the need for additional investigation and cleanup in the future; however, focus during the initial mitigation effort should be on the more easily recoverable media such as affected waters or slurries. Initiating recovery tactics as soon as possible after a release of AFFF will greatly reduce the footprint of PFAS-contaminated materials and lower the cost of the total mitigation effort.

3.9 Immediate Investigative and Cleanup Actions

A series of immediate investigative actions can be taken after the use of AFFF at the site of a fire to determine the level, nature, and extent of the contamination. First responders should collect, to the best of their ability, information regarding the volume of AFFF discharged, its concentration, active ingredients, and discharge location information.

Information about actions to be taken after the immediate actions is included in <u>Section 10</u>, Site Characterization; <u>Section 11</u>, Sampling and Analysis; and <u>Section 12</u>, Treatment Technologies.

Traditional field-screening methods used for other types of contaminants (for example, PID field screening for petroleum) are not effective for PFAS due to their unique chemistry, generally low volatility, and lack of development of colorimetric or reactive chemistry technologies. Some efforts have been made to develop mobile analytical laboratories, which are covered in <u>Section 10.3.1.3</u> of this document.

3.9.1 Visual Site Delineation

Visual site delineation refers to outlining the affected area of contamination based on visual clues, such a visible foam and wet ground, as a guide. The extent of foam should be marked using survey tape, lathe, and pin flags placed to identify locations of AFFF contamination. This technique of determining the initial expanse of the contamination is simple to perform directly after a discharge and can be useful for reference in future testing on the site. In addition, photographs of the site taken during or immediately after the incident can be used to determine the extent of AFFF impacts.

3.9.2 The Shake Test

The shake test is an informal qualitative field-screening method that provides a visual analysis of the site contamination. The shake test can apply to both water and soil-water solutions. In the shake test, a small sample (10-25 mL) is collected on site by the field personnel and shaken. After it is shaken, if there is foaming in the sample, it should be noted and then submitted for analysis (Transport Canada 2017). Photographs of the samples may be helpful. If AFFF foam was used to fight the fire, then the presence of foam strongly suggests the sample may be contaminated with PFAS. This test is a good indicator for high concentration contamination. It may not be able to detect lower concentrations of contaminants, so lab testing may still be required. This may be true of soil and water samples taken around the foam application location where the shake test does not show foaming but the sample media may still have PFAS above background in it.

3.9.3 Initial Investigative Sampling

Investigative sampling is used to determine the nature and extent of contamination, including concentrations at and surrounding release areas. Initial investigative sampling can help to determine whether additional characterization is necessary, in addition to informing the need for and extent of interim or permanent remedial actions. Combining the information gained from investigative and confirmation sampling with information from a CSM will inform project managers as to whether further site characterization and remediation or mitigation efforts are needed. See <u>Section 5</u>, Environmental Fate and Transport Processes, <u>Section 10</u> and <u>Section 12</u> for additional information on the actions that may be needed following initial response.

3.9.4 Interim Removal

Following the information gathering described above, or possibly prior to initial investigative sampling, additional source control can be achieved through removal of soils that are expected to be highly contaminated. During an initial removal

action intended to target PFAS hot spots, soil excavation can be guided by shake tests (Section 3.9.2). An interim removal is not necessarily designed or expected to remove all contamination but can help to reduce the migration of PFAS into other media, including groundwater and surface water. After this initial removal effort, it may be appropriate to hire an environmental professional to perform further mitigation efforts. To determine how to dispose of the soil, see Section 12.

3.9.5 Confirmation Samples

Once removal actions take place, confirmation samples are taken to confirm that an excavation or interim removal successfully removed the soil contamination that exceeds applicable regulatory or risk-based levels. If confirmation sampling determines that soil contamination still exists at levels of concern, additional removal actions or other types of remediation or mitigation may be required. The type, number, and distribution of confirmation samples is determined on a site-specific basis according to local regulatory guidance. If confirmation sampling is delayed due to weather events—for example, a rainfall event—the results from such sampling should be interpreted carefully.

3.10 AFFF Disposal

BMPs recommend that volumes of AFFF foam concentrate be carefully monitored and recorded at each storage location, from fire trucks to suppression systems to storage containers (see <u>Table 3-3</u>). Weights of other AFFF system components requiring disposal should be similarly observed. Disposal certificates for materials bound for removal should indicate volumes of AFFF concentrate or solution or weights of system components or debris, as applicable. Total volumes or weights generated for disposal should match that indicated on disposal certificates.

Disposal of AFFF concentrate represents a significant challenge for any owner of firefighting foam concentrates. The disposal of AFFF concentrates through standard disposal options may carry risks. Practitioners should be aware of possible disposal options, best management practices, and disposal hierarchy, as explained by USEPA (<u>USEPA 2020</u>). Manufacturers' product literature and local regulatory agencies should be consulted for information regarding the specific foam concentrate to be disposed. Some disposal options that are currently available for AFFF concentrates and AFFF-impacted natural media are presented in USEPA's *Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances* (<u>USEPA 2020</u>). Additional information can be found in Stoiber, Evans, and Naidenko (2020) and Aleksandrov et al. (2019).

As of February 2021, the USEPA interim PFAS destruction and disposal guidance (USEPA 2020) is closed for public comment. EPA plans to update the interim guidance by December 2023. Currently available AFFF concentrate disposal options are briefly presented below and in <u>Table 3-4</u>. Table 3-4 also presents advantages and disadvantages associated with each disposal method and new disposal technologies that were under development when this table was prepared. The disposal options that are currently available for materials impacted with dilute AFFF wastes are presented in <u>Section 12</u>, and include stabilization and landfilling, incineration, and deep well injection.

As stated in the USEPA interim PFAS destruction and disposal guidance (<u>USEPA 2020</u>), one option for addressing disposal concerns related to environmental releases of foam, byproducts, or other possible releases is to store AFFF in warehouse storage to provide time for completion of studies for destruction, disposal, or stabilization of the AFFF. Stakeholder concerns regarding AFFF waste disposal practices are presented in <u>Section 13.1.11</u>.

Each of the currently available disposal options presented below and in <u>Table 3-4</u> has different advantages and disadvantages that the practitioner should consider when deciding how to dispose of AFFF concentrates, including availability, cost, effectiveness, and potential long-term risks associated with nondestructive disposal options.

3.10.1 Stabilization and Landfill Disposal

Waste stabilization and landfilling is a nondestructive disposal methodology wherein waste, including AFFF concentrates, are mixed with stabilizing materials (for example, Portland cement) and disposed at a landfill that is licensed to accept and manage these wastes. This disposal method is nondestructive in that the waste is not destroyed but immobilized and encapsulated to prevent exposure and reduce potential mobility. Ultimately the stabilized and landfilled AFFF concentrate is managed with other wastes disposed of at the same landfill through landfill best management practices (for example, liners, leachate collection, cap management, groundwater monitoring, etc.). Stabilization and landfill disposal is an accepted waste management strategy in some states, though the long-term stability of stabilized AFFF concentrate is not well understood.

Practitioners with AFFF concentrates requiring disposal should collaborate with their local or state agency waste management personnel, as applicable, to determine current availability and acceptability of stabilization and landfill disposal as a waste management practice. AFFF concentrate bound for disposal should be properly documented (for example, a proper manifest or bill of lading) as a best practice and in compliance with state and federal transportation regulations (as discussed in <u>Section 3.6.2</u>). After the concentrate product has been disposed of, a certificate of disposal may be generated by the disposal facility, transmitted to the product owner, and retained by the disposal facility. This certificate of disposal may be transmitted to the state regulatory agency for review and maintained on file by the product owner.

3.10.2 Incineration

Incineration is a destructive disposal technology wherein AFFF concentrate is destroyed, or mineralized, through the application of heat. Heat is applied to the AFFF concentrate at incineration facilities that have the capability to manage high temperatures and residence times required to destroy AFFF concentrate, as well as vaporized combustion products (flue gases) that are captured and/or further incinerated. Most AFFF concentrate has historically been disposed of using incineration in the United States (FFFC 2016). However, the effectiveness of incineration, and the temperature and time conditions required to achieve complete PFAS destruction, are not well understood (USEPA 2020). Legal, technical, and political challenges to incinerating AFFF exist based on gaps in research on the effectiveness of incineration (Earthjustice 2020). For example, the New York State DEC prepared a sampling report in 2021 near one incineration facility in response to concerns about emissions from the facility (NY DEC 2021). USEPA researchers are currently studying PFAS incineration, sampling and analytical methods development, and industrial field sampling. Thermal stability of PFAS, the ability to fully capture and identify PFAS and their thermal decomposition byproducts, and the efficacy of emission control technologies are areas of targeted research (USEPA 2020). The NDAA for fiscal year 2022

(https://www.congress.gov/bill/117th-congress/senate-bill/1605) establishes a temporary moratorium on incineration of AFFF generated by DOD. The temporary moratorium began no later than 120 days after enactment of the NDAA FY22 (4/26/2022) and will be in place until the Secretary of Defense issues guidance for implementing the USEPA's destruction and disposal guidance (USEPA 2020) or the USEPA Administrator publishes a final rule in the Federal Register regarding destruction and disposal. The DOD published a memo about the temporary prohibition on April 26, 2022 (USDOD 2022). The DOD published a memo with interim guidance about destruction or disposal of materials containing PFAS on July 11, 2023 (USDOD 2023).

This technology is currently the only known AFFF destruction technology in widespread use, though the efficacy of incineration as an effective disposal option for AFFF concentrate is an area undergoing further study (<u>USEPA 2020</u>). At the time of publication there are a number of studies ongoing to evaluate destruction temperatures and treatment time required to achieve complete AFFF destruction, the potential to generate products of incomplete combustion, flue-gas analyses to assess mobilization of AFFF concentrates, and other risk factors. Owners of AFFF concentrates requiring disposal should consider contacting their local or state agency waste management personnel, as applicable, to determine current acceptability of incineration as a disposal practice prior to disposal.

3.10.3 Deep Well Injection

Another disposal approach, available in some states, is to dispose of AFFF concentrate through deep-well injection. In some cases, disposal via landfilling of a stabilized concentrate or deep well injection at a licensed hazardous waste management facility has been used. This disposal option eliminates discharges to surface water and shallow groundwater, similar to stabilization and landfilling, but does not destroy or degrade disposed wastes. Deep well injection is an available option that is being used given the currently limited number of disposal options for AFFF concentrate. Class I deep injection wells, as defined by USEPA, accept both hazardous and nonhazardous liquid wastes (USEPA 2019), including AFFF waste materials such as dilute AFFF (fire water) and AFFF concentrates. The USEPA has published guidance on the requirements for the use of deep injection wells, including siting, construction, operation, monitoring, testing, record keeping, reporting, and closure (USEPA 2019). The USEPA has also studied the risks associated with underground injection wells (USEPA 2001), and these risks are documented for consideration by generators prior to disposal of AFFF concentrates through deep-well injection.

3.10.4 Potential Future Disposal Technologies

The currently available disposal options for AFFF waste are limited and carry inherent unknowns in terms of long-term reliability. This is of particular importance when considering nondestructive disposal means such as stabilization and landfill disposal and deep well injection. These unknowns translate into short- and long-term risks for the practitioner. Additional disposal options may be available in some areas (for example, deep well injection) for AFFF concentrate wastes and AFFF- impacted materials. Alternate treatment and disposal technologies are presented in <u>Section 12</u>. New treatment and disposal

technologies are an active area of research and development by a number of groups; some are presented in <u>Table 3-4</u>. All technologies will require extensive evaluation to ensure they are fit-for-purpose.

Table 3-4 PFAS Waste Materials Disposal Options

Current as of October 2022

Current Disposal Practice	Advantages	Disadvantages		
Stabilization and Landfill Disposal (Section 3.10.1)	 AFFF concentrate mass is encapsulated and immobilized in a stable form Disposal is at a licensed landfill with monitoring programs and leachate collection systems designed to ensure disposed mass remains controlled Long-term management of the disposed waste is part of the overall landfill management and monitoring program 	 Disposed AFFF concentrate mass remains in place with no known and documented destruction mechanisms Risks associated with comingled waste disposed of at the waste management facility Long-term testing of stabilized PFAS waste materials under landfill conditions is limited. Some studies are available (<u>CONCAWE 2016</u>; Oliaei et al. 2013; Weber et al. 2011) PFAS mass from disposed wastes can form mobile leachates, which require long-term collection, management, and disposal (<u>Stoiber</u>, <u>Evans</u>, and Naidenko 2020) Some PFAS may be emitted by the landfill gas collection and management system 		
Deep Well Injection (<u>USEPA, 2019;</u> <u>USEPA, 2020; Marine 2020)</u> (<u>Section 3.10.3</u>)	 AFFF concentrate mass is injected deep underground in previously defined tectonically stable strata Waste is injected well below drinking water aquifers, reducing potential for future impacts to drinking water resources Waste immobility and lack of potential for unacceptable migration must be documented prior to waste injection Long-term management of the injected waste is the responsibility of the operator while the disposal facility is in operation 	 Disposed AFFF concentrate mass remains in place with no documented destruction mechanism known Waste materials are injected with no modifications or additives to reduce migration potential or enhance degradation Deep well injection facilities are generally operated with limited mandated monitoring to document lack of long-term waste migration The long-term stability of injected wastes is undocumented 		
Incineration—General (<u>Section 3.10.2</u>)	 Incineration (at properly licensed and operated disposal facilities) is the only disposal technology currently available that has the potential to result in the destruction of PFAS PFAS destruction through incineration has been documented in laboratory studies (e.g., <u>Aleksandrov et al. 2019</u>; <u>Khan et al. 2020</u>) but known studies analyzed only for a subset of PFAS PFAS destruction reduces/eliminates future risk 4. Some incineration facilities maintain successful track records of operating within permit requirements based on system performance monitoring data collection 	 The efficacy and operational requirements of incineration are currently under question and require additional study (USEPA 2020) Existing laboratory experiments on the incineration of PFAS do not address the full spectrum of potential PFAS byproducts that could form during incineration (Stoiber, Evans, and Naidenko 2020; USEPA 2020) Current regional and local moratoria exist in some locations against incinerating PFAS waste. Practitioners should confirm disposal vendor licensing and operational status prior to shipping AFFF concentrate for disposal 		
Incineration—Municipal	1. Municipal incinerators are readily available and offer a comparatively low-cost disposal option if operated at sufficient temperatures and residence times and if equipped with appropriate emissions controls	 Municipal incinerators may not be permitted to accept AFFF concentrate for disposal Temperatures, residence times and emissions controls may not be adequate to fully degrade PFAS Potential for partial decomposition of PFAS to shorter carbon chain-length PFAS (USEPA 2020) Existing laboratory experiments on the incineration of PFAS do not address the full spectrum of potential PFAS byproducts that could form during incineration (Stoiber, Evans, and Naidenko 2020; USEPA 2020) 		

Current Disposal Practice	Advantages	Disadvantages		
Incineration—Hazardous Waste	 Some specialized incinerators exceed minimum temperature required Some are designed to handle flue gases and scrubber wastes Generators may be able to obtain a disposal certification from the incineration facility 	 Temperatures, residence times, and emissions controls may not be adequate to fully degrade PFAS at some standard commercial facilities Potential for partial decomposition of PFAS to shorter carbon chain-length PFAS (<u>USEPA 2020</u>) Difficulty handling high-water content wastes 		
Incineration—Cement Kiln	 Temperatures and residence times in excess of minimum required (1100°C and 2 seconds) Effective permanent capture of fluorine No extra energy required above normal kiln processing 	1. Potential for partial decomposition of PFAS to shorter carbon chain-length PFAS (<u>USEPA 2020</u>)		
Experimental Disposal Technologies (Sec	tion 3.10.4)			
Electrochemical Oxidation (<u>Le et al.</u> 2019; Ensch et al. 2020)	PFAS is degraded in a closed-cell reactor using metallic electrodes and electrical current. Several different types of electrodes (titanium oxide, boron-doped diamond, etc.) have degraded some PFAS to varying degrees of success and several studies were underway in 2020. In previous laboratory-scale studies, PFAS destruction was achieved, though at relatively low throughput rates. This disposal technology is applicable to liquid waste streams only.			
Enhanced Contact Plasma Reactor (<u>Singh et al. 2019</u>)	PFAS are degraded in a closed system using water, electricity, and argon gas to degrade PFAS through a series of sequential destruction steps. At laboratory scale the destruction of PFAS was observed within their ability to measure, limited by analytical method detection limits. Air Force Civil Engineering Center (AFCEC) and Clarkson University were field testing this technology at Wright-Patterson Air Force Base, Ohio in 2020.			
Alkaline Hydrothermal Treatment (HaLT) (<u>Wu et al. 2019</u>)	Perfluorooctane sulfonate (PFOS) and potentially other PFAS are degraded through the application of hydrothermal conditions (condensed water at high temperature [200-350 °C] and high pressure [2-16.5 MPa]) to solutions amended with NaOH. Initial studies document PFOS destruction within 90 minutes. Expanded laboratory studies continue to investigate efficacy over a broader range of PFAS compounds.			
Supercritical Water Oxidation (<u>SERDP-</u> ESTCP 2020)	Supercritical water oxidation at high temperature (c 22 MPa) has been demonstrated to degrade PFAS. E called PFAS Annihilator to apply this technology for supported study at Duke University began in May 20 higher throughput rates (approximately 907 kg of w	greater than 373 °C) and high pressure (greater than Battelle Memorial Institute has patented a process the destruction of PFAS. In addition, an ESTCP- 020 to demonstrate the efficacy of this technology at vaste material per day).		

3.10.5 Fire Water and Flush Water Containing AFFF

Fire water produced during training or emergency response, as well as flush water produced during the rinsing of firefighting systems and equipment, may be managed and disposed of as a generated waste because these waters contain dilute concentrations of PFAS. Practitioners may consult with local regulatory agency personnel ideally prior to the generation of fire- and flush water so that there is a good understanding of local laws and regulations governing disposal. Standard practices for foam containment and cleanup should be developed prior to use such that response teams have the needed equipment and training before an event occurs; Table 3-1 provides additional information for BMPs. Some fire water disposal options are focused on reducing the volume of wastewater through concentration and disposal of the generated concentrate via incineration, landfilling, stabilization, or other mechanisms. See Section 3.10.1 for comments related to these disposal methods. Widely used treatment methods, as presented in Section 12 are as follows:

- granular activated carbon treatment
- discharge to and treatment at a wastewater treatment plant
- pumping AFFF-impacted fire water into watertight, secure containment basins and allowing the water phase to evaporate, leaving behind a solid or semi-solid material containing the AFFF concentrate. The remaining material is then disposed of at a certified waste management facility (<u>USDOD 1997</u>). This method is an option only in some localities and where climatic conditions are favorable.

3.11 Firefighting Foam System Replacement

The AFFF application design is specific for each foam and use case and system design can vary significantly by location, manufacturer, foam product, and system objective. Changing between foam types or application objectives could require a

complete system review and, potentially, redesign and modification of system components to meet the new objectives or material and performance requirements. When objectives or requirements are changed, each subject system should be evaluated and modified individually to ensure that operational objectives are met.

Procurement at U.S. airports is primarily driven by regulatory performance requirements, notably the DOD Mil-Spec, MIL-PRF-24385, as well as FAA requirements (<u>ACRP 2017</u>). DOD recommends complete replacement of the required AFFF concentrate supply and rinsing of the storage and discharge system prior to refilling with a different concentrate product (<u>USDOD 2017</u>). This not only prevents any unforeseen incompatibility issues, but also greatly reduces possible crosscontamination and the uncertainty of AFFF formulations (PFAS profile and content).

Applicable replacement products standards include NFPA Standards 11 (<u>NFPA 2016</u>) and 16 (<u>NFPA 2019</u>) for foam water sprinkler and foam water spray systems and NFPA Standards 1901 (<u>NFPA 2016</u>) and 412 (<u>NFPA 2020</u>) for equipment.

3.11.1 Replacement Products

Replacing foams and foam systems generally follows four steps:

- 1. Assess and understand the specific hazards and application objectives.
- 2. Ensure that foam product to be adopted is listed and approved for use on the specific assets that are being protected and the hazards that that are being mitigated.
- 3. Ensure that the foam product storage system and the foam/water application system meet product storage (for example, materials compatibility and storage temperature), proportioning, and application requirements.
- 4. Ensure that the selected foam product(s) meet applicable requirements (Requirements are based on where and how the foam is being used and rely on sector-specific standards such as Mil-Spec, Underwriters Laboratories (UL), or Factory Mutual compliance). These organizations audit manufacturers to ensure compliance with their standards.

Where two or more foam products meet applicable performance requirements, the foam with the best environmental performance may be considered for use. Alternatives currently available as replacement products for legacy AFFF include products discussed in the following sections.

3.11.1.1 Fluorine-Free Foams (F3)

Most foam manufacturers now produce Class B F3s. Performance of these foams should be evaluated carefully as future purchasing decisions are made. As of spring 2023, there are no military-specified F3s approved for use on Class B fires at federal- and FAA-regulated facilities that require Mil-Spec-compliant AFFF. Approved and certified military-specific foams are expected to be available and listed on the DOD Qualified Products Database by the Fall of 2023. But a mandate within the FAA Reauthorization Act of 2018 (enacted October 5, 2018) directs the FAA to stop requiring the use of fluorinated foam no later than 3 years from the date of enactment (October 4, 2021), so F3 use is anticipated at FAA-regulated facilities in the near future (FAA 2018).

There continues to be robust discussion regarding the replacement of AFFF products with F3 formulations. For example, the organization IPEN has published a document titled *Fluorine-Free Firefighting Foams (3F): Viable Alternatives to Fluorinated Aqueous Film-Forming Foams (AFFF)*, which states that F3 products are as effective in combating Class B fires as AFFF and concludes that because of the lower environmental impact of F3 products, the use of AFFF should be discontinued (IPEN 2018). The Fire Fighting Foam Coalition (FFFC) produced a three-page document responding to the IPEN paper, which discusses technical details regarding differences in foam performance for certain types of Class B fires and performance standards (as opposed to composition standards) that continue to necessitate the use of AFFF or other fluorochemical products for certain hazards. Additional challenges to the replacement of AFFF with F3 foams are also described in the FFFC document (FFFC 2018).

3.11.1.2 Modern Fluorotelomer Foams

If it is determined that the performance of a fluorinated Class B foam is required for a specific hazard (for example, the federal regulation requiring AFFF use for military applications, at FAA-regulated airports, and/or other high hazard Class B fires and potential incidents), users should purchase modern fluorotelomer foams. Most foam manufacturers have transitioned to the production of only short-chain (C6) fluorosurfactants, so it is likely that any AFFF bought today meets that

requirement. But foams made with only short-chain (C6) PFAS may still contain smaller quantities (parts per billion) of PFOA and PFOA precursors as byproducts of the manufacturing process. This should be confirmed with the supplier.

Although there are currently mandated specifications requiring the use of fluorinated foams at airports and military installations, users should be aware that some compounds in modern fluorotelomer foams are regulated by several states and are known to have probable effects on human health (<u>Section 7.1</u>). Use of these foams may be restricted to emergency situations only and not for use in firefighting training activities. Local and state regulations may require reporting of their release, including emergency use. <u>Section 3.12</u> discusses the current state of regulations on AFFF use.

3.11.1.3 Replacements, Certifications, and Alternatives Assessments

Several efforts are underway to evaluate F3 AFFF replacements for environmental and human health effects, as well as performance effectiveness. SERDP and ESTCP programs continue to "fund several research and development projects to evaluate performance, lifecycle impacts, and health and safety implications of commercially available, non-fluorinated alternatives." For example, Jones et al. (2022) examined the direct lethal effects of seven F3 and a PFAS-containing AFFF on 14 aquatic species using a series of lethal concentration (LC50) tests. Across all aquatic species tested, they discovered that exposure to at least one F3 was more or as toxic as exposure to the PFAS-containing AFFF. This illustrates that more research is needed to understand new F3 formulations to ensure they are not regrettable substitutions. Additional information regarding PFAS toxicity, data gaps, and research needs is presented in <u>Section 7.1</u>. The DOD SERDP program has invested heavily in these efforts; representative studies supporting these efforts are listed in <u>Section 3.13</u>.

In related efforts, some organizations have developed certification processes to help consumers understand which products are considered "PFAS-free" (see Section 2.5.3). For example, Clean Production Action developed the first-ever ecolabel for firefighting foam products via their GreenScreen certification process, which identifies products as eco-labeled but does not include a release of liability. They worked with a technical review team of scientists, firefighting foam researchers, and governments to ensure the PFAS-free standard is protective, achievable, and supports purchasers to choose foam products that are safer and better for the environment. Clean Production Action defines PFAS-free as zero PFAS intentionally added to the product and PFAS contamination in the product less than 0.0001 percent by weight of the product (1 part per million) total organic fluorine as measured by combustion ion chromatography. There are currently more than two dozen certified firefighting foam products available. Go to https://www.greenscreenchemicals.org/certified/fff-standard for more information.

Alternatives assessments have been another mechanism to further evaluate F3 alternatives in terms of regrettable substitution. The first-ever alternatives assessment for AFFF (Wood Environment & Infrastructure, 2020) was completed for the European Commission and European Chemicals Agency. This assessment included an evaluation of substances in formulation, a market analysis, emissions and hazards evaluation, remediation costs and technology, an analysis of alternatives and socioeconomic impacts, and regulatory management options. As a result, a Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) restriction proposal for AFFF was submitted in 2022. Tickner (2022), funded by SERDP, completed an alternatives assessment for AFFF. The assessment focused on understanding alternatives assessments completed, supporting assessment and decisions about substitutes regarding "safer" and "sufficient performance," and supporting needs related to adoption. Tickner (2022) developed six guiding considerations, including:

- 1. "Determine the function of the chemical of concern for the specific application. Understand this function within the production chain.
- 2. Define the application-specific use scenario(s). Identify alternatives that are fit for that particular purpose.
- 3. Establish and/or use performance standards independent of the standards dependent on using chemicals/materials of concern. Adjust based on available alternatives or alternatives on the horizon.
- 4. Use a range of performance standard benchmarks, e.g., 'inadequate' to 'sufficient' to 'best in class.'
- 5. Consider technical performance separately from technical feasibility.
- Consult stakeholders for determining acceptable tradeoffs between performance results and other elements such as environmental health and safety."

3.11.2 System Decontamination and Sampling During Foam Replacement

The replacement of Mil-Spec legacy foam with the modern foams requires review of system components, particularly the proportioning system, to ensure that appropriate system performance will be maintained. During foam replacement, a thorough clean-out of storage tanks and associated pipework is highly recommended prior to filling with replacement foam concentrate. There is potential for PFOS and PFOA contamination from legacy AFFF, as described in <u>Section 3.1</u>, and from PFOA and other PFAS from fluorotelomer foams. For nonmilitary applications, legacy AFFF and replacement modern foams may not be compatible. In these cases, the foam manufacturers should be consulted when a foam change is required and current best practices for foam replacement, system decontamination, and verification sampling should be considered. The degree of cleanliness required and the cost balance between cleaning and replacing system components should be considered during the planning phase of a foam concentrate change-out event.

Currently, there are no regulatory guidelines or requirements pertaining to the clean-out of AFFF firefighting systems when foam concentrates containing legacy foams are replaced with alternative foams; however, local and state governments and other organizations continue to develop policy and guidance on replacing foams. DOD (and other foam users) have performed a triple water rinsing step after the legacy AFFF is removed. The rinse water is containerized and managed as a waste material as presented in Section 3.6.2. After the rinse water is removed, the modern fluorotelomer AFFF concentrate is added to the system and the system is function tested and placed back into service. Specific department or facility fire wastewater management considerations may be outlined in the facility or installation spill response plan, which should include information and resources available within the facility or on the installation to contain and recover AFFF-containing fire water to protect the environment. Proprietary cleaning solutions and coagulants have also been used for AFFF clean-out (CTDEEP 2022). These methods have been compared to the triple water rinse. No single cleaning method has yet been proven to be 100% effective in eliminating residual PFAS concentrations (CTDEEP 2022). Use of proprietary methods is more costly than triple water rinse, but these methods are more effective at reducing PFAS concentrations (>99% compared to approximately 95% removal) (CTDEEP 2022). Organizations should check with local and state regulatory agencies regarding local policies and guidance for foam change-out and system clean-out requirements or recommendations. Sampling of rinsate to ensure that residual contamination has been removed may be considered before adding replacement foams, and sampling of replacement foams that have gone through the system may provide the best assurance that PFAS will not continue to be released when the systems are used.

3.11.3 AFFF Transition Planning

Protocols around transition planning and execution of foam change-out are becoming ever more important to understand. Several factors need to be carefully considered when F3 alternatives, including but not limited to:

- What will the foam be used for and max volume of fuel source handled?
 - Fuels fires and max volume (large atmospheric storage tanks or other)
 - Chemical fires and max volume (large atmospheric storage tanks or other)
 - Other
- What are the current performance specification requirements for the foam?
 - Mil-Spec
 - Other
- What application and application technique are anticipated?
 - Fire suppression system
 - Fire response vehicles
 - Industrial fire extinguisher
 - Other
- What water type is used for mixing?
 - Fresh water (compatible with most foam products)
 - Salt water (incompatible with some foam products)
- What other types of foam characteristics should be considered? (<u>NFPA 2020</u>)
 - Viscosity of the foam concentrate (Newtonian and thixotropic)
 - Suitability for use with existing proportioning hardware
 - Homogeneous mixing of concentrate with water
 - Compatibility with materials in the system (for example, plastic, rubber seals, metals)
 - Stability of foam concentrate or premix solution (separation, stratification, sedimentation)

- Suitability for use on the flammable liquids in question
- Suitability of application method (aspirated, non-aspirated, forceful, gentle)
- Extremes of ambient temperature that may be encountered in an incident
- Suitability of the expansion ratios produced by existing equipment for effective firefighting performance
- Suitability of the application rates produced by existing equipment for effective firefighting performance
- Suitability in specific climate (extreme ambient temperatures, both high and low)

<u>Table 3-5</u> (provided as a separate Excel file) is presented to provide example case studies for transition planning and execution. Case studies from the aviation industry and the oil and gas industry are provided. Case studies also vary by geography to illustrate potential variability by country. They are provided only as examples of how sites are implementing transition planning, but are not intended to represent guidance to be applied at other sites. The following items are included in the table:

- foam procurement, including selection criteria used to evaluate and select alternatives
- system decontamination and sampling, specifically how replacement versus clean-out was evaluated, how and whether sampling was conducted, and the definition of "clean"
- treatment and disposal, including type of cleaning reagent, waste streams generated, and how they were managed.

Because there are currently no federal or state standards on how much residual fluorine contamination in replacement foam is acceptable, each foam user is responsible for determining whether sampling and analysis of the replacement foam is necessary, and if sampled and analyzed, if the cross-contamination of replacement foam is considered acceptable for their use.

3.11.3.1 AFFF Replacement and System Clean-out

Both system replacement and system clean-out are options when transitioning to F3. There is currently no known standard practice for AFFF system clean-out procedure that is widely recommended by state or federal regulatory agencies. However, system clean-out using triple water rinse has been used by the U.S. Department of Defense, and hot water rinse (<100° F) is approved for use in some states (for example, Connecticut and New York) and is recommended in an article published by the International Fire Fighter website (Preiss 2022). U.S. vendors are developing clean-out methodologies that may be more effective than currently used methodologies—for example, rinsing with low- or high- temperature solvents or acids. Most methodologies are currently being performed as demonstration projects, are not widely used, and have not been proven on a wide scale as of the publication of this document.

When selecting a methodology for cleaning out a system, practitioners should aim to achieve the maximum level of cleanout to minimize potential for future PFAS release when the system is deployed, considering both objectives and costs. It's important to understand that more aggressive clean-out procedures will generally be more expensive and generate more waste that will require proper management and disposal. However, inadequate system clean-out may result in the presence of residual AFFF, which may contaminate new F3 with PFAS when the system is refilled.

DOD recommends a triple rinse using water (heated or unheated) that is employed after the old AFFF foam has been drained from the system and containerized. After the system is drained, the system is iteratively rinsed and drained with water to flush out accessible AFFF residuals, and each successive rinse water volume is containerized for management and disposal (<u>USDOD 2018</u>). During each successive rinse, the system is completely filled with rinse water and allowed to sit for some period of time. The State of Connecticut recommends a sitting time of 30 minutes with hot water or 1–2 hours with cold water for municipal systems such as trailers and trucks (<u>State of Connecticut 2022</u>). Note that there are no established standard guidelines for cleaning procedures due to the immense variety of foam delivery systems for which the procedures can vary greatly even among the same manufacturer. All rinsing fluids and other waste generated during the system clean-out process should be containerized, labeled, and managed for proper future disposal. After the system has been cleaned out and rinse waters have been completely drained, new foam concentrate can be added. The practitioner should be aware that changing foam products may necessitate changes to system components, such as proportioners and discharge nozzles.

Foam change-out practitioners should also be aware of and take measures to mediate potential hydrogen sulfide generation in rinse waters that are improperly stored (<u>Sheinson and Williams 2007</u>). Hydrogen sulfide can be generated when foam

contains sulfate (such as PFOS) or the water source itself contains sulfate. As a result, hydrogen sulfide may be in foam change-out rinse waters that are stored in sealed containers and that are allowed to transition into anoxic conditions. The hydrogen sulfide is generated through anaerobic microbial transformation of sulfate in the rinse water to sulfide followed by complexation of sulfide and hydrogen. Hydrogen sulfide generation can result in risk to site workers, particularly if starting sulfate concentrations in the rinse water are high. Regular inspection of stored rinse waters is necessary to detect any potential hydrogen sulfide generation, allowing for early implementation of mitigation steps.

3.12 Federal, State, and International Regulations and Guidance

3.12.1 Overview

This section summarizes representative information on the regulation of PFAS-containing firefighting foams (AFFF). Although federal law currently does not prohibit the use of existing stocks of legacy AFFF, any discharge of foam containing PFAS to public waters can be considered a release of a "pollutant or contaminant" under CERCLA, 42 U.S. Code § 9601, and therefore subject to remediation requirements. In February 2019, the USEPA announced in its PFAS Action Plan that the agency is beginning to evaluate designating PFOA and PFOS as "hazardous substances" through one of the available statutory mechanisms, including potentially CERCLA Section 102 (USEPA 2019). In October 2021, the EPA published the *PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024* (USEPA 2021). The USEPA's stated goals for addressing PFAS are focusing on research, restriction, and remediation. The strategic roadmap includes actions across the different divisions of USEPA. More information about USEPA's actions in 2021 to address PFAS are available on their website (USEPA 2021).

As of February 2021, 18 states have established restrictions on the use of AFFF, ranging from limitations on training, notification of PFAS content and/or release, storage, and firefighter personal protective equipment (PPE) (Horst et al. 2021). AFFF use is explicitly regulated by some states, such as the State of Washington and the State of New York (Table 3-6); however, other states regulate PFOA, PFOS or their salts, and other PFAS in AFFF as hazardous substances or hazardous waste. These regulations effectively limit the storage and/or environmental release of legacy AFFF (both legacy PFOS AFFF and legacy fluorotelomer AFFF), as well as potentially triggering cleanup actions. Similar bills, banning the use of AFFF for testing and training, have been passed in other states such as Arizona, Colorado, Georgia, Kentucky, and Minnesota.

Examples of hazardous substance and hazardous waste regulations, as well as other federal, state, and international guidance pertaining to AFFF, are presented below. For more information pertaining to the regulation of PFAS, see <u>Section 8</u>. This section addresses only regulations related to AFFF.

Table 3-6. Representative state AFFF regulatory and legislative activity
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State	Regulation or Bill	Initial Effective Date	What is Regulated?	Specific Requirement	Reference
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State	Regulation or Bill	Initial Effective Date	What is Regulated?	Specific Requirement	Reference
New York	6NYCRR Part 597	March 2017	PFOS, PFOA, and Class B foams	PFOS and PFOA are hazardous substances. Storage and registration requirements for class B foams if those foams contain at least 1% by volume of PFOS and PFOA (acid and salt) and prohibit the release of 1 pound or more of each into the environment during use. If a release exceeds the 1-pound threshold, it is considered a hazardous waste spill and must be reported. Clean-up may be required under the state's superfund or brownfields program (NYDEC 2017). New York's Chemical and Bulk Storage regulations may also trigger further registration and storage requirements for foams that contain one of the four PFAS designated as hazardous substances (NY CRR Parts 596-599).	(<u>NY DEC</u> 2017)
Washington	WAC 296-24-33001	July 2020	Class B foams	Class B firefighting foams cannot be used or discharged for training purposes, and manufacturers of firefighting personal protective equipment must provide written notification to purchasers if the equipment contains PFAS. Beginning July 1, 2020, manufacturers of class B firefighting foams may no longer manufacture, sell, or distribute for sale PFAS-containing class B firefighting foams except for the following uses: applications where the use of a PFAS- containing firefighting foam is required by federal law, including but not limited to the requirements of 14 CFR 139.317 (such as military and FAA-certified airports). Other exceptions include: Petroleum Terminals (as defined in RCW 82.23A.010), Oil Refineries, Chemical Plants (WAC 296-24-33001)	
Virginia	House Bill 2762ER	January 2020	PFAS-containing AFFF	Virginia Department of Fire Programs and the Virginia Fire Services Board begin assisting municipal fire departments to transition to F3, where possible. Effective the same date, the bill bans the discharge or use of PFAS-containing AFFF foams for testing or training unless the facility has implemented containment, treatment, and disposal measures to prevent release to the environment.	(<u>State of</u> <u>Virginia,</u> 2019)

3.12.2 Take-Back Programs

Several states have implemented "take-back" programs for AFFF. For example, in May 2018, the Massachusetts Department of Environmental Protection (MA DEP), in partnership with the Massachusetts Department of Fire Services, implemented a take-back program to assist fire departments in the proper disposal of legacy firefighting foams that could impact water resources (MA DEP 2018). MA DEP provided funding to assist local fire departments in identifying these foams in their stockpiles and for MA DEP to dispose of them. Any AFFF manufactured before 2003 is eligible under the take-back program. Vermont also announced a take-back program (VT ANR 2022). Users should contact their state regulatory agency for information on available take-back programs.

3.12.3 Federal Guidance

As of publication, F3s do not meet the performance requirements of the Mil-spec and therefore are not used at federal- and FAA-regulated facilities. A mandate within the FAA Reauthorization Act of 2018 (enacted October 5, 2018) directs the FAA to stop requiring the use of fluorinated foam no later than 3 years from the date of enactment (October 4, 2021), however, per Cert Alert 21-05, no fluorinated Mil-Spec existed as of that date. In January 2023, the FAA released a Cert Alert to all Title 14 CFR Part 139 Certificated Airport Operators and Aircraft Rescue and Firefighting Departments and Mutual Aid Providers (FAA 2023). The alert noted that FAA will accept the airport operator's use of the new F3 extinguishing agent at certificated Part 139 airports once the agent passes the military performance standards and qualification testing and is added to the Navy's Qualified Products' List/Qualified Products' Database. The alert further noted that currently, the FAA will not require certificated Part 139 airports to transition to the new F3, and airport operators are authorized to continue using AFFF, but should check with their state and local municipalities for any local requirements. The National Defense Authorization Act of fiscal Year 2020 (signed into law Dec 20, 2019) requires the DOD to phase out its use of AFFF at all military installations by Oct. 1, 2024, with limited exceptions, and immediately stop military training exercises with AFFF.

In January 2023, DOD released a new Mil-Spec (MIL-PRF-32725) to replace AFFF with F3s at military installations. The F3 Mil-Spec contains a product qualification step that requires a "non-detect" for PFAS as measured by Draft USEPA Method 1633, and also a specification limitation on PFAS content, prohibiting F3s from containing more than one part per billion PFAS (<u>USDOD 2023</u>).).

3.12.4 International Guidance on AFFF

Internationally, there are many governmental agencies that have developed guidance or operational policy for AFFF. Some examples are briefly presented in <u>Table 3-7</u>. The international guidance and regulations are shaped by the unique regulatory structure and regional history of the areas in which they are implemented. As such, they may not necessarily provide informative insights to readers who are unfamiliar with those specific contexts.

Country	Initial Effective Date	What is Regulated?	Specific Requirement	Reference
Canada	January 2018	PFOS, PFOA, long-chain PFCAs	Canada prohibits the manufacture, use, sale, or import of a number of PFAS- containing chemicals and products, such as AFFF, that have these chemicals. Canada allows certain exemptions, including the use of AFFF that contains residual levels of PFOS at a maximum concentration of 10 ppm; the use and import of AFFF contaminated with PFOS in military equipment returning from a foreign military operation; and the import, use, sale, and offer for sale of AFFF that contains PFOA and/or LC-PFCAs used in firefighting.	(<u>ECCC 2017</u>)

Table 3-7. Representative international	I AFFF	regulatory	and	guidance	activity
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Country	Initial Effective Date	What is Regulated?	Specific Requirement	Reference
Canada	2022	PFOS, PFOA, long-chain PFCAs, polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCD)	The proposed prohibition would remove or provide time limits for exemptions for PFOS, its salts and precursors, PFOA, its salts and precursors, long chain PFCAs, PBDEs, and HBCD to further restrict the manufacture, use, sale, and import of these substances, and products that contain them. It would also prohibit the manufacture, import, use, sale, and offer for sale of Dechlorane Plus (DP) and decabromodiphenyl ethane (DBDPE), and products that contain them, with exemptions.	(<u>ECCC 2022</u>)
Germany	May 2013	AFFF	The German Federal Environment Agency released a Guide for the Environmentally Responsible Use of Fluorinated Fire- fighting Foams. The guidance discusses what AFFFs are, when it is necessary for use, why it endangers humans and the environment, and the consequences of use.	(German Federal Environment Agency 2013)
Australia	July 2016	Firefighting foam	The Queensland Department of Environment and Heritage Protection issued an Operational Policy on the Environmental Management of Firefighting Foam. The objective of the policy was to define the requirements and expectations for the handling, transport, storage, use, release, waste treatment, disposal, and environmental protection measures of AFFF.	(<u>Australia</u> Government DOD 2007)
Australia	July 2016	Firefighting foam	Australia's state of Queensland established restrictions on application and procurement of C8-AFFF (eight carbon- fluorine bonds or greater) and designated that C6-AFFF (six carbon-fluorine bonds or less) replacement foams contain less than 10 mg/kg PFOS and less than 50 mg/kg of PFOA, PFOA precursors, and their long- chain homologues.	Queensland DES 2021 (replaced Queensland DES 2016)
Australia	January 2018	Firefighting foam	Australia's state of South Australia instituted a ban on fluorinated firefighting foams with a grace period of 2 years to complete foam transition.	<u>SA EPA May 2019</u>

Country	Initial Effective Date	What is Regulated?	Specific Requirement	Reference
European Union	July 2020	PFOA, its salts, and related substances	Prohibit the manufacture of PFOA and related substances on their own from 4 July 2020. Products manufactured after 4 July 2020 should not contain PFOA and its salts greater than 25 ppb or sum of PFOA- related substances (e.g., precursors) greater than 1,000 ppb.	European Commission 2017
European Union	December 2021	PFHxA, its salts, and related substances	Proposed a restriction on the manufacture of PFHxA and related substances on their own, as well as in products that contain concentrations equal to or above 25 ppb for the sum of PFHxA and its salts or 1,000 ppb for the sum of PFHxA-related substances.	European Chemicals Agency (ECHA) 2021
European Union	February 2023	C9-C14 PFCAs, their salts, and C9-C14 PFCA-related substances	Prohibit the manufacture of C9-C14 PFCAs and related substances on their own from 23 February 2023. Products manufactured after 25 February 2023 should contain less than 25 ppb for the sum of C9-C14 PFCAs and their salts or less than 260 ppb for the sum of C9-C14 PFCA-related substances.	European Commission 2021

3.13 Foam Research and Development

Current modern AFFF fluorosurfactant alternatives are largely short-chain C6 telomer-based fluorosurfactants. The fluorosurfactants do persist in the environment, and they have the potential to create breakdown products that are also persistent. Although numerous fluorine-free alternatives are already on the market, there is still a need to develop novel firefighting foams that provide the desired firefighting performance while not being harmful to human health and the environment. Research is currently being conducted to further evaluate modern fluorotelomer and fluorine-free alternatives. Research is discussed below.

3.13.1 Research on Current AFFF

Research is being conducted to provide a better understanding of AFFF in the environment and to develop novel technologies to clean up or remove AFFF at contaminated sites. Due to the ability of these legacy AFFF to spread quickly and prevent re-ignition of fuel fires, combined with the fact the USEPA did not require manufacturers to remove their long-chain inventory as part of the 2010/2015 PFOA Stewardship Program, some legacy stockpiles are still being used today (Barclift 2013).

Since 2017, the Strategic Environmental Research and Development Program (SERDP) has been funding research intended to identify and test F3s that meet the performance requirements defined in MIL-PRF-24385. New formulations must be compatible with existing AFFF and supporting equipment. Projects include evaluation of persistence and aquatic toxicity of the alternative materials and will provide human health and environmental impact assessments on the ingredients, formulations, and byproducts being studied. <u>Table 3-8</u> summarizes the current AFFF alternatives studies supported by SERDP-Environmental Security Technology Certification Program (ESTCP). The user is encouraged to view the results and full reports of these and future projects on the SERDP-ESTCP website (<u>https://serdp-estcp.org/</u>).

Table 3-8. Summary of the AFFF alternatives studies supported by SERDP-ESTCP

Lead Investigator	Objectives	Expected Completion	Project Link
Dr. Joseph Tsang, Naval Air Warfare Center Weapons Division	Proof-of-concept for the development of the next generation of fluorine-free firefighting foam formulations as a replacement for existing aqueous film-forming foam (AFFF). The novel foam systems produced in this research are derived from polysaccharide copolymers and nanoparticles that are sustainable, nontoxic, and water- soluble (or water- dispersible), and will be applied using existing military firefighting equipment.	Aug-18	https://serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2737/WP-2737
Dr. John Payne, National Foam	Improve understanding of the physical and chemical processes that underlie firefighting foams, and how the components of a foam formulation can deliver the properties required for good fire- extinguishing performance while minimizing environmental burdens. Statistical method will be employed to develop a fluorine- free surfactant formulation that meets the performance requirements defined in MIL- F-24385. A life cycle assessment will compare the environmental impact of each foam type and identify routes to improving environmental performance	Sept-19	https://serdp-estcp.org/Frogram-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2738/WP-2738
Dr. Ramagopal Ananth, U.S. Naval Research Laboratory	Develop a fluorine- free firefighting surfactant formulation that meets the performance requirements of MIL- F-2438F and is an environmentally friendly drop-in replacement for the current environmentally hazardous AFFF.	Dec-20	https://serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2739/WP-2739
Prabhat Krishnaswamy Engineering Mechanics Corporation of Columbus (Emc2)	wr22-7321. This project's technical objective is to develop a novel approach for fighting gasoline pool fires based on fire-retardant additive releasing smart beads.	Initiated 2022	https://www.serdp-estcp.org/projects/details/352aa6f8-fae0-4cf6-8080-0fc319700142/wp22-7521-project-overview
Dr. Girish Srinivas TDA Research, Inc.	WP22-7456. TDA Research, Inc.'s objective is to collect baseline data for the PFAS-free foam under MIL- PRF-24385F to inform what specifications could be adjusted to fully evaluate PFAS-free foams for fire suppression and environmental impact.	Initiated 2022	https://www.serdp-estcp.org/projects/details/baa72637-e3c8-40ee-a007-f295311c72ad/wp22-7456-project-overview

Lead Investigator	Objectives	Expected Completion	Project Link
Dr. Tirumalai Sudarshan Materials Modification Inc.	WP22-3456. This project's technical objective is to develop a novel approach for fighting gasoline pool fires based on fire-retardant additive releasing smart beads.	Initiated 2022	https://www.serdp-estcp.org/projects/details/h4cada93-5acf-47ff-ab68-c115a9c6c6ab/wp22-3436-project-overview
Eric Sievert Naval Air Warfare Center Weapons Division	WP21-3461. During this follow-on effort, the capabilities of the top fluorine-free products will be assessed and validated against the test configurations used to assess the capabilities of AFFF 30-40 years ago.	2021	https://www.serdp-estcp.org/projects/details/1bed98f7-dbe6-4bdd-98d2-1f9cfeb5f3d9/wp21-3465-project-overview
Dr. Satya Chauhan Battelle Memorial Institute	WP20-5335. The objective of this project is to provide comparative and unbiased demonstration and validation of mature Fluorine-Free Fire Suppression Alternatives (FF_FSA) against military specifications (MIL- SPEC), specifically MIL-PRF-24385F, as amended, to permit transition to field use as a firefighting agent.	2020	https://www.serdp-estcp.org/projects/details/164cac28-0322-4d7a-8980-80a1146b5afa/wp20-5335-project-overview
Kevin Roth ADA Technologies, Inc.	WP20-5381 Testing of New Fluorine-Free Green Surfactants Mixture to Replace AFFF	4/20/2022 Project Brief	https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/project_documents/WP20-5381%2BProject%2BOutbrief.pdf?VersionId=5e69zE0HUHjoVs.NrGmWPp1ZiZM1wWjH
Dr. Bridgett Ashley Air Force Civil Engineer Center	WP 20-5381. The goal of a water mist system in an aircraft hangar is to suppress and mitigate fire events and prevent damage to aircraft surfaces that are directly above and/or adjacent to the fuel spill fire.		https://www.serdp-estcp.org/projects/details/cb97638e-8d4e-4892-adce-343575ca862c/wp21-5212-project-overview

Examples of other ongoing research includes:

- European Chemicals Agency, 2020. Assessment of Alternatives to PFAS-Containing Fire-Fighting Foams and the Socio-Economic Impacts of Substitution.
- European Commission, 2020. The Use of PFAS and Fluorine-Free Alternatives in Fire-Fighting Foams.
- The Fiscal Year 2020 National Defense Authorization Act (NDAA), passed in December 2019, included \$49M in research funding for AFFF and F3 activities.
- The Fiscal Year 2022 National Defense Authorization Act (NDAA), passed in December 2021, included more than \$500 million for PFAS provisions
- NFPA Research Foundation (2022), Fire Fighting Foams: Fire Service Roadmap.

Updated September 2023.

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