BIODEGRADABILITY OF FLUORINATED FIRE FIGHTING FOAMS

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Abstract

Fluorinated fire fighting foams provide superior performance for extinguishing Class B flammable liquid fires when compared to other types of fire fighting foams. Perfluorocarboxylates and perfluorosulfonates have historically been surfactants used in these foams with a recent shift to fluorotelomer-based foams due to environmental and health concerns surrounding perfluorinated compounds such as PFOA and PFOS. Releases of aqueous film forming foams from training, accidental spills, or fire events where wastewater is not captured have, among other sources, led to detectable concentrations of fluorinated compounds in groundwater, surface water, and drinking water supplies globally. Persistence, toxicity, and bioaccumulation potential of these substances are areas of ongoing research.

Biodegradability data for these AFFFs in published studies and manufacturers' material safety data sheets may be based on a comparison of BOD and COD measures. The present study concludes that COD is an inappropriate measure of organic content for fluorinated compounds due to the carbon-fluorine bond strength, and thus published biodegradability data must be critically evaluated for validity. TOC measured an average of 91% of carbon content for four fluorinated test substances, recommending it for use as an analytical parameter in biodegradability tests when specific compounds' identities are not required, e.g. in the absence of an LC/MS.

Biodegradability of three fluorinated foams (AFFF, AR-AFFF, and FP) purchased from a major U.S. manufacturer measured in the range of 77-96% based on DOC die-away during a 28-day test using activated sludge inoculum. This meets OECD criteria for "ready biodegradability" and NFPA biodegradability recommendations in Standards 18, 18A, and 1150. Defluorination of two foams was measured using ion chromatography and, based on an estimate for total fluorine content developed in part from manufacturer MSDSs, was found to liberate a detectable level of fluorine that was 1 to 2 orders of magnitude less than the estimated value. In this 28-day test, foams underwent significant biodegradation but fluorinated compounds' biodegradation was likely incomplete.

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1. Introduction

Aqueous film forming foams (AFFFs) are used to extinguish Class B fires where flammable, volatile liquids are the fuel source. Surfactants are key ingredients in these foams which reduce surface tension, allowing the foam to blanket the fuel with a film, suppress vapors and block the oxygen source while water content in the foam also cools flames. To provide the most effective extinguishment, surfactants used in these foams have historically included fluorinated components, such as the perfluorinated acid and salt PFOA and PFOS (perfluorooctanoic acid, perfluorooctane sulfonate) with carbon chain lengths of 8 [1] due to the superior performance fluorinated compounds provide beyond other types of surfactants.

In the past two decades, PFOA, PFOS, and other long-chain perfluorinated compounds have been tracked in global environments and found in detectable levels in numerous organisms, including humans as a result of to their presence in the environment, drinking water and foods, consumer goods, and due to other possible exposure routes including occupational exposure [2-5]. These compounds have proven to be persistent in the environment and bioaccumulative, raising ecological, human health, and environmental concerns as research continues [6-9]. PFOS has been listed as a Persistent Organic Pollutant in the Stockholm Convention [10]. In January, 2009, the U.S. Environmental Protection Agency (EPA) issued provisional health advisories of drinking water concentrations of 0.4 µg/L PFOA and 0.2 µg/L PFOS although at that time it was reported that adverse health outcomes in humans remained inconclusive [11]. In 2006, the EPA Science Advisory Board reported that PFOA is “likely to be carcinogenic to humans” based on a draft risk assessment of PFOA and is currently in the process of evaluating all information [12].

Firefighting foams with these or other fluorinated ingredients may end up in groundwaters, surface waters, and wastewater treatment plants as a result of their use during firefighting or training, contributing to potential environmental threats and/or overwhelming of wastewater treatment facilities with wastewaters bearing high organic loadings [13]. As a result of some of these concerns, surfactants with shorter carbon chains and different structures have been developed and used in AFFFs with the goal of providing the same or better performance while reducing environmental and health impacts [14]. The fire industry uses other types of foam to suit different applications, some of which also include fluorinated surfactants.

The manufacturing process called electrochemical fluorination is used to produce fully fluorinated compounds such as PFOA and PFOS with linear or branched chains. An alternative process, telomerization, produces linear fluoroalkyl chains consisting of a fluorinated portion attached to an ethyl group followed by some non-fluorinated end-group [15]. Chain lengths and functional group identities may vary. Compounds produced through telomerization have been shown to biodegrade more readily than perfluorinated compounds while still being able to offer the surfactant properties desired in AFFFs [14]. In many foams currently manufactured, a combination of fluorotelomer surfactants and hydrocarbon surfactants are used [16] which is able to reduce fluorine content by 30 to 60% [14]. The difference in degradability can be attributed to the degree of fluorination—compounds with a greater number of carbon-fluorine bonds require much greater energies to cleave the stronger and more numerous bonds. The bond between carbon and fluorine is the strongest of known bonds due to the electronegativity of fluorine and the overlap between the 2s and 2p orbitals of fluorine and corresponding carbon orbital, making fluorocarbons particularly recalcitrant in the environment [17].

3M, the major manufacturer using the electrochemical fluorination process, withdrew from the fire fighting foam market in 2002, citing environmental reasons associated with emerging research into PFOA and PFOS [18]. In 2006 the EPA launched a Global Stewardship Program encouraging the country's eight major fluoropolymer and telomer manufacturers to reduce PFOA/PFOS content in products and emissions to the environment by 95% by 2010 and completely by 2015 [19]. These companies report annually to demonstrate compliance with this voluntary stewardship program. Accordingly, any manufacturers that formerly used PFOA or PFOS-based foams have developed new foam formulations devoid of these and other long-chain perfluorinated compounds. Fluorotelomers in particular have been used as replacements, though fluorotelomers had already been used in many foams for decades [14].

Foam manufacturers conduct rigorous studies to ensure their foams meet standards to extinguish fires effectively, rapidly and safely for emergency responders. A balance between the required performance and prudent minimization of environmental and biological impacts is sought. Biodegradability in particular is an important property of foams since these products may be released into uncontrolled environments where they may accumulate for years if not degradable by the microorganisms present in natural systems. The National Fire Protection Association (NFPA) recommends that foams used on wildland and structural fires (Class A fires) reach 60% biodegradability within 42 days, where this value represents the amount of carbon in solution that is converted to carbon dioxide by microorganisms [20]. If foam used on these wildland fires is assumed to pose the greatest environmental threat since less of this foam may reach municipal wastewater treatment plants and the majority may remain in the environment, this 60% level of biodegradation offers one reference point for the determination of prudent biodegradability values. This level remains only a recommendation made by NFPA until referenced in statute. Class B AFFFs meeting U.S. military specifications must attain 65% biodegradability based on a ratio of the 20-day biochemical oxygen demand (BOD) to the chemical oxygen demand (COD) [21].

These biodegradability values are believed to be quite stringent, accepted to demonstrate "rapid and complete biodegradation in the environment" [22] since the additional 35-40% of carbon remaining is understood to be either converted to biomass or mineralized to carbon dioxide soon after the testing period ends. However, for fluorinated foams, these threshold levels as well as standard biodegradability test methods may not be entirely appropriate. Since most fluorinated foams are composed largely of water, solvents, freeze point depressants, etc. with low overall fluorine content, a foam may pass this 60% biodegradability threshold during testing if the majority of the foam is degraded. If the high strength of carbon-fluorine bonds render them non-amenable to biodegradation, the fluorinated constituents of interest may remain in solution even if the overall foam is deemed biodegradable by standard test methods. Additionally, biodegradability test methods relying on a comparison of observed BOD or carbon dioxide formation during bacterial metabolism as a percentage to the overall measured COD or TOC may be inherently inaccurate if COD or TOC tests are unable to break C-F bonds and produce falsely low COD or TOC measures. Recent biodegradability studies of AFFFs [23-25] and some manufacturers' AFFF material safety data sheets [26-30] have reported wide ranges of biodegradation, from less than 1% up to 126%, indicating the need for further testing and a critical evaluation of the test methods themselves. This study will perform biodegradability testing of two fluorinated foams and will investigate the accuracy of COD and TOC analysis of fluorinated compounds.

2. Objectives

Objectives of this study are:

1. To quantify the biodegradability of various fluorinated fire fighting foams, using a standard OECD test as recommended by NFPA
2. To quantify defluorination and breakage of any C-F bonds during biodegradation of foams
3. To evaluate the appropriateness of TOC and COD analysis when determining biodegradability of solutions containing fluorinated compounds

3. Background

3.1 Types and Characteristics of Fire Fighting Foams

Fire fighting foams are mixtures of liquid foaming agents and air-filled bubbles that form a blanket over burning fuel. This foam blanket can exist on top of the fuel due to lower density, lowered surface tension, and/or a polymeric membrane separating fuel from foam. Foams stop and prevent further combustion through multiple mechanisms: smothering the flame to disconnect the oxygen supply, separating the fuel and the fire, cooling the fuel, and suppressing flammable vapors [31]. To generate this foam, water is first mixed with a viscous foam concentrate, which contains foaming agents, in a water:foam concentrate ratio typically between 99:1 and 94:6, and then the solution is aerated immediately prior to use. The foam's final air content may be over 80% [16]. Foams are typically used when either the location or the fire type make water use undesirable.

Foams are used primarily for Class B fires, but may also be used for Class A fires. Class B fires involve flammable liquids and volatile vapors, which are not effectively extinguished with water and instead require foam. If water was used on a Class B fire with flammable hydrocarbon fuels, the applied water would form a layer below the hydrocarbons, which are typically less dense than water, and be ineffective in suppressing flames. Furthermore, water application on flammable hydrocarbons could lead to water submersion and subsequent boiling, creating a water vapor pressure that has the potential to propel some amount of fuel outwards, spreading the fire, and creating dangerous conditions [32]. Foams are formulated with surfactants and aerated to form a continuous layer on top of Class B fuels. Class A fires are structural and wildland fires with ordinary combustible material such as wood and paper. These fires may be extinguished with water and in certain cases foam may be used to help rapidly penetrate into tight areas, such as bales of hay or piles of leaves. In areas with limited water supplies, foams may be used on Class A fires to reduce the overall water requirement.

There are a number of types of foam with different expansion levels and performance characteristics based on either synthetic (detergent) or protein ingredients. Protein foams and fluoroprotein foams use keratin protein as raw materials. Protein foams are rarely used today [31]. Instead, synthetic foams, either aqueous film forming foams (AFFF) or alcohol resistant – AFFFs (AR-AFFF) are used more heavily due to the wider range of fuels they may be used on, their compatibility with foams used by other groups, and their long storage lives. Different types of foams have different storage lives, resistance to freezing, viscosity, and may be preferred for use on different types of fires. For example, alcohol-resistant (AR) foams are effective on polar solvent fuels whereas foams without this alcohol resistance are wholly ineffective on this type of fire and would collapse.

Required foam performance properties include rapid extinguishment, prevention of burnback (during which the fuel burns holes in the foam blanket), high water retention (which allows the foam to remain intact and effective for longer before the water seeps out of the foam), resistance to high temperatures, etc. After application, the water content of foams either vaporizes due to the heat or drains from the foam. Therefore, effective foams must retain their structure and water content while blanketing as large of the fuel's surface area as possible [31].

3.1.1 Active Ingredients: Surfactants

Active ingredients in fire fighting foams are surfactants, which achieve two main features in foams: the high retention of air bubbles and the spreading of foam across large fuel surface areas. Surfactants, or surface-active agents, lower surface tension of solutions by selective adsorption at the interface between two phases. At an interface between two immiscible phases, attractive forces within the bulk liquid phase are stronger than the interactive forces between the two phases. This tends to draw solvent molecules from the surface (interface) back into the bulk phase, and work must be done in order to increase the surface area between the two phases [33]. Surface tension is defined as the work per area required to expand this interface. Surfactants, or surface-active agents, decrease this surface tension. This stems from the amphiphilic nature of surfactants, meaning the attraction to two types of media—in each molecule there is a polar, water-soluble hydrophilic part of the surfactant and a nonpolar, water-insoluble hydrophobic part. Fluorinated surfactants' hydrophobic end is also oleophobic, or incompatible with fats and hydrocarbons. In fire fighting foams, this allows the surfactant solution to repel hydrocarbon fuel surfaces and avoid boiling of foams' water content by forming the film spread across fuels [33]. In solution, surfactants orient themselves such that the hydrophilic ends of surfactant molecules point toward water and hydrophobic ends point toward air or the burning fuel. In fluorinated surfactants which are often used in fire fighting foams, the fluorinated component is in the oleophobic group [13].

For fire fighting foam applications, the two interfaces between immiscible phases of interest are the foam-air interface and foam-fuel interface. At the foam-air interface of a solution with high surface tension, the surface tension would cause the solvent enclosing the air bubbles to be drawn back into the bulk solvent phase, decreasing surface area and collapsing the foam. Through the use of surfactants, the surface tension in fire fighting foams is low enough to allow air bubbles to remain intact while covering a larger surface area of fuel. At the foam-fuel interface, a solution with high surface tension (and assuming lower density after aeration) would flatten onto the fuel surface due to its own weight but would reach some shape where it can balance forces of gravity while maintaining a minimum surface area [33]. With a lower surface tension through the use of surfactants, the foam solution can flatten out and spread onto the fuel surface to a greater degree since surface area may be more easily increased. This allows any gaps in foam application to be "healed over" as the aqueous film spreads across the fire to form a continuous foam blanket to smother flames.

Other ingredients in AFFF and AR-AFFF foam concentrates include water, glycols, alcohols, and other solvents. In some cases, multiple surfactants are used, up to above 10% by weight, which may include both fluorinated and nonfluorinated types. Typical fluorinated surfactant concentrations range from 0.5-10% by weight [26-30, 34-42]. Water is the main component of foam concentrates, at times composing up to 98% of some foam concentrates [43]. AR-AFFF foams include a polymeric gumming agent such as xantham gum to form the alcohol resistant film. Surfactants within foam concentrates are the active ingredients responsible for foam formation.

3.1.2 Fluorinated Foams – AFFF, AR-AFFF, FP

Many foams, both protein based and synthetic, include a fluorinated surfactant to lower surface tension and allow for the formation of a water-foam layer floating on top of the fuel layer, separated by a thin film interface between the two layers. Synthetic foams of this type are called aqueous film forming foams, or AFFFs. Other types of non-fluorinated surfactants may be used in foams, but fluorinated surfactants offer superior performance and resistance to high fire temperatures and oxidative conditions. In this discussion, AFFFs will be taken to include fluorinated surfactants. AFFFs are extremely valuable in the fire fighting industry.

Fluorinated surfactants differ from hydrocarbon surfactants in that their non-polar perfluorocarbon tail is both hydrophobic and oleophobic, or oil-repelling, as opposed to a solely hydrophobic tail of hydrocarbon surfactants. This gives the surfactant its film-forming capability on hydrocarbon fuels [13]. The fluorination of surfactants gives foams increased chemical and thermal stabilities compared to hydrocarbon surfactants while reducing surface tensions to very low levels [16]. Surfactants may be perfluorinated, meaning that all hydrogen atoms have been substituted by fluorine atoms, or polyfluorinated if not all hydrogen atoms have been replaced. The hydrophobicity of a CF_2 group is equal to 1.7 times the hydrophobicity of a CH_2 group in a surfactant differing in structure by only this CH_2 or CF_2 group [44]. For perfluorinated chains, this leads to surface tension reduction to about 10-20 dynes per centimeter at 20°C as compared to the 30-40 dyne/cm level achieved with hydrocarbon surfactants [16]. This lower surface tension as compared to hydrocarbon surfactants reduces the amount of surfactant required—fluorinated surfactants are often used in 10-100 times smaller quantities than hydrocarbon surfactants [16].

The film-forming properties of AFFFs may also be conferred to alcohol-resistant formulations, called AR-AFFFs, for use on polar solvents such as ethers, ketones, or alcohols. AR-AFFFs form more defined membranes between polar fuel and aqueous foam layers due to polysaccharide gumming agents, such as xanthan gum, which are designed for use on polar solvents where AFFFs alone would rapidly breakdown and cause foam drainage. A polysaccharide, when it comes into contact with the polar solvent, precipitates and forms the interfacial barrier between foam and polar solvent [16]. The polymer barrier retards drainage, and increases the foam’s stability when it would otherwise be destroyed by a polar solvent [33]. AR-AFFFs can be used on any flammable liquid, nonpolar or polar, and are also available from many manufacturers in a single product that can be used at either 3% concentration for nonpolar solvent fires or at 6% for polar solvent fires (or 1% for nonpolar and 3% for polar depending on the manufacturer). These function the same as AFFFs when used on hydrocarbon fires and produce a floating gel-like layer when used on polar solvent fires. These preferred properties have led to high AR-AFFFs usage, perhaps more than AFFF usage. In particular, as hydrocarbon fuels' ethanol content is increasing, car fires with punctured gas tanks have been cited as one reason for AR-AFFF preference over AFFF alone—the capability to extinguish a broad range of fires is an excellent property [45]. Some locations, such as airports and training facilities may continue to use AFFF if wastewater containing foam is collected and treated since any polymer precipitate from an AR-AFFF would cause problems to wastewater treatment facilities (See Section 7).

Fluoroprotein (FP) foams are protein-based with the addition of fluorinated surfactants. Protein and fluoroprotein foams provide excellent heat resistance and vapor suppression. Ingredients include keratin protein hydrolysis products (e.g. hoof meal, chicken feathers), stabilizers, corrosion inhibitors, and bacterial inhibitors [46]. These do not necessarily form defined films across fuel surfaces unless formulated as Film Forming Fluoroprotein (FFFP) foams. Alcohol resistant AR-FFFPs also exist which form a polymer layer for use on polar solvents.

3.2 The Carbon-Fluorine Bond

It is the carbon-fluorine bond that gives fluorinated surfactants their resistance to oxidation at high temperatures, making them excellent for fire fighting applications. Fluorine is the most electronegative element, meaning it has the greatest tendency to attract electron density from an atom it bonds with. When fluorine draws electron density from carbon, the carbon becomes more electronegative than it would be when bonded to other elements. This inductiveness creates strongly polarized bonds which are 43% ionic in character [47]. Other carbon-halide bonds are much less ionic, most closely the carbon-chlorine bond with 12% ionic character [47]. As the number of fluorine atoms bonded to a carbon atom increases, the ionic character of bonds increase, bond length shortens, and bond strength increases (Table 1). This occurs because increased fluorine substitution withdraws more charge and lowers the electron density of carbon, increasing the positive nature of carbon which results in more ionic bonds. The 2p orbitals of carbon are likely where this charge density is lost, therefore increasing the s bond character and shortening bond lengths. This increase in ionic bond character is a cause for the great strength of C-F bonds. Table 1 shows that C-F bonds possess higher bond strengths than other carbon-halogen bonds that are less ionic in nature [48]. Based on this, perfluorinated carbons can be expected to feature greater C-F bond strengths than polyfluorinated carbons.

Table 1: Carbon-halogen bond lengths and energies in halomethanes [49]

	X = Fluorine		X = Chlorine		X = Bromine	
	Bond Length, Å	Bond Strength, kcal	Bond Length, Å	Bond Strength, kcal	Bond Length, Å	Bond Strength, kcal
CH_3X	1.385	107.0	1.782	78.0	1.9390	66.6
CH_2X_2	1.358	109.6	1.772	77.9	1.9340	66.4
CHX_3	1.332	114.6	1.767	78.3	1.9300	66.1
CX_4	1.317	116.0	1.766	78.2	1.9420	66.6

Specifically, the single bond formed between carbon and fluorine is the strongest of any known bond. The bond energy of the carbon-fluorine bond is significantly greater than other carbon-halogen single bonds (Table 2). The strength of single bonds that fluorine forms with other elements decrease as the electronegativity of the other element increases, so while C-F bonds are the strongest, other F-X bonds are not all similarly as strong. When compared with other halogens, the fluoride ion is the smallest halide ion, leading to the highest charge density. This causes the fluoride ion to form stronger hydrogen bonds than other halide ions [48].

Table 2: Bond strengths [48]

Bond	**E, kcal**
C-F	107-121[a]
C-Cl	81
C-Br	68
C-I	57
C-H	98.7
H-F	135
H-Cl	103.1
H-Br	86.5
N-F	65
S-F	68

[a] Authors estimate ranges; energy varies with bonding environment

Since fluorine has a low energy of dissociation (Table 3), a “kinetically significant” number of fluorine atoms are available to form bonds at room temperature [48]. Highly reactive and electronegative, fluorine atoms rapidly form stable C-F and F-H bonds. Fluorine bonds with low selectivity during this process.

Table 3: Dissociation energies ($X_2 \rightarrow 2X\bullet$) [48]

Element	Dissociation Energy, kcal
F_2	37
Cl_2	58
Br_2	46
O_2	118
N_2	225

3.2.1 Properties and Reactivity of Fluorocarbons and Hydrocarbon Analogs

The effect of fluorination upon surface tension is the primary reason for the widespread use of fluorocarbons in surfactants and detergents. As previously stated, perfluorinated alkanes have the lowest recorded surface tension, from 10-20 dynes per centimeter at 20°C, and fluorinated surfactants also require lower concentrations than hydrocarbon surfactants to reduce surface tension to the same levels. Additionally, some polyfluorinated compounds have the ability to similarly decrease surface tensions. A solution of "less than 1% of perfluorocarboxylic acids [in] water decreases the surface tension from 72 to 20 dyne/cm" [17].

Fluorinated compounds always have greater densities than corresponding nonfluorinated compounds. Fluorinated or perfluorinated compounds often have negligible solubilities in water and may form two-phase systems with organic solvents. Solubility generally decreases with increasing chain length and increasing fluorine substitution. Critical micelle concentrations (cmc) depend on the structure of the hydrophobe and hydrophile which affect cohesive forces between hydrophobic tails and the water affinity of hydrophilic groups [33].

Strong bonding properties give fluorinated surfactants their resistance to harsh conditions, acids, alkali, reduction, and oxidation, even at elevated temperatures. Likewise, these properties make fluorinated surfactants less reactive than their hydrocarbon analogs and more persistent when released into the environment. The strength and short length of the C-F bond prevents attacking groups from interacting with carbon, making fluorocarbons more stable than other halocarbons. Any fluorine displacement occurs at slower rates than other halogen displacement due to the energy required to break the C-F bond, usually significant in the rate limiting step [48]. Rigid C-F bonds stiffen carbon backbones and limit reactions, while small fluorine atoms also shield carbon atoms without steric interference.

3.3 Historical Foam Components

Historically, many AFFF foams have featured long-chain perfluorinated surfactants as the active ingredients. Perfluorinated surfactants offer the lowest surface tensions, making their use highly attractive when the strength of C-F bonds under high temperature and oxidative conditions is also considered, as would exist during fire applications. Perfluorocarboxylic acids and perfluoroalkane sulfonic acids in particular are considered the most thermally stable fluorosurfactants [33]. One production method for perfluorinated compounds is electrochemical fluorination (ECF) in which a substance is dissolved in hydrofluoric acid. An electric current is applied and all hydrogen atoms on a carbon backbone are replaced by fluorine [13]. This method was used by the 3M Company, the principal U.S. producer [9], in their AFFFs as well as by a few other major companies internationally [43]. This method can produce perfluoroalkyl acids such as perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and other perfluorinated compounds with even or odd chain lengths. Many side products are formed in ECF and yields are moderate to low, but acceptable electricity and reagent costs made this manufacturing process attractive [13].

The 3M Company was a major foam concentrate producer, using these perfluorinated surfactants manufactured from their ECF process. In 2000, an estimated 3650-4500 tons of perfluorooctanesulfonyl fluoride, a raw material used during PFOS manufacturing, were produced globally [50]. At the time, other foam concentrate producers purchased their fluorinated surfactants from external sources such as major chemical companies. These other fluorochemical manufacturers used a fluorination process called telomerization [43]. This process starts with a telogen and reacts this with two or more unsaturated taxogens, forming a telomer. Telomers have carbon chain lengths of even numbers and feature a characteristic ethyl group between the alkyl chain and the end group [13]. These are named as X:Y fluorotelomers where X is the number of carbons in the perfluorinated chain and Y is the number of carbons in the ethyl group.

From 1965-1974, perfluorocarboxylates were the primary surfactants used in AFFFs. In the 1970's, perfluorosulfonate-based AFFFs became more predominantly used. During this time fluorotelomer AFFFs also entered the market but gained less than half the market share. Until 2000, perfluorosulfonates were the primary component of AFFFs [51]. Currently, fluorotelomers are used in foams.

3.4 Environmental and Health Impacts of Fluorinated Foams

The C-F bond stability and resistance to degradation, the same properties making long-chain fluorinated components attractive for use in fire fighting foams, also lead to persistence in the environment and bioaccumulation in wildlife and humans [9]. Prevedouros et al. has estimated historical perfluorocarboxylate emissions from the 1950's to present to be 3200-7300 tons from both direct (e.g. manufacturing, consumer products, AFFFs) and indirect sources (e.g. impurities, degradation) [51]. Perfluorinated chemicals (PFC) are particularly recalcitrant and have been deemed persistent, bioaccumulative, and toxic (PBT) by EPA [9]. The United Nations has listed PFOS as a Persistent Organic Pollutant under the Stockholm Convention Annex B, which specifies restriction of production and use [10]. Potential long-term adverse health effects on humans continue to be investigated [5]. Provisional health advisories issued by the EPA for drinking water concentration are 0.4 µg/L PFOA and 0.2 µg/L PFOS [11]. The concentration of PFOA detected in drinking water near one fluorochemical manufacturing site in the U.S. has been reported to be 3.55 µg/L. Groundwater concentrations of 120 µg PFOS/L, 105 and µg PFOA/L resulted from operations at a different U.S. fluorochemical manufacturing site [50]. In 2006, the EPA Science Advisory Board reported that initial findings suggested PFOA is "likely to be carcinogenic to humans" and review of data is ongoing [12]. In 2009, EPA reported that adverse health outcomes in humans remained inconclusive [11].

PFCs have been detected in human blood serum collected globally. Highest concentrations were found for PFOS, PFOA, and perfluorohexane sulfonate (PFHxS) [9]. These compounds may enter blood or other bodily fluids due to exposure to vapor or dust of fluorinated surfactants (particularly at industrial sites), aerosols [33], contaminated drinking water, consumer goods [4], PFC-affected fish, birds, or mammals, or other routes [9]. PFOA and PFOS have been of the greatest concern. A great number of studies have investigated the global occurrence, physiological effects, and persistence and bioaccumulation of fluorinated compounds [3, 5-6, 52]. They have potential for long-range transport. Atmospheric and oceanic long-range transport have been suggested as major routes contributing to global dispersion and global mass balances have been written to trace this transport and accumulation in certain areas [53-55]. Environmental sinks have been identified as deep oceans and soil burial below levels that may interact with water columns [51].As a result of increasing concerns regarding the toxicology and environmental persistence of certain fluorinated components, particularly perfluorinated, many major manufacturers of fluorinated compounds have adjusted or ceased their production.

In May, 2000, the 3M Company announced its withdrawal from the PFOS market due to concerns regarding internal research indicating PFOS detection in wildlife and at low concentrations in humans. This phase out of electrochemically fluorinated surfactants was completed by 2002 [18]. The fire fighting foam industry began a substantial shift in 2001 from perfluorinated chemicals to fluorotelomer-based foams while maintaining equal effective or superior performance. Prior to this shift, some foam concentrate manufacturers did already use fluorotelomers [43]. Newer, fluorotelomer based foams redeveloped during and after this transition period contain 30-60% less fluorine than PFOA/PFOS-based AFFF [14]. The Fire Fighting Foam Coalition, a nonprofit organization, was formed by representatives from major foam manufacturers to provide reliable technical information about AFFF products and cooperate with regulatory authorities [14].

The U.S. Environmental Protection Agency launched a voluntary global environmental stewardship program in 2006, asking eight of the country's largest fluorochemical manufacturers to reduce PFOA and related chemicals' production and emissions with the following goals:

> "1) To commit to achieve, no later than 2010, a 95% reduction, measured from a year 2000 baseline, in *both:*
>
> - facility emissions to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and

- product content levels of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals.

> 2) To commit to working toward the elimination of PFOA, PFOA precursors, and related higher homologue chemicals from emissions and products by five years thereafter, or no later than 2015." [56]

Participating companies were Arkema, Asahi, BASF Corporation, Clariant, Daikin, 3M, DuPont, and Solvay Solexis. At that time, companies reported baseline data on emissions and product content from 2000 and subsequently reported annual progress towards the 2010/2015 goals [19]. This program was voluntary, though all companies committed. In the meantime, products containing PFOA, precursors, or related higher homologues were not banned or taken back. Fire fighting foams and other products therefore could, and still have the legal opportunity to, contain PFOA or related chemicals. However, in fire fighting foam formulations, a shift away from PFOA had started prior to this PFOA Stewardship Program [14]. In the European Union, a 2006 Commission Directive [57] required fire fighting foams to be PFOS free as of June, 2011 and called for more research on PFOA.

3.5 Current Foam Components

In accordance with the phase out of PFOA and long-chain fluorocarbons, newer fire fighting foam formulations can no longer contain PFOA, precursors, or related long-chain homologues. Existing foams with these components may still be used in the U.S. until stocks are depleted, as there is no current product reclamation program. However, many foams on the market have not included PFOA or similar compounds for 20 years [14]. The use of different, less toxic and biopersistent fluorinated components as well as the combined use of multiple surfactants, both hydrocarbon and fluorocarbon, can enable the reduction of overall fluorine content while still achieving desired properties.

Production methods have a significant impact upon the structure and degradation byproducts of fluorochemicals. Instead of electrochemical fluorination which produces fully fluorinated compounds, telomerization is now the primary production method for fluorinated surfactants used in fire fighting foams. Fluorotelomers do not break down to form PFOS, PFOA, or any perfluorinated compounds [13]. Instead, other byproducts are formed, the identities and impacts of which have been the subject of many recent studies. Use of shorter chain fluorinated compounds as starting reagents also eliminates production of long-chain heavily fluorinated compounds as degradation byproducts. FFFC reports that fluorotelomers with a six-carbon backbone represent more than 75% of fluorosurfactants used in telomer-based AFFF formulations [58]. Perfluorobutane sulfonate (PFBS) has been used as a starting reagent by some fire fighting foam manufacturers, leading to shorter chain fluorinated components. PFBS, compared to PFOS and perfluorohexane sulfonate (PFHxS) has a lower potential for human bioaccumulation [59]. Companies such as Chemguard report that any PFOA or PFOS in their foams are trace levels, on the ppb to ppm scale, resulting from impurities in their raw materials [60].

Foam manufacturers continue to work beyond EPA guidelines in attempts to develop foam products with low fluorosurfactant levels. However, due to the superior performance provided by fluorination, efforts are focused on reduction of fluorine content rather than complete elimination [14]. Telomer-based AFFFs contain already 30-60% less fluorine than PFOS-based AFFFs [14]. Foams that are completely fluorine-free may not perform as well as AFFFs. A study comparing a PFOS-based AFFF and three fluorine-free foams available in Australia found that the AFFF was the most effective at suppressing the formation of flammable vapors leading to flash fires, and it prolonged reignition to the greatest degree when exposed to a direct flame [61].

3.5.1 Identified Fluorine Components in AFFFs

The identities of surfactants in fire fighting foams are not disclosed due to formulations' proprietary nature. This presents challenges in determining the environmental and physiological impacts if studies cannot be done with specific compounds of interest. To address this need, experimental work in recent years has identified structures of some compounds and certain byproducts found in commercial formulations and contaminated sites.

A 2012 study by Place and Field identified major components of AFFFs collected from military sites in the U.S. [62] Patents were also evaluated for confirmation of structures identified using mass spectrometry. Foams from 7 manufacturers produced between 1984 and 2011 were used, including 3M foams produced using electrochemical fluorination as well as foams from National Foam, Ansul, Angus, Chemguard, Buckeye, and Fire Service Plus using the telomerization process. Components identified in the 3M AFFF included PFOS-based products and other shorter chain derivatives: C6-C8 perfluoroalkyl sulfonates, C4-C6 perfluoroalkyl sulfonamides with carboxylic acid and tertiary amine functional groups, and C5-C6 perfluoroalkyl sulfonamide compounds with or without an additional propanoic acid branch. In foams from the other manufacturers using fluorotelomerization process, the 6:2 fluorotelomer thioether amido sulfonate identified occurred in three manufacturers' foams: Ansul, Angus, and Chemguard. Other telomer-based fluorocompounds detected include fluorotelomer sulfonamide betaines with perfluoroalkyl chain lengths of 4, 6, 8, or 10, fluorotelomer betaines with quaternary amine and carboxylic acid functionalities, 4:2 and 6:2 fluorotelomer sulfonamide amine, 4:2, 6:2, 8:2 and 10:2 fluorotelomer thioether amido sulfonate, and 4:2, 6:2, 8:2 and 10:2 fluorotelomer sulfonamide with dimethyl quaternary amine and carboxylic acid functionalities, 6:2 thioether amido sulfonate [62]. From this study it is evident that fluorinated compounds with carbon chains lengths up to 10 may still be used in foams, though the manufacturing dates of each foam and the fluorocompounds identified were not indicated in this paper. These specific compounds identified are not perfluorinated, will not biodegrade to PFOA or PFOS, and may potentially be biodegradable.

Schultz et al. had previously identified 6:2 and 8:2 fluorotelomer thioether amido sulfonate (also referred to as thioamidosulfonates) in one AFFF used at a U.S. military base [15]. Backe et al. found 4:2, 6:2, and 8:2 fluorotelomer thioamidosulfonates in fluorotelomer-based AFFF formulations collected from U.S. military sites [63]. The study by Backe et al. used the same foams collected by Place and Field and found 6 out of the 7 same major fluorotelomer groups, in some instances with previously unreported fluoroalkyl carbon chain lengths, in addition to 4:2, 6:2, and 8:2 fluorotelomer sulfonates which were not previously identified. Authors report no perfluoroalkyl sulfonates or carboxylates were detected in these fluorotelomer-based AFFFs. These two major perfluoroalkyl and fluorotelomer groups of compounds, with variable end chains, differ in the presence of an ethyl group separating the fluorinated portion and rest of the compound in fluorotelomers.

Weiner et al. identified common AFFF components in 11 AFFF samples collected by the Ontario Ministry of the Environment from sites where AFFF were used in Ontario, Canada, and one purchased AFFF [64]. Components identified include 6:2 fluorotelomer thioether amido sulfonate (also referred to as fluorotelomermercaptoalkylamido sulfonate) which was identified in 9 out of 11 foams and also identified by previous studies, and perfluoroalkyl sulfonates as the most frequently occurring compounds including PFOS and PFBS. Perfluoroalkyl carboxylates and fluorotelomer sulfonates were also identified. This study also used total organofluoride-combustion ion chromatography to measure total ion content. Comparison of fluorine content in quantified compounds identified and author’s measured organofluorine concentration revealed that for half of the samples, only compounds comprising less than 10% of total fluorine were identified. Additionally, they conducted a 42-day biodegradation test of 6:2 fluorotelomer thioether amido sulfonate using activated sludge inoculum and withdrew samples periodically to identify metabolites using GC/MS. Perfluoroalkyl carboxylates, fluorotelomer carboxylates, and fluorotelomer sulfonates were among byproducts.

D’Agostino and Mabury subsequently identified a total of 103 AFFF-related compounds in ten AFFF formulations, including 22 classes of perfluoroalkyl substances with few or no reported identification in published studies as of 2014 [65]. The major groups of compounds identified in AFFFs were fluorotelomer thioether amido sulfonates including previously unreported 10:2, 12:2, and 14:2 forms, fluorotelomer sulfonamide betaines with or without acetic acid groups, fluorotelomer betaines including previously unreported perfluoroalkyl chain lengths of 11 and 13, fluorotelomerthiohydroxyl ammonium, perfluoroalkylsulfonamido amino carboxylates and perfluoroalkylsulfonamido amine oxides. Authors conclude that the tremendous number of perfluoroalkyl substances including intermediates, side products, and/or degradation products complicate the analysis of AFFF-related compounds likely existing in the environment and their biodegradation potential. Foams from the same manufacturer did not necessarily contain the same components.

The fluorinated surfactant Forafac®1157, manufactured by DuPont (Wilmington, DE), has been identified by Moe et al. as a 6:2 fluorotelomer sulfonamide alkylbetaine with molecular formula $C_{15}H_{20}F_{13}N_2O_4S$ [66]. This is one surfactant that may be used in AFFF formulations. The deprotonated form of the fluorotelomer betaine Forafac® 1157 was detected by Place and Field as well as D'Agostino and Mabury. From these studies, a number of primary compounds in AFFFs have been identified as well as potential biodegradation products. Increasing accuracy in analytical methods may allow for continued detection of new compounds, for example of shorter-chain analogues [63]. It should be noted that although these studies have successfully identified likely AFFF fluorinated compounds as well as biodegradation products, controlled biodegradability testing was not performed to observe biodegradation rates.

3.6 Biodegradability

Biodegradability is a measure of the extent to which microorganisms may aerobically or anaerobically degrade a substance. The microorganisms in natural water and soil degrade pollutants with a carbon source, in "the most important degradative mechanism for organic compounds in nature" [67]. This measure of biodegradability is used to assess the persistence of a substance in the environment and is often used in conjunction with toxicity data to evaluate environmental threats. In addition to a substance's persistence, other concerns may include the toxicity of any intermediates formed during degradation. Studies to measure biodegradability can offer kinetic data somewhat representative of a realistic degradation environment, though variables such as pH, temperature, salinity, dissolved oxygen content, concentrations of organics, microorganism content, and other nutrients or metals present also impact biodegradation rates in the environment [67].

The biodegradability of fire fighting foams is particularly relevant due to the release of foams into the environment through the course of their use. In addition to entry into surface water bodies or groundwater, this foam may reach stormwater drains and enter wastewater treatment facilities, where biodegradation plays a major role during traditional biological treatment. Knowledge of the biodegradability of foams and the impact their organic content would play in a wastewater treatment facility is important.

3.6.1 Standard Tests of Biodegradability

There are a number of accepted tests to evaluate biodegradability of compounds based on different analytical methods. Tests involve the inoculation of the aqueous test substance with bacteria and incubation for a time period during which measurements are made to monitor carbon dioxide produced during bacterial digestion, decreases in the carbon content of the solution, or oxygen uptake under aerobic conditions. The test substance must be the only carbon source in the sample.

The international Organization for Economic Co-operation and Development (OECD) has published guidelines for six such tests to screen chemicals for "ready biodegradability" [68].

Ready biodegradability tests run for 28 days and measure mineralization of carbon-containing substances by monitoring carbon content reduction, CO_2 production, or oxygen consumption. Readily biodegradable substances must meet a 60-70% threshold of organic carbon reduction, CO_2 production, or O_2 consumption. Table 4 lists the six OECD 301 tests, their analytical parameters used to measure biodegradation, details of the calculation of biodegradation, and pass levels. Pass levels must be met within a 10-day window within the 28-day test, which begins when biodegradation has reached 10%. If the pass level is not met during the 10-day window, the test may be continued for the 28 days and the substance may be regarded as biodegradable if it meets the pass level in 28 days, but not readily biodegradable. In OECD ready biodegradability tests, a high concentration of the test substance (2-100 mg/L) is typically used and conditions are considered to be very stringent. Respirometric tests involve the continuous supply of oxygen to test substance at a monitored rate throughout test duration.

Table 4: OECD guidelines for testing of ready biodegradability, adopted July 1992 [68]

Number	Name	Analytical Parameter	Biodegradability Calculation	Pass Level*
301A	DOC Die Away	Dissolved organic carbon (DOC)	$1-\left(\frac{DOC_t - DOC_{blank,t}}{DOC_0 - DOC_{blank,0}}\right)$	70%
301B	CO_2 Evolution (Modified Sturm)	Respirometry: CO_2 production	$\frac{mg\ CO_2 produced}{ThCO_2 \cdot mg\ test\ substance}$ or $\frac{mg\ CO_2 produced}{mg\ TOC\ in\ test\ substance\ \cdot 3.67}$	60%
301C	Modified MITI	Respirometry: Oxygen consumption	$\frac{BOD}{ThOD}$	60%
301D	Closed Bottle	Respirometry: Dissolved oxygen	$\frac{BOD}{ThOD}$ or $\frac{BOD}{COD}$	60%
301E	Modified OECD Screening	Dissolved organic carbon	$1-\left(\frac{DOC_t - DOC_{blank,t}}{DOC_0 - DOC_{blank,0}}\right)$	70%
301F	Manometric Respirometry	Oxygen consumption	$\frac{BOD}{ThOD}$ or $\frac{BOD}{COD}$	60%
*Pass level must be met within a 10-day period during the 28-day test, beginning on the day that 10% biodegradation is achieved				

Equation 1 shows carbon consumption and carbon dioxide production during biodegradation for a completely mineralized carbon source. This simplification does not consider compounds containing any number of other elements in solution which may exert a variable oxygen demand (and produce carbon dioxide). Equations 2 [69] and 3 [68] are used to calculate theoretical oxygen demand (ThOD) and theoretical carbon dioxide (ThCO$_2$) for use in biodegradability calculations.

$$C + O_2 \rightarrow CO_2 \qquad \text{(Equation 1)}$$

$$ThOD\left(\frac{mg\ O_2}{mg\ test\ substance}\right) = \frac{16\left[2C+\frac{H-Cl-3N}{2}+3S+\frac{5P}{2}+\frac{Na}{2}-O\right]}{Molecular\ weight} \qquad \text{(Equation 2)}$$

$$ThCO_2\left(\frac{mg\ CO_2}{mg\ test\ substance}\right) = mg\ TOC\ in\ test\ substance\ \cdot 3.67 \qquad \text{(Equation 3)}$$

In instances where theoretical oxygen demand (ThOD) or carbon dioxide production (ThCO$_2$) may not be calculated (ie, substance identity is unknown), replacement parameters based on chemical oxygen demand (COD) or total organic carbon (TOC) may be used. However, OECD warns that if COD tests do not fully degrade all carbon sources in the test substance, falsely high biodegradability percentages may result. In all tests, blanks are run in parallel and test substances are corrected for blanks' values (O$_2$ consumption, CO$_2$ production, DOC) prior to calculations of biodegradability [68].

Pass levels for tests based on oxygen uptake or carbon dioxide production are lower than for tests tracking organic carbon since a portion of the carbon in the test substance is converted to biomass, resulting in lower observed CO$_2$ production or O$_2$ consumption. There have been suggestions to reduce the respirometric pass level to 50%, but this change has not been made [70]. A test substance deemed readily biodegradable after passing one of these tests is assumed to degrade rapidly and ultimately in the environment, at which point no further testing is typically needed [68]. Since test conditions are stringent, negative test results may indicate a need for further testing in the form of a simulation test more representative of the specific environmental conditions expected (surface water or groundwater with other organics present, soil type) or an inherent biodegradability test allowing microbial acclimation, longer exposure times, or low test substance to biomass ratios. Ready biodegradability tests do not consider rate constants, contributing to test stringency. Tests may be more or less appropriate for various test substances based on the analytical parameter selected, concentration of test substance or inoculum, or available equipment.

3.6.2 Biodegradability Standards for Fire Fighting Foams

The National Fire Protection Association (NFPA) publishes a series of standards for various aspects of fire prevention, treatment equipment, and operations. Standards relevant to fire fighting foams (composition, not application or apparatus) include NFPA Standard 11 for Low-, Medium- and High-Expansion Foams, Standard 18 and 18A on Wetting Agents and Water Additives, and Standard 1150 on Foam Chemicals for Fires in Class A Fuels [20, 71-73]. Like all

NFPA Standards, these are recommendations made by boards of technical experts, company representatives, and other members representing a balance of interests. NFPA is an international nonprofit organization seeking to "reduce the worldwide burden of fire and other hazards on the quality of life by providing and advocating consensus codes and standards, research, training, and education" [75]. In order to hold force of law, NFPA standards must be referenced by statute or statutory code (e.g. building code or fire code).

NFPA Standard 11 features an annex devoted to Foam Environmental Issues included for informational purposes. Primary environmental concerns are identified as "toxicity, biodegradability, persistence, treatability in wastewater treatment plants, and nutrient loading" [71]. It is noted that fluorochemical surfactants are known to biodegrade slowly and/or only partially, and specifically the fluorine-containing components are likely to remain undegraded and may continue to foam or pose toxicity issues. The importance of cleanup of foam waste from training exercises is stressed. To this end, many foam manufacturers offer training foams to mimic foaming during application but which do not contain the active fluorinated surfactants. In NFPA Standard 11, this biodegradability information is included in an annex for informational purposes only and no biodegradability standards are set for foams.

Since fire fighting foam concentrates are considered water additives, they are included in Standard 18 on Wetting Agents and Standard 18A on Water Additives for Fire Control and Vapor Mitigation. In both standards, mammalian and fish toxicity are specified and biodegradability is addressed [72-73]. Wetting agents should be biodegradable in accordance with EPA Office of Prevention, Pesticides, and Toxic Substances document 835.3110 [74], Section M, a CO_2 Evolution (Modified Sturm) Test when tested for 28-42 days. This is the same as the OECD 301B test. If the 60% threshold is met within 28 days, the substance is readily biodegradable. If met within 29-42 days, it may be considered biodegradable. This longer time frame differs from the OECD definition of "ready biodegradability" which is based on a 10-day window within a 28-day test. Again, this NFPA guideline holds no force of law until referenced in a statutory code manufacturers must comply with.

The same NFPA biodegradability standard is set in NFPA Standard 1150 for Foam Chemicals for Fires in Class A Fuels—60% CO_2 evolved in 28 or 42 days [20]. Class A fires include combustible material such as wood or cloth, and in particular structural fires or outdoor fires in wooded areas. For these fires, water use is also appropriate and foams may be used when specific conditions warrant their use. This standard is relevant if wildland fires are considered to include the most vulnerable environmental areas (i.e. where releases may be unlikely to reach wastewater treatment facilities and would instead partition to groundwater, surface water, soil, or air) and the biodegradability recommendations made in NFPA 1150 are considered to be the most stringent required with regards to the environmental threats posed by foams.

Foams used by the U.S. military must meet performance and quality requirements set forth in MIL-F-24385 [21]. Biodegradation of at least 65% as defined as BOD_{20}/COD must be met. Manufacturers may offer AFFF products for civilian use as well as an AFFF product meeting this military specification.

3.6.3 Manufacturer-Reported Biodegradability of Fire Fighting Foams

Some manufacturers disclose BOD, COD, TOC, and/or biodegradability information for their products. Some give direct values for COD and 5-day or 20-day BOD, others report biodegradability percentages directly. Table 5 summarizes biodegradability data available from MSDS available online from Chemguard, National Foam, Angus, and Ansul for select AFFF, AR-AFFF, and FP foams [26-30, 34-42, 76-80]. These foams were selected to represent 3% foams from each manufacturer for general applications (i.e. not specialized formulas for low viscosity, cold temperatures, etc) and not all foams were evaluated for each manufacturer before selecting these particular foams. Therefore, these foams may not necessarily be representative of all foams available. If a foam is the only 3% formulation for that type (AFFF, AR-AFFF, or FP) from a particular manufacturer, this is indicated in Table 5 by an asterisk. From National Foam, there is no AFFF/AR-AFFF combination both named “Aer-o-lite” or “Aer-o-water” so these are instead compared to one another. Military Specification AFFFs are included for Chemguard, National Foam, and Angus. BOD and COD values are provided for foam concentrates and not for foam concentrations applied to fires. Values provided in units other than kg O_2/kg test substance were converted to these for comparison among manufacturers, using specific gravities available in product MSDS’s and no rounding was performed. If a range of specific gravities was provided, the median value was used for calculations.

Table 5: Selected biodegradability data reported by foam manufacturers [26-30, 34-42, 76-80]

Manufacturer/ Foam	COD, mg O_2/kg test substance	BOD$_{20}$ mg O_2/ kg test substance, Other BOD Test Durations Noted	Ratio of BOD/COD, %	Additional Notes Reported on MSDS
Chemguard				
3% AFFF (C303)*	205781	78197	38	
3% Mil Spec AFFF (C301MS)*	241458	306673	127	
3% AR-AFFF (C333)	982318	782908	80	
3x3% AR-AFFF (C135)	304000	141000 (BOD$_5$)	46	
3% Fluoroprotein (CP2302)*	Not Reported			
National Foam				
Aer-o-lite 3% AFFF *(Only "Aer-o-X" 3%)	400000	239000 (BOD$_5$)	60	
Aer-o-water 3% Mil Spec AFFF*	516000	480000	93	
Universal gold 3% AR-AFFF	290000	91500 (BOD$_5$)	32	
Centurion 3% AR-AFFF	243000	91000 (BOD$_5$)	37	
Aer-o-Foam XL 3% FP	760000	158000 (BOD$_5$)	21	
Angus				
Tridex 3% AFFF	Not Reported			Product is biodegradable
Tridol 3% AFFF	637000**	220000 (BOD$_5$)	35	Readily biodegradable
Tridol 3% Mil Spec AFFF*	518533	Not Reported	67	
Tridex 3% AR-AFFF	243000	91000 (Unknown Test Duration)	37	Product is biodegradable
Tridol 3% AR-AFFF	Not Reported			Product is biodegradable
FP70 Plus 3% FP*	460000	440000 (Unknown Test Duration)	96	Readily biodegradable
Ansul				
Ansulite 3% AFFF (AFC-3-A)	Not Reported			
Ansulite Premium 3% Mil Spec AFFF (AFC-5-A)				
Ansulite 3% AR-AFFF	Not Reported			
3% FP	Not Reported			

*This is the only 3% formulation of this type listed by manufacturer online

**Angus Tridol 3% AFFF has reported COD of 0.65 g/L and BOD$_5$ of 0.22 g/g. Based on the specific gravity of 1.02, these correspond to COD of 637 mg O_2/kg test substance and BOD$_5$ of 220,000 kg O_2/kg test substance, resulting in a biodegradability ratio far exceeding 1. Reporting error is likely in this case. If units were both g/g, the BOD$_5$/COD ratio would lead to a calculated biodegradability of 35% (reported in Table 5)

Each manufacturer's military specification AFFFs exceeded the non-military specification AFFFs in reported biodegradability by 55% (National Foam), 97% (Angus), and 334% (Chemguard). This is due to the 65% minimum BOD_{20}/COD biodegradability value required for military specification Class B Foams [21], where non-military AFFFs must meet no specific biodegradation value. Although NFPA has published standards 18, 18A, and 1150 which do specify 60% biodegradability, no enforceable biodegradability standards are currently in place for fire fighting foams for civilian use.

Excluding military specification AFFFs, biodegradability of Chemguard AR-AFFF exceeded their biodegradability of their AFFF, while National Foam AR-AFFF had lower reported biodegradability than their AFFF. Angus AFFF and AR-AFFF were comparable. Based on these results, no clear conclusions regarding differences in AFFF, AR-AFFF, or FP biodegradability can be formed. Stabilizers and inhibitors used in FP foams could contribute to reduced biodegradability.

Chemguard's military specification 3% C301MS AFFF has reported BOD_{20} and COD that would result in a biodegradability level greater than 100%; that is, the BOD is greater than the COD. Theoretically, COD should be a measure of maximum oxygen demand if COD reagents are strong enough oxidants, and BOD is assumed to be a value lower than this COD. Excluding the possibility of human error in testing or reporting, this suggests COD is not an accurate measure of the total possible oxygen demand. Indeed, such a high BOD indicates that this foam is very biodegradable. But without accurate COD measures to represent a total possible oxygen demand, biodegradability calculations of the ratio of BOD:COD may be falsely high, in this case exceeding 100%.

3.6.4 Published Biodegradability Testing of Fire Fighting Foams and Fluorinated Surfactants

A limited amount of testing of the biodegradation of fire fighting foams has been done in recent years. Some studies on fire fighting foams specifically have been conducted, others on the biodegradability of fluorosurfactants that may also be used in other industries, and recently many on the biodegradation of specific fluorocompounds likely to be ingredients of telomer-based foams or their byproducts. Varying degrees of biodegradability were observed in these studies, due to differences in starting concentration and possible toxicity effects on microorganisms, testing procedures, and inoculum sources.

A 2012 study by Zhang et al. found 89%, 85 %, and 89% biodegradation of three (unnamed) Class A foams in 28 days according to the CO_2 Evolution Test (OECD 301B), starting with foam concentrations of 15 mg/L [23]. Zhang et al. used activated sludge to inoculate tests. Theoretical carbon dioxide values were calculated based on measured TOC using Equation 3.

A 2010 study by Tureková and Balog found much lower biodegradation values for four AFFFs, from 0.23% to 0.47%, using a 5-day standard BOD test and standard dichromate test to obtain their BOD_5/COD ratio [24]. However, concentrations were much higher in the Tureková and Balog study—between 1% and 3% in water as applied to fires, which corresponds to 10,000-30,000 mg foam concentrate/L. Overwhelming of bacteria with high concentrations likely resulted in dissolved oxygen depletion and bacterial death since a continuous supply of oxygen was not provided to BOD bottles, or toxicity may have played a role since some solvents in foams may be toxic in high concentrations. Falsely low biodegradation results are suspected.

A study by Król et al. with 40 foam concentrates using a modified manometric respirometry method (OECD 301F) was performed to compare biodegradability of synthetic, protein, fluoroprotein, AFFF, AR-AFFF, and film forming fluoroprotein (FFFP) foams from manufacturers in seven countries [25]. BOD was evaluated at 5 and 20 days and compared to COD, using concentrations from 0.77 g/L to 3.50 g/L to target COD values close to 1000 mg/L. These concentrations represent a small fraction of typical foam formulation concentrations, which would be in the range of 10-60 g/L (1-6% foam). Biodegradability values after 5 days range from 9-50% and 18-92% after 20 days. Six AFFFs from five manufacturers had measured biodegradation of 23-31% in 5 days and 50-76% in 20 days. For four AR-AFFFs from four manufacturers: 10-23% in 5 days and 28-58% in 20 days. For four FPs from three manufacturers: 14-18% in 5 days and 30-42% in 20 days. Król et al. used activated sludge inoculum from a local wastewater treatment facility, and aerated the sludge for 72 hours but did not preadapt it to the test substances.

With the 5-day biodegradation information, the study by Król et al. can be compared to that of Tureková and Balog (5-day not reported by Zhang et al.). One foam, Shthamex F-15 3% AFFF (Germany), was studied by two groups-- Tureková and Balog report 0.34% biodegradability in 5-days, while Król et al. report 31% in 5 days and 58% in 20 days [24-25]. Much higher AFFF biodegradability was observed by Król et al., again likely due to dissolved oxygen depletion caused by Tureková and Balog’s high concentrations.

Król et al. also compared the biodegradation of different types of foams, developing the ranking of foam types in order of decreasing biodegradability reported as BOD_{20}/COD: Synthetic > AFFF > Class A > AR-AFFF > FFFP > FP > P. Synthetic, AFFF, and Class A foams were found to be more easily biodegraded than other types, including protein foams. This greater biodegradability of synthetic foams compared to protein foams was not anticipated since protein foams are made from natural proteins and are advertised as biodegradable. Król et al. note that Devonshire [81] and Ruppert et al. [82] have suggested that low biodegradability of protein foams may be caused by the presence of iron (II) sulfate, zinc (II) chloride, hexylene glycol, preservatives, and any protein hydrolysis products formed.

A caveat must be considered when regarding biodegradability reports that include COD or TOC analysis as opposed to ThOD or calculated carbon content. Due to the strength of the C-F bond there is reason to question whether COD or TOC analysis has broken these bonds in fluorinated components of fire fighting foams. If not, carbon bound to fluorine will not be measured by these tests and COD or TOC values will be falsely low, leading to falsely high biodegradability calculations. The possibility that COD tests using dichromate oxidation do not accurately measure total chemical oxidation has been acknowledged by many sources, including OECD, EPA, and NFPA publications. This was a general statement made, not specific to fluorinated compounds. Standard Methods for Water and Wastewater Analysis lists pyridine, volatile aliphatics, and related compounds as resistant to the standard dichromate COD test [69].

If a test substance's chemical structure is known biodegradability calculations can ideally use theoretical oxygen demand or calculated carbon content. However, since foam concentrate compositions are proprietary information and unique to each formulation, biodegradability calculations must rely on COD and TOC tests. One or the other may be more or less effective for analysis of fluorocarbons. If there are any inaccuracies in the results from Król et al. showing synthetic foams as the most biodegradable, they would likely be due to the inability of the COD testing to fully oxidize all of the foam. The authors do state that the measured COD values are in line with manufacturers' reported COD values.

Based on results from Król et al. and Zhang et al., it seems that significant biodegradation occurs. The obvious question is whether this includes solvents, hydrocarbon surfactants, and other additives only or if fluorinated compounds with strong C-F bonds are biodegraded. In many foam formulations, fluorinated components represent a small percentage of the overall components. Table 6 lists the reported percentages of fluorinated surfactants in foams from Table 5. From this, it appears that the concentration of fluorinated surfactants in a foam concentrate is typically less than 10% by weight though this is not an inclusive list and some manufacturers do not disclose any information on fluorine-specific concentrations.

If significant biodegradation of all non-fluorinated components occurs, this may dwarf the level of biodegradation of the fluorinated components—or possible lack of biodegradation. This is also noted by Król et al., who explain that the biodegradation of other components, either solvents or additives, impact overall biodegradation substantially even if fluorinated components "probably do not undergo complete degradation in the environment" [25]. A substance that passes a ready biodegradability test may have achieved full biodegradation of all non-fluorinated components while undergoing a lesser degree of biodegradation of fluorinated components.

Table 6: Selected fluorinated component content data reported by foam manufacturers [26-30, 34-42, 76-80]

Manufacturer/Foam	**Fluorinated Surfactant Listed**	**Weight % of Fluorinated Surfactant**
Chemguard		
3% AFFF (C303)	Proprietary fluorosurfactant	Not Listed
3% Mil Spec AFFF (C301MS)	Fluorosurfactant	Proprietary
3% AR-AFFF (C333)	Proprietary fluorosurfactant	Proprietary
3x3% AR-AFFF (C135)	Proprietary fluorosurfactant	Not Listed
3% Fluoroprotein (CP2302)	Fluorosurfactants	<5
National Foam		
Aer-o-lite 3% AFFF	Fluoroalkyl surfactant	0.5-2.0
Aer-o-water 3% Mil Spec AFFF	Fluoroalkyl surfactant	0.5-2.0
Universal gold 3% AR-AFFF	Fluoroalkyl surfactant	0.5-2.0
centurion 3% AR-AFFF	Fluoroalkyl surfactant	0.5-2.0
Aer-o-Foam XL 3% FP	Fluoroalkyl surfactant	0.1-0.5
Angus		
Tridex 3% AFFF	Fluoroalkyl surfactant	0.5-2.0
Tridol 3% AFFF	Fluorosurfactant	5-10
Tridol 3% Mil Spec AFFF	Fluorosurfactant	5-10
Tridex 3% AR-AFFF	Fluoroalkyl surfactant	0.5-2.0
Tridol 3% AR-AFFF	Fluoroalkyl surfactant	1-5
FP70 Plus 3% FP	Surface active agents and fluorosurfactant	1-5
Ansul		
Ansulite 3% AFFF (AFC-3-A)	Other components below reportable levels	>90
Ansulite 3% AR-AFFF	Other components below reportable levels	>90
3% FP	Other components below reportable levels	>90

3.6.5 Published Biodegradability Testing of Related Poly- and Perfluorinated Compounds

A number of studies have investigated microbial degradation of fluorinated compounds, some of which are used as replacements for PFOA or PFOS, some are raw materials or degradation byproducts of these or other fluorinated surfactants, and some are possible firefighting foam components. Review articles are available that summarize specific strains of microorganisms that are capable of defluorinating fluoroaliphatics and fluoroaromatics to varying degrees [83-84] though these are not fire fighting foam specific. A review by Parsons et al. concludes that aerobic defluorination is thermodynamically possible although microorganisms obtaining useful energy from this defluorination have not yet been identified since halogenated substances require cometabolism [85]. The comparison is made between this thermodynamically favorable defluorination and successful microbial dechlorination demonstrated by Dolfing, among others, for compounds such as 2-chlorobenzoate (see Table 7) [86]. Anaerobic biodegradation of fluorinated compounds is more thermodynamically favorable than aerobic [85].

Table 7: Gibbs free energy values for reductive dehalogenation [86]

Reaction	ΔG° (kJ/mol)	
	Defluorination	Dechlorination
2-Halobenzoate + $H_2 \rightarrow$ Benzoate + H^+ + halide$^-$	-132	-145
3-Halobenzoate + $H_2 \rightarrow$ Benzoate + H^+ + halide$^-$	-138	-137
4-Halobenzoate + $H_2 \rightarrow$ Benzoate + H^+ + halide$^-$	-142	-144

Liou et al. attempted reductive defluorination of PFOA (average oxidation state of +2.25) under anaerobic conditions using five different microbial populations (activated sludge, industrial site soil, agriculture soil, soils from two fire training sites) [87]. Cometabolism of PFOA with trichloroethylene and with nitrate, iron, sulfate, and methanogenesis was also attempted. PFOA concentrations were observed to decrease and fluoride ions were detected, however, no metabolites could be successfully identified and without evidence of changes to the molecular structure of PFOA, authors conclude that PFOA is inert under the tested conditions. This conclusion is contrary to thermodynamic indications that anaerobic defluorination will occur.

Quinete et al. studied the biological (aerobic) and chemical degradation of “new substitutes for perfluorinated surfactants” using the manometric respirometry test and a UV/hydrogen peroxide advanced oxidation process (AOP) [88]. These included perfluorobutane sulfonate (PFBS) which is a 4-carbon perfluorinated analog of PFOS, two fluoroaliphatic esters NOVEC FC-4430 and NOVEC FC-4432 from 3M, and fluorosurfactant Zonyl from DuPont. With the manometric respirometry testing, biodegradation of 25, 28, 13, 40, and <1% were seen for the two fluoroaliphatic esters, fluorosurfactant Zonyl, 10-(trifluoromethox)decane-1 sulfonate, and PFBS, respectively. During AOP testing authors linked fluoride ion increase over time to TOC decrease, as the carbon structure degraded and fluorine was liberated. PFBS was degraded only 1.5% by UV/H_2O_2 and 1% of theoretical fluorine content was liberated. For the two fluoroaliphatic esters and fluorosurfactant Zonyl, degradation with UV and UV/H_2O_2 led to fluoride ion liberation equivalent to 6, 10, and 16 weight percent of the total organic content of solutions. Authors were not able to quantify the degree of defluorination for these since compounds’ identities are proprietary. For 10-(trifluoromethox)decane-1 sulfonate, full degradation and 96% defluorination were observed with UV degradation (without H_2O_2). These results indicate that biodegradation ranges for various fluorinated compounds are broad, AOP of these do not necessarily increase degradation (as for PFBS), but some C-F bond cleavage and fluoride liberation does occur using UV exposure or UV/H_2O_2.

A 1996 study by Remde and Debus on the biodegradation and defluorination of three fluorosurfactants, including PFOA, according to the closed-bottle test (OECD 301D) compared biodegradation activated sludge inoculum from three domestic wastewater plants serving populations of 1,000, 15,000, and 30,000 individuals [89]. This study also ran a number of controls in parallel with their test substances: an inoculum blank (nutrient media and inoculum), procedural control (nutrient media, inoculum, and reference compound), toxicity control (nutrient media, inoculum, reference compound, and test substance), and abiotic sterile control (nutrient media, inoculum, test substance, and sterilizing agent). The toxicity control in particular is of interest here since toxicity effects is one possible reason for the range of biodegradability values for firefighting foams found in published studies. Under aerobic conditions, their Surfactant 1 (a combination of fluorosurfactants with 10 wt% fluorine) was found >80% biodegradable. Surfactant 2 (a highly fluorinated oxethylate, ~50 wt% fluorine) was found increasingly biodegradable by activated sludge from increasingly larger wastewater plants—28, 52, and 77% biodegradable by the 1,000, 15,000, and 30,000-person facilities. Since the largest plant treated industrial wastewater in addition to domestic, increased biodegradation with that sludge may have been due to greater microorganism population diversity or better adaptation to fluorinated or halogenated compounds. With the three sources of sludge, no differences in the time course of biodegradation was observed, indicating no impact of differing toxicity requiring different acclimation periods or initial inhibition. PFOA (Surfactant 3, 51.3 wt% fluorine) was not degraded by any of these sources of inoculum. Authors report that none of these fluorosurfactants (concentrations of 100 mg/L) showed negative influence on the activity of microorganisms.

In a Closed Bottle Test (OECD 301D) of 8 perfluorocarbons and 3 fluorotelomers (carbon chain lengths 4-10) throughout aerobic and anaerobic conditions over 15 weeks, Saez et al. observed some possible but inconclusive evidence of aerobic degradation of perfluorohexanoic acid, 6:2 fluorotelomer and 8:2 fluorotelomer since these concentrations also decreased during their controls [90]. A study on the biodegradation of 2-N-ethyl(perfluorooctanesulfonamido)ethanol by bacteria in marine sediments over 120 days identified multiple perfluorinated metabolites including PFOS [91].

Fluorotelomer alcohols have been an area of significant focus, including aerobic biodegradation of 6:2 fluorotelomer alcohol [92] and 8:2 fluorotelomer alcohol [93-95]. Some studies have identified metabolites indicating the removal of some CF_2 groups in soil, activated sludge, and mixed bacterial culture. The 8:2 fluorotelomer alcohol aerobic biodegradation pathway proposed by Wang et al. indicates stable metabolites including PFOA and perfluorohexanoic acid [95]. Average PFOA yield from 8:2 fluorotelomer in soil after 90 days was 25%, based on a carbon mass balance [95]. Fluoride ion formation after 90 days corresponded to 12% biodegradation of the 8:2 fluorotelomer alcohol [93].

An aerobic biodegradation pathway was proposed for 6:2 fluorotelomer also [92]. The major metabolites of 6:2 fluorotelomer alcohol in mixed bacterial culture after 28 days were 6:2 fluorotelomer unsaturated acid and 5:2 secondary alcohol. Interestingly, 6:2 FTOH half life in mixed bacterial culture was estimated at 1.3 days and major metabolite concentrations were found to stabilize within 14-28 days which may have been due to adsorption to test vessels. Fluoride detection in mixed bacterial culture after 90 days corresponding to 16% biodegradation of 6:2 FTOH was reported. Major metabolites of aerobic degradation in soil were perfluoropentanoic acid and 5:3 polyfluorinated acid. Other metabolites from both microbial populations included perfluorohexanoic acid, perfluorobutyl acid, and 6:2 fluorotelomer saturated acid, as well as temporary intermediates.

These biodegradation studies indicate that some biodegradation of fire fighting foam-related fluorocompounds may occur under aerobic conditions, with the thermodynamic potential to occur under anaerobic conditions as well. In either case, biodegradation is not likely to lead to complete defluorination or mineralization. Based on identified metabolites of some studies, biodegradation does not lead to complete mineralization, e.g. even in the 180-day, long-term study of 6:2 fluorotelomer alcohol [92]. Instead, stable byproducts are formed in what may be rapid initial biodegradation. Some products formed may pose persistence or toxicity threats equivalent to or greater than those of the parent compound. In particular, the formation of PFOA and other perfluorinated compounds during the biodegradation of fluorotelomer alcohols can contribute to PFOA presence in the environment.

3.7 Foam Ultimate Fate or Disposal

Fire fighting foams are not classified as hazardous material during disposal and therefore are not regulated by the EPA under the Emergency Planning and Community Right-to-Know Act (EPCRA) [96]. There are no official EPA procedures for foam disposal, either in the form of foam concentrate that is expired or no longer desired, or in wastewater after fire application. Foam concentrate MSDSs often recommend only to dispose of foam concentrate or solution in accordance with federal, state or provincial, and local regulations. In the case of large spills, these should be absorbed on non-combustible material such as vermiculite, sand or earth, then transferred to a sanitary landfill for disposal [78]. Some MSDSs recommend spills be reported to the National Response Center and state and/or local agencies, since runoff from fire application can cause pollution [26]. Others consider the treatability of solutions of foam and fuel, recommending users obtain approval before discharging into sewer treatment systems [41]. The release of some components in foams, such as freeze point depressant ethylene glycol in excess of 5000 pounds, must be reported under US EPA Comprehensive Environmental Response Compensation & Liability Act (CERCLA) while others do not, such as glycol ethers [71].

3.7.1 Entry into Wastewater Treatment Plants

When fire fighting foam solutions reach wastewater treatment plants, primary concerns involve excess foaming and high nutrient loading which can both potentially contribute to the release of untreated wastewater to natural water bodies. Very low concentrations of foam concentrate in water, despite the even lower concentrations of actual surfactants in water, may still foam, keeping in mind that some formulations require only 1% foam concentrate and 99% water for their use. This foam can inhibit treatments by creating hydraulic difficulties for equipment or disrupting biological treatment.

Recommended disposal is defoaming or metering solutions into a wastewater treatment plant until sufficiently low concentrations are achieved [43]. In the Environmental Issues Annex of NFPA Standard 11, adequate dilution is specified as a concentration of foam solution in plant effluent not exceeding 1700 ppm. This is a ratio of 588 gallon plant influent per gallon of foam solution. This can be accomplished by the collection of wastewater and dilution to the maximum practical level, then metering of the solution into the sewer at a gradual rate to achieve the appropriate concentration. It is also recommended that discharges should be discussed with individual wastewater treatment facilities since each case differs [71]. However, when applied to fires, collection and gradual metering of wastewater solutions can be a difficult if not impossible task. One exception may be if a fire occurs at a location that has existing storage tanks available to capture the foam wastewater, for example at a chemical plant.

High BOD and COD levels are also likely in wastewaters containing fire fighting foam, which can challenge the effectiveness of biological treatment during secondary wastewater treatment. Perfluorinated chemicals that may be used in older AFFF formulations are known to biodegrade incompletely [43]. Typical BOD_5 levels in domestic wastewater may range from 100-300 mg O_2/L and COD levels from 250-1000 mg O_2/L [97]. For some foams, reported BOD and COD levels largely exceed these values by 1-2 orders of magnitude. Chemguard C-303, an AFFF concentrate composed of 85-90% water, reports a 20-day BOD of 79,800 mg O_2/L and COD of 210,000 mg O_2/L [26]. When proportioned in 3% solution as used, BOD is 2,394 mg/L and COD is 6,300 mg/L—still much greater than that of domestic wastewater. These BOD values are more typical of industrial wastewaters, for example tannery waste which typically has 700-7,000 mg/L BOD_5 [97]. According to the FFFC, accepted practice is to collect and treat fluorine-containing foams that are used for training purposes [98].

3.7.2 Fate in Surface Water, Groundwater, and Soil

Foams can also enter surface and groundwater supplies, and a number of studies have been conducted to quantify the impact of these releases. This can be a serious threat to aquatic organisms or if drinking water supplies are affected. In 1999, perfluoroalkyl carboxylates with six to eight carbon chain lengths were detected at fire-training sites on U.S. military bases in Nevada and Florida in total concentrations from 125 to 7090 μg/L at various sampling wells [99]. Military sites were chosen since the military is the largest U.S. AFFF consumer, resulting in detected concentrations that would be much higher than the average location. At the training sites tested, untreated wastewater containing AFFF used for training activities routinely entered groundwater and surface water. At the time of this study, one site had been inactive for seven years and the other for ten. Perfluorocarboxylates with 6, 7, or 8 carbon chain lengths were identified in varying proportions in different locations. Authors cite C-F bond strength and perfluorocarbon chain rigidity as contributors to the detection of these compounds up to 10 years after their use.

In 2003, groundwater at a Michigan air force base decommissioned 10 years prior was found to contain PFOA, PFOS, perfluorohexanoate, and perfluorohexanesulfonate in concentrations from 3 to 120 µg/L [100]. In groundwater samples from these three U.S. military sites tested in 1999 and 2003, a 2004 study identified 4:2, 6:2, and 8:2 fluorotelomer sulfonates in two of the bases [15]. The maximum fluorotelomer sulfonate concentrations detected in groundwater was 14,600 µg/L. An AFFF sample provided by one military base was analyzed in the same study and concentrations of 6:2 and 8:2 fluoroalkylthioamido sulfonates were estimated to be 12,000 and 6,000 µg/L, respectively. Since these were not detected in groundwater samples from the same base, authors conclude the degradation of fluoroalkylthiomadio sulfonates to fluorotelomer sulfonates is possible.

In these studies, the specific foams used at military sites are unknown. Perfluorinated carboxylates and sulfonates were likely produced with the electrochemical fluorination process and may have originated from 3M foams no longer in production. Fluorotelomer sulfonates identified in AFFF-impacted groundwater in 2004 [15] do not directly match the fluorotelomers identified in AFFF formulations by published studies [62-65], thus these may be degradation products. These studies from fire training facilities focused on detection methods and identification of the range of individual fluorinated compounds and metabolites that may exist. These represent much higher concentrations than would be found in typical groundwater or surface water bodies with the exception of large spills or releases. Concentrations in surface waters may range from picogram to microgram per liter levels [3, 50] and concentrations in drinking water up to micrograms per liter have been detected [3, 50].

The use of PFOA or PFOS-based foams on fires has resulted in contaminated groundwater and drinking water in multiple global occurrences. In these cases, releases have been at areas not on military training facilities and some of these releases have seriously impacted drinking water supplies. Foam use at an airport in The United Kingdom in the 1990's led to elevated PFOS concentrations that remained above 10 µg/L in some local ponds and boreholes as of 2009. Maximum drinking water concentration was 98 µg/L [50].

If fluorinated foams enter groundwater, their interaction with soil plays a role in their transport and persistence. Guelfo and Higgins [101] argue that while sorption and transport of some perfluoroalkyl acids have been studied [102], AFFF-specific solutions must be understood.

These may include fluorinated and hydrocarbon surfactants as well as foam solvents and stabilizers and a mixture of any unspent fuel. Microbial populations in soil may contribute to degradation and form a complex mixture of metabolites. Competitive adsorption of these co-contaminants and metabolites must be considered. In this study, authors concluded that carbon chain length impacts transport and co-contaminants generally increased sorption to soil.

4. Procedures

4.1 Chemicals

Pentadecafluorooctanoic acid (PFOA, 96%), 2,2,3,3,3-pentafluoro-1-propanol (97%), ethyl trifluoroacetate (99%), heptadeca fluorooctanesulfonic acid (PFOS, 40% in water), 2,2,2-trifluoroethyl perfluorobutyl sulfonate (95%), and 1H,1H,2H,2H,-perfluoro-1-decanol (8:2 fluorotelomer alcohol, 97%) were purchased from Sigma Aldrich (St. Louis, Missouri). Linear formulas are given in Table 8. Fire fighting foams concentrates purchased were manufactured by Ansul (Marinette, Wisconsin), a Tyco International Company: Ansulite 3% AFFF (AFC-3A) (product code 1010-2-016 Ana), Ansulite ARC 3x6 AR-AFFF (1011-2-032 ANa), and Ansul 3% Fluoroprotein (FP) Foam (1050-3-001 SBg). Intended foam proportioning is 3% in water for AFFF and FP, and either 3% or 6% for AR-AFFF. Reagent water was prepared using a Thermo Scientific Barnstead Nanopure Life Science UV/UF system with TOC analyzer, for which effluent TOC was ≤ 5 ppb.

Table 8: Test substances

Test Substance	Linear Formula
Pentadecafluorooctanoic acid (PFOA)	$CF_3(CF_2)_6COOH$
2,2,3,3,3-Pentafluoro-1-propanol	$CF_3CF_2CH_2OH$
Heptadecafluorooctanesulfonic acid (PFOS)	$CF_3(CF_2)_7SO_3H$
Ethyl trifluoroacetate	$CF_3COOC_2H_5$
2,2,2-trifluoroethyl perfluorobutylsulfonate	$CF_3(CF_2)_3SO_3CH_2CF_3$
8:2 fluorotelomer alcohol (FTOH)	$CF_3(CF_2)_7CH_2CH_2OH$

4.2 Solution Preparation

Solutions of 100 milligrams fluorinated test substance per liter of water purified with the Thermo Scientific ultrafiltration system were prepared. This concentration was used for most tests. Solubility of two fluorinated compounds, 2,2,2-trifluoroethyl perfluorobutyl sulfonate and 8:2 fluorotelomer alcohol, did not allow preparation of 100 mg/L solutions. For these two substances, solutions were prepared decreasing in concentration from 100 mg/L to 5 mg/L but remained above saturation concentrations. For 8:2 FTOH, this is confirmed by the reported solubility value of 0.137 mg/L at 21°C [103]. A solubility value for 2,2,2-trifluoroethyl perfluorobutylsulfonate was not available. Measurement of COD or TOC of solutions less than 5 mg/L would be below the lower bounds of the sensitivities of the methods and instrument and therefore testing of these solutions was not continued.

Table 9 gives foam concentrate specific gravities, based on the most current available Ansul MSDS, and concentrations in water that correspond to the 3% solution applied to fires.

MSDS's are in Appendix A. Solutions of 100 mg/L were used for biodegradability testing in the current study, more than 300 times diluted from concentrations used for fire applications.

Table 9: Foam concentrate specific gravities and concentrations for 3% solution [78-79]

Foam Concentrate Type	Specific Gravity	3% Solution Concentration, mg Foam Concentrate/L water
AFFF	1.02	30,600
AR-AFFF	1.00	30,000
Fluoroprotein	1.15	34,500

All glassware was washed with detergent and rinsed with purified water six times. Glassware used for TOC analysis was acid-washed in 20% sulfuric acid (minimum of 2 hrs) and rinsed with purified water six times. Glassware was confirmed to be organic free using TOC analysis of purified water in cleaned glassware.

4.3 Analytical Methods

Organic carbon content and chemical oxygen demand were used as measures of organic content in solutions. Samples of known chemical composition were tested using these methods, to first establish the effectiveness of the analytic methods in measuring organic content of fluorinated compounds. Theoretical and measured values could be compared. Subsequently, the foam samples of unknown chemical composition were measured. Free fluorine in solution was measured using ion chromatography.

4.3.1 Chemical Oxygen Demand

Chemical oxygen demand was measured using dichromate oxidation with Bioscience, Inc. (Allentown, PA) low-range (5-150 mg COD/L) accu-Test vials which contained premixed dichromate reagents. Bioscience COD test vials are consistent with Standard Methods for the Examination of Water and Wastewater Method 5220 for COD analysis.

Samples (2.5 mL per vial) were added to the test vials, the sample vials shaken, incubated at 150°C for 2 hours, and then cooled to room temperature. Using a Cary WinUV spectrophotometer, light absorbance at 440 nm was measured and correlated to COD with a standard curve made with potassium hydrogen phthalate (KHP, E.M. Science, Cherry Hill, NJ) standards with theoretical oxygen demands from 0 to 150 mg O_2/L. When necessary, samples were diluted prior to COD analysis in order to fit within this range.

Two KHP stock solutions were mixed and two calibration curves correlating KHP concentration (and therefore ThOD or COD) to light absorbance at 440 nm were developed. These were found to be nearly identical with R^2 values greater than 0.998. One calibration curve yielded the equation given by Equation 4.

$$COD = (Abs\ at\ 440\ nm - 0.3403)/-0.0023,\ R^2 = 0.9994 \qquad \text{(Equation 4)}$$

4.3.2 Total Organic Carbon

A Shimadzu TOC-5000A Analyzer was used for TOC analysis as non-purgeable organic carbon (NPOC). This analyzer used a high temperature furnace to oxidize all carbon present in solution to carbon dioxide. Test substances were first acidified with HCl (Fisher Chemicals, Fair Lawn, NJ) to convert bicarbonate or carbonate in solution to carbon dioxide. Samples were then sparged with zero-grade carbon dioxide-free air to remove inorganic carbon (CO_2) present in samples.

Solutions were diluted based on known or estimated carbon content to reach final carbon concentrations no greater than 80 mg/L in accordance with the optimum testing range of the TOC analyzer. A new calibration curve using KHP concentrations in the appropriate range was created prior to each round of sample measurement. Samples (10-20 mL) were added to autosampler vials, acidified with 6N HCl (1 uL/mL test solution), and sparged for 3 min. Between 3-5 injections per sample were used for repetitive measurements with an allowable 2.0% coefficient of variation between replicates. The injection syringe was washed 4 times and needle was washed 1-2 times to prevent interference in results from previous samples retained in the equipment. When blanks were run in between samples, no artifacts were observed.

All glassware was organic-free (washed in 1% solution of Fisherbrand Sparkleen 1 laboratory detergent or 20% HCl solution, HCl purchased from Fisher Chemicals). Potassium hydrogen phthalate standards run as samples were included in sampling racks at a frequency of 1 standard per 5-8 samples to verify the accuracy of the calibration curve throughout testing duration. Procedural blanks were used when possible to measure equipment contribution to background TOC.

Sample hold time was minimized when possible, however due to equipment maintenance, samples corresponding to day 14 and 21 of the fluoroprotein DOC die-away test were held up to test day number 28 (7-14 day hold time) until DOC was measured. These were refrigerated and acidified to reduce biological activity. When measured, DOC concentrations of the two FP solutions at days 14 and 21 fell within the anticipated range and these values were used.

4.3.3 Ion Chromatography

Ion chromatography was used to identify fluoride ions in samples. A Thermo Scientific Dionex ICS-2100 ion chromatography system was used with Dionex AS-15 4X150mm analytical column and Dionex AG-15 4X50mm guard column. A Dionex ASRS 300 4mm suppressor and DS6 conductivity cell were used. A calibration curve of fluoride standards purchased from Dionex was developed for concentrations ranging from 10 to 500 ppb. Fluoride elution time was approximately 3.3 minutes; sample run time was 31 minutes to ensure all ions were eluted. In nutrient media solutions, other known ions which were added to provide nutrients for biomass growth were detected but not included in analysis. No fluoride was added to nutrient media solutions and blanks were run to measure any background fluoride levels in samples.

4.4 Oxidation of Fluorine-Containing Compounds

Based on COD results indicating dichromate is an insufficiently strong oxidant, Fenton oxidation and ozonation were also used to attempt to break recalcitrant C-F bonds using stronger oxidants than dichromate. Again, this was first performed on samples of known chemical composition and concentration prior to samples of unknown composition (foam solutions). Each sample's TOC before and after oxidation were compared to determine how effective the oxidative process was. Additionally, any free fluoride, a product of successful C-F bond breakage, was measured after oxidation using ion chromatography.

4.4.1 Fenton Oxidation

Fenton oxidation of PFOA and pentafluoropropanol with molar ratios of ferrous sulfate:hydrogen peroxide:fluorinated organic test substance of 100:5:1 and 200:10:1 was conducted. Test substance concentrations were 100 mg/L. For Fenton's oxidation of the foam concentrations, for which molar analysis was not possible, similar masses of reactants were used as for the 100:5:1 molar ratio to pentafluoropropanol, which required the larger mass of reagents out these test substances. This was based on a conservative estimate that the fluorine content of foams was likely to be a maximum of 10% (10 mg/L) and carbon content closer to a 30% (30 mg/L) maximum since water is often the major component. Table 10 gives the carbon and fluorine content of solutions and the amounts of reactants used for Fenton's oxidation.

Table 10: Reagents used during Fenton oxidation

Test Substance	**Calculated Carbon Content, mg/L**	**Calculated Fluorine Content, mg/L**	**Mass of Ferrous Sulfate Heptahydrate, mg into 50 mL**	**Volume of 30% H_2O_2, uL into 50 mL**	**Mass of Ferrous Sulfate Heptahydrate, mg into 50 mL**	**Volume of 30% H_2O_2, uL into 50 mL**
Known Hydrocarbons			100:5:1 Molar Ratio		200:10:1 Molar Ratio	
PFOA (pentadecafluorooctanoic acid)	23.21	15.97	16.79	125	33.57	245
Pentafluoropropanol	24.01	15.20	46.32	340	92.64	680
Foam Formulations	**Estimated Carbon Content, mg/L**	**Estimated Fluorine Content, mg/L**	**Mass of Ferrous Sulfate Heptahydrate, mg into 50 mL**		**Volume of 30% H_2O_2, uL into 50 mL**	
AFFF	<50	<10	50		350	
AR-AFFF	<50	<10				
Fluoroprotein foam	<50	<10				

Solution volumes of 50 mL were used. After the addition of ferrous sulfate heptahydrate (>99%, Sigma Aldrich) and hydrogen peroxide (30%, Fisher Chemicals), solution pH was measured and adjusted if necessary to reach 2.5-3.0, then solutions were covered with aluminum foil and stirred continuously for 48 hours. After 48 hours, solutions' pH levels were adjusted to 8.0 with the addition of 10 N and 0.5 N NaOH (Fisher Chemicals) to precipitate ferric hydroxide, and solutions were vacuum filtered through 0.22 um Millipore Durapore GV membrane filters (Billerica, MA). Samples were analyzed using dissolved organic carbon analysis after filtration. The impact of residual hydrogen peroxide in solution on TOC analysis was investigated by measuring the TOC of deionized water with hydrogen peroxide added directly to it (from 1 to 8 uL H_2O_2/L water). These samples gave TOC values less than the error seen when calibrating the analyzer using KHP standards, and no correlation between concentration and TOC was observed (R^2=0.087). Residual hydrogen peroxide effects were taken to be negligible.

4.4.2 Ozonation

Samples were also subjected to ozonation to observed achievable oxidation and determine any fluorine liberation. Ozone was generated on-site from compressed oxygen using an Ozonology ozone generator (Ozonology Inc, Northbrook, IL). Solution pH was adjusted to 10 with the addition of NaOH prior to ozonation to encourage the formation of free radicals. Though ozone maximum solubility in water is 40 mg/L, concentrations below this were anticipated in solution during the 2-hour exposure period. Sample volumes of 50 mL were sparged with ozone for 2 hours. Following ozonation, samples were agitated in an ultrasonic bath for 15 minutes to remove residual ozone from solution. Samples were then analyzed using TOC analysis. Again, the impact of residual ozone in solution on TOC analysis was investigated by ozonating a blank water sample and measuring the TOC immediately following ozonation and following a 15 minute period in the ultrasonic bath. This sample showed negligible interference from residual ozone or other species in solution.

4.5 DOC Die-Away Test (Respirometry)

4.5.1 Method and Equipment Selection

The biochemical oxygen demand of the foam solutions was initially tested using a 4-bottle automatic respirometer from Challenge Technology (Springdale, AK) according to the Manometric Respirometry Test (OECD 301F). This test tracks oxygen consumption, while evolved carbon dioxide is trapped by a 30% potassium hydroxide solution in a tube suspended from the vessel's cap. First, nutrient media and test substance were added to 500-mL bottles. Oxygen was supplied through needles inserted through septa on bottle caps, connected to a cylinder of compressed oxygen regulated at ≤5 psi. This oxygen line was also connected to the Challenge measuring block to measure oxygen consumption by each bottle which was reported in one-minute intervals. Oxygen not consumed by the test bottles exited to the room.

However, due to undetermined complications with either the equipment's oxygen-measurement blocks or calibration software, etc., the equipment's ability to accurately measure oxygen consumption degraded rapidly. After ~6 months of use, no oxygen consumption was reported by any bottles during testing. It is important to note that though the equipment's functionality was obviously impaired, DOC measurements made during biodegradability test trials did show a reduction in DOC due to biological activity for all tests that DOC was measured for. For example, the easily biodegradable reference compound sodium benzoate achieved 96% DOC reduction in 7 days using the Challenge equipment although no oxygen demand was reported by the software. Biological growth (flocs) was visible in bottles. The author is confident that although the equipment/software reported no oxygen demand, the oxygen supply mechanism was undamaged and continued to function properly during all tests (i.e. anaerobic conditions did not result).

As a result of these equipment complications, the principle of the DOC Die-Away Test (OECD Method 301A) was used instead. For this method, samples are withdrawn from the test bottles in frequent intervals during the 28-day test, filtered through a 0.45 micrometer filter, and measured for dissolved organic carbon content. This method uses the same nutrient solutions and inoculum concentration as the Manometric Respirometry Test. The DOC Die-Away Test specifies the use of conical flasks (250 mL-2L) shaken by an automatic shaking machine (temperature controlled) in order to maintain aerobic conditions. In the current study, the Challenge respirometer equipment was instead used. This was regarded as a non-ideal solution used in order to still obtain meaningful results with the available equipment. However, monitoring of DOC throughout biodegradability testing may still be recommended in parallel with functioning automatic respirometric measurements in order to allow comparison of the two data sets.

4.5.2 Test Solution Preparation

The procedure described below is for the DOC Die-Away Test as used in this study with equipment originally intended for a Manometric Respirometry Test. The initial concentration of test substances was specified by the test method as 10-40 mg DOC/L, with the test substance as the sole source of organic carbon. Recommended solubility of the test substance in water is at least 100 mg/L. Stock solutions of AFFF, AR-AFFF, and fluoroprotein foam solutions (10 g/L) and sodium benzoate (J.T. Baker, Phillipsburg, NJ), the reference substance, (4 g/L) were prepared in water. A stock solution of PFOA was not made since solubility was too low. Instead, PFOA was added directly to nutrient media in the appropriate concentration to minimize dilution of the nutrient solution. Table 11 gives concentrations of foams used to achieve DOC within this window, all of which did exceed this minimum solubility.

Table 11: Initial concentration and DOC of foam solutions during biodegradation testing

Solution	Initial Concentration (mg foam concentrate/L)	Initial DOC (mg/L)
AFFF	200	14.5
AR-AFFF	450	20.0
FP	200	21.4

The nutrient media for bacteria growth was prepared as specified by OECD 301A: potassium dihydrogen orthophosphate, KH_2PO_4 (85 mg/L); dipotassium hydrogen orthophosphate K_2HPO_4 (217.5 mg/L); disodium hydrogen orthophosphate dehydrate, $Na_2HPO_4 \cdot 2H_2O$ (334 mg/L); ammonium chloride, NH_4Cl (5 mg/L); calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$ (36.4 mg/L); magnesium sulphate heptahydrate, $MgSO_4 \cdot 7H_2O$ (22.5 mg/L); and iron (III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$ (0.25 mg/L). All chemicals' purities were above 98%. Potassium dihydrogen orthophosphate, ammonium chloride, and calcium chloride dehydrate were purchased from Fisher Chemicals. Disodium hydrogen orthophosphate dehydrate was purchased from EMD Chemicals (Gibbstown, NJ). The remaining nutrients were purchased from J.T. Baker. Nutrient media was made immediately prior to testing. No precipitate was observed.

4.5.3 Inoculum

Inoculum was obtained from the secondary biological treatment tanks of the Upper Blackstone Pollution Abatement District (Millbury, MA) the day of the testing, a maximum of 3 hours prior to the start of the test. This is a 56 average MGD facility (160 MGD maximum) treating primarily domestic wastewater. No preconditioning or preadaptation of the activated sludge to the test conditions was performed. Samples were aerated using an air stone aerator for one hour to prevent anaerobic conditions from developing in the sample while the test setup was prepared.

To measure MLSS concentration, a sample was filtered and dried at 105°C, and solids concentration was determined gravimetrically. The mixed liquor suspended solids (MLSS) concentration reported by the facility was within 10% difference of the measured value for the first three samples taken for inoculation; subsequent samples' MLSS measurement was taken from the WWTP and was not measured in-house. MLSS ranged from 2800-4200 mg/L on the dates that samples were taken. A seed concentration no greater than 30 mg/L was specified for the DOC Die-Away Test. A target 25 solids concentration of mg/L was used to inoculate bottles during this study. OECD reports that use of a larger concentration of microorganisms to inoculate tests usually leads to a smaller variation between replicates.

4.5.4 Preparation of Flasks

To set up tests, nutrient media and the appropriate concentration of stock solution were added to two out of four glass sample bottles to achieve concentrations equivalent to 10-40 mg

DOC/L. According to Challenge instructions intended for use with the Manometric Respirometry Test, volumes of 500 milliliters are to be used. Since the DOC Die-Away test allows volumes between 250 mL and 1 L, initial volumes of 550-600 mL were used to also compensate for the volume of sample that would be removed at intervals during the testing to measure DOC. The remaining two bottles were used as inoculum blanks and contained only nutrient media.

Solution pH was measured and, all samples within the acceptable 7.4 ± 0.3 range were not adjusted. Bottles were then inoculated with activated sludge to reach a total solids concentration of 25 mg/L. Immediately prior to inoculating the four test bottles, the sample of sludge was inverted to resuspend microorganisms. A portion of the upper aqueous phase was transferred to each test bottle, avoiding coarse materials. Potassium hydroxide solution (Fisher Chemicals, 45% as purchased, 30% prepared) used to trap evolved carbon dioxide was added to the appropriate tube within the respirometer bottle (did not mix with test solution) and bottles were sealed. Needles connected to the oxygen regulated at ≤5 psi were inserted through the septa on bottles. A needle was inserted briefly through each septa to equalize bottle pressure. Approximately 5 cm^3 of headspace gas was withdrawn with needle and syringe from each bottle in attempts to register some measurement of oxygen consumption on the respirometer software, however, this was not successful in later trials. Tests were run for between 7-28 days. Solutions were magnetically stirred and supplied with oxygen throughout the duration of the test.

No flasks were used for abiotic control or toxicity control. Testing with sodium benzoate as a reference compound was conducted during initial trials but was not possible to perform in parallel with AR-AFFF, AFFF, or fluoroprotein foams during 28-day testing due to the limited number of bottles that could be used simultaneously. Testing with inoculum blanks was always performed in parallel.

Testing was conducted in a temperature-controlled environment. Measured temperatures of a beaker of water in the room with the respirometer equipment were in the range of 19.5-21°C during 28 days. Continuous magnetic stirring of samples increased sample temperatures up to 24°C.

4.5.5 DOC Analysis

Throughout the 28-day test, samples were withdrawn from each bottle for DOC analysis. Samples were taken on days 0, 3, 7, 14, 21, and 28. This frequency was selected based on time constraints; more frequent sampling would provide greater detail into degradation rates. At each interval, DOC of test solutions and inoculum blanks was measured in parallel.

Samples (15-20 mL) were withdrawn from well-mixed test bottles and filtered through 0.45 Whatman Puradisc AQUA 30 cellulose acetate syringe filters sold prewashed specifically to reduce organic contamination via desorption for use with DOC or COD analysis. Both syringes and filters were rinsed prior to use with 25 mL of purified water, followed by the collection of a

20 mL filtrate for DOC analysis to verify low organic concentration contributions from all syringes and filters. Syringes underwent 20% sulfuric acid cleaning and rinsing similar to all glassware used for TOC. In early testing, 0.45 Fisherbrand syringe filters were used. These, not designed specifically for DOC or COD analysis, were rinsed three times each. Filtrate from these filters was similarly collected for DOC analysis to quantify organic contributions from syringe or filter. After rinsing syringe filters, the initial 3-5 mL of filtrate from test solutions was discarded to avoid dilution of the sample by residual rinse water in the filter's holdup volume.

Contributions to DOC from syringes and both types of filters ranged from 0.05 to 0.5 mg carbon/L. Since for DOC measurements on any date, the same type of filters and the same cleaning procedure was used for all samples (i.e. both test solutions and inoculum blanks), this contribution to DOC measurements from syringe or filter can be assumed to be consistent for all samples. Therefore, when calculating the DOC of test solutions by subtracting the DOC of inoculum blanks, any contribution from glassware, syringes, or filters can be assumed to be factored out. Any adsorption of samples' organic content onto syringes or filters was not controlled in this study.

4.5.6 Calculation of Biodegradability

Equation 5 was used to calculate percentage degradation, D_t, based on DOC reduction at each sampling interval.

$$D_t = \left[1 - \frac{C_t - C_{b(t)}}{C_0 - C_{b(0)}}\right] * 100 \qquad \text{(Equation 5)}$$

Where

D_t = percentage degradation at time t
C_0 = mean starting DOC concentration in test solutions (mg DOC/L)
C_t = mean DOC concentration in test solutions at time t (mg DOC/L)
$C_{b(0)}$ = mean starting DOC concentration in blank inoculum controls (mg DOC/L)
$C_{b(t)}$ = mean DOC concentration in blank inoculum controls at time t (mg DOC/L)

This calculation was used to determine the 10-day window beginning after 10% DOC degradation occurred, and during which the 70% DOC removal threshold needed to be met in order for the test solution to be considered readily biodegradable.

According to OECD guidelines for test validity, the "test is considered valid if the difference of extremes of replicate values of the removal of the test chemical at the plateau, at the end of the test or at the end of the 10-d window, as appropriate, is less than 20% and if the percentage degradation of the reference compound has reached the pass levels by day 14." Repeat testing is recommended if either of these conditions is not met. In this study, reference compounds were not used in parallel.

4.5.7 Fluoride Detection

At the beginning and end of 28-day biodegradation tests, filtered samples (0.45 micron filters) were measured for fluoride concentration using ion chromatography as described previously. Initial samples on day 0 were expected to have no fluoride since nutrient media did not contain any fluoride. Chloride and sulfate were anticipated in nutrient media solution but these total quantities were not of interest. Calibration curves for other anions were not developed for this study and no cationic species were analyzed.

5. Results and Discussion

5.1 Effectiveness of TOC and COD Analysis for Fluorinated Substances

The TOC and COD of four fluorocompounds were measured to evaluate the effectiveness of these test methods in breaking C-F bonds and giving accurate measures of organic content of fluorinated compounds. Figure 1-Figure 4 show molecular structures of these compounds. Solutions of 100 mg/L were used for each compound, equivalent to molar concentrations of 0.20-0.70 millimoles/L. Two compounds, PFOA and PFOS, were perfluorinated while the other two were polyfluorinated.

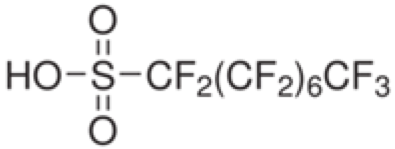

Figure 1: Structure of heptadecafluorooctane sulfonic acid (PFOS)

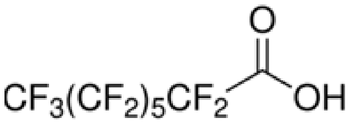

Figure 2: Structure of pentadecafluorooctanoic acid (PFOA)

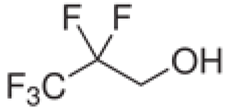

Figure 3: Structure of 2,2,3,3,3-pentafluoro-1-propanol

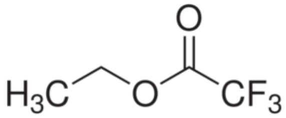

Figure 4: Structure of ethyl trifluoroacetate

Figure 5 presents the correlation between theoretical and measured organic carbon content of PFOA, PFOS, pentafluoropropanol and ethyl trifluoroacetate measured in this study. Solutions of 100 mg fluorinated organic/L were used, corresponding to carbon content up to 34 g/L. Carbon content was calculated based on molecular structure. For PFOS, pentafluoropropanol, and ethyl trifluoroacetate solutions, the measured TOC is slightly lower than the calculated carbon content. However, on average, it was able to measure 81-100% (91% average) of the carbon in the four fluorocompounds tested. The TOC injection syringe, flow line, and needle were rinsed between each sample and thus carryover from one sample to the next was not suspected, which was confirmed by the use of blanks and periodic measurement of calibration standards.

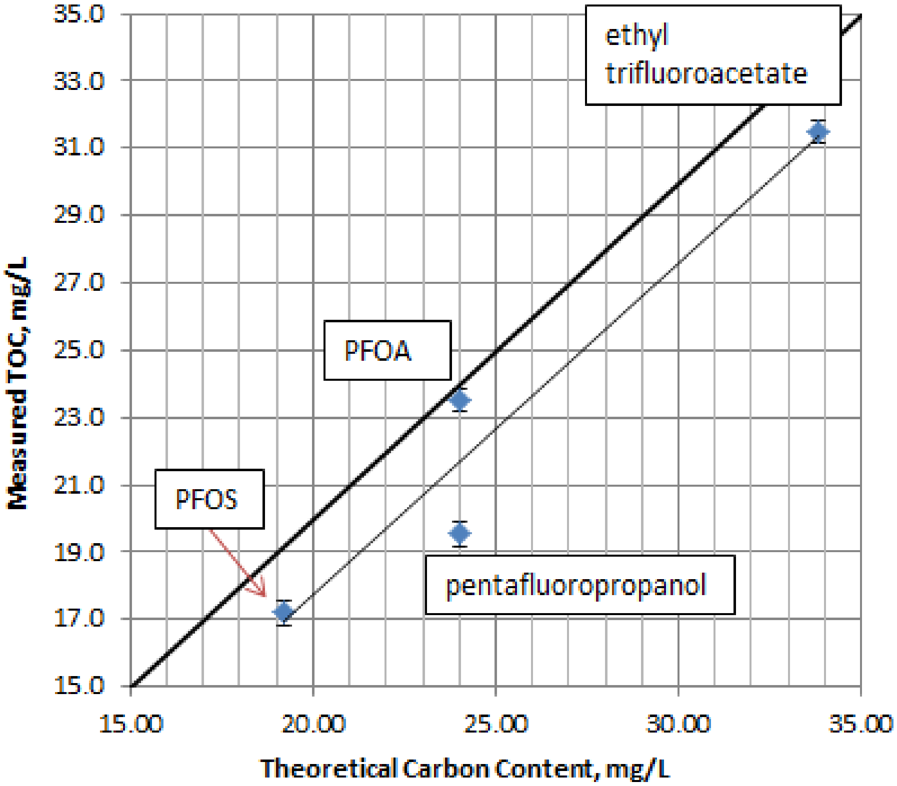

Figure 5: Theoretical and measured total organic carbon values for known fluorocompounds

Table 12 lists typical bond dissociation energies for carbon single and double bonds relevant for fluorinated compounds used in this study [104]. These bond energies represent average dissociation energies for a number of molecules which may feature variable functional groups adjacent to these bonds rather than absolute values for a particular molecular. Authors cite the example that C-O single bond strength was the average of bonds in methanol, ethanol, and dimethyl ether. Carbon-halogen (C-X) bond strengths are similar to those reported by Glocker for molecules of the form C-X_4.

Table 12: Average carbon dissociation energies [104]

Bond	Bond Dissociation Energy	
	KJ	kcal
C-H	412	98
C-C	348	83
C-O	360	86
C=O	743	178
C-F	484	116
C-Cl	338	81
C-Br	276	66

These bond strengths were used to calculate an approximate summation of bond strengths between carbon and other species in the four fluorocompounds, Table 13. The proportion of this total bond strength that carbon-fluorine bonds represent is calculated also. A comparison of this proportion of overall bond strength and the percentage of calculated carbon that was measured by the TOC test (Figure 5) does not seem to show a correlation.

Table 13: Comparison of TOC effectiveness to C-F bond frequency and proportion of carbon bond strengths

Fluorinated Test Substance	Number of C-F Bonds	Total Number of Bonds Involving Carbon	Frequency of C-F Bonds (% Out of Total Bonds Involving Carbon)	Summation of Energies of Bonds Involving Carbon (kcal)	Percentage of Bond Energy Contributed by C-F Bonds (%)	Percentage of Calculated Carbon Content Measured by TOC Test (wt% of Carbon)
PFOA	15	24	63	2581	**67**	**98**
PFOS	17	25	68	2549	**77**	**89**
Ethyl trifluoroacetate	3	13	23	1355	**26**	**93**
Pentafluoro-propanol	5	10	50	1028	**56**	**81**

Another possible cause for deviation of measured TOC from calculated organic carbon content could be test substance volatilization and loss during initial sample sparging to remove inorganic carbon from solution. Volatile test substances could be partially stripped from solution resulting in lower measured TOC values. Table 14 reports the Henry's Law constants (H) for the four fluorinated test substances. Henry's constants are written for volatilization reactions in the form of Equation 6 where larger Henry's constants correspond to greater volatility.

$$A \cdot nH_2O \leftrightarrow A(g) + nH_2O \qquad \text{Equation 6}$$

Temperature data is not available for PFOS, however, it is assumed based on the source's focus on environmental conditions that a reasonable temperature may be 20-25°C. For PFOA, at a solution pH of 3.8, above the pKa of 3.4, the dissociated anionic form perfluorooctanoate (PFO^-) dominates (representing 72% of solution). The vapor pressure and Henry's Law constant for PFO^- are undetermined but assumed to be negligible [105]. The pKa of PFOS has been calculated as -3.27 [106]; it is presented in the completely ionized form in the test solutions used.

Table 14: Henry's constants for fluorinated test substances

Test Substance	Henry's Constant, atm·L/mol	Temperature, °C	Source
Perfluorooctanoate (PFO-)	ND, assumed negligible	20	[105]
Heptadecafluorooctanesulfonic acid (PFOS)	$3.1*10^{-6}$	Not Specified	[106]
Ethyl trifluoroacetate	8.33	20	[107]
2,2,3,3,3-Pentafluoro-1-propanol	$2.2*10^{-2}$	25	[108]

If H is less than about $3*10^{-4}$ atm·L/mol, "the substance is less volatile than water and its concentration will increase as the water evaporates" [109]. It is essentially non-volatile. For H values between 10^{-2} and 10^{-4}, the substance will volatilize to some degree based on H. Based on these guidelines, PFO- and PFOS may be characterized as negligibly volatile. Pentafluoropropanol is a medium-volatility compound, and ethyl trifluoroacetate is volatile. Nevertheless, 93% of organic carbon in ethyl trifluoroacetate was detected using TOC. It is concluded that substance volatility for these compounds played an insignificant role in TOC analysis effectiveness. Difference between calculated and measured carbon content for these four fluorocompounds may be due to human error in solution preparation, sampling, or some adsorption to glassware although the average 91% of calculated values that was measured indicates losses on average were minor during TOC testing.

There is a weak correlation between theoretical oxygen demand calculated according to Equation 2 and measured COD, shown in Figure 6. For PFOA and PFOS samples, no COD was detected at all, indicating no C-F bond breakage during the COD analysis reactions. These two compounds had the highest proportion of carbon-fluorine bonds of the compounds measured. Organic content of ethyl trifluoroacetate was most effectively measured by COD, followed by pentafluoropropanol—49% and 14% of theoretical oxygen demands, respectively. The average percentage of ThOD detected for these four compounds was 16%.

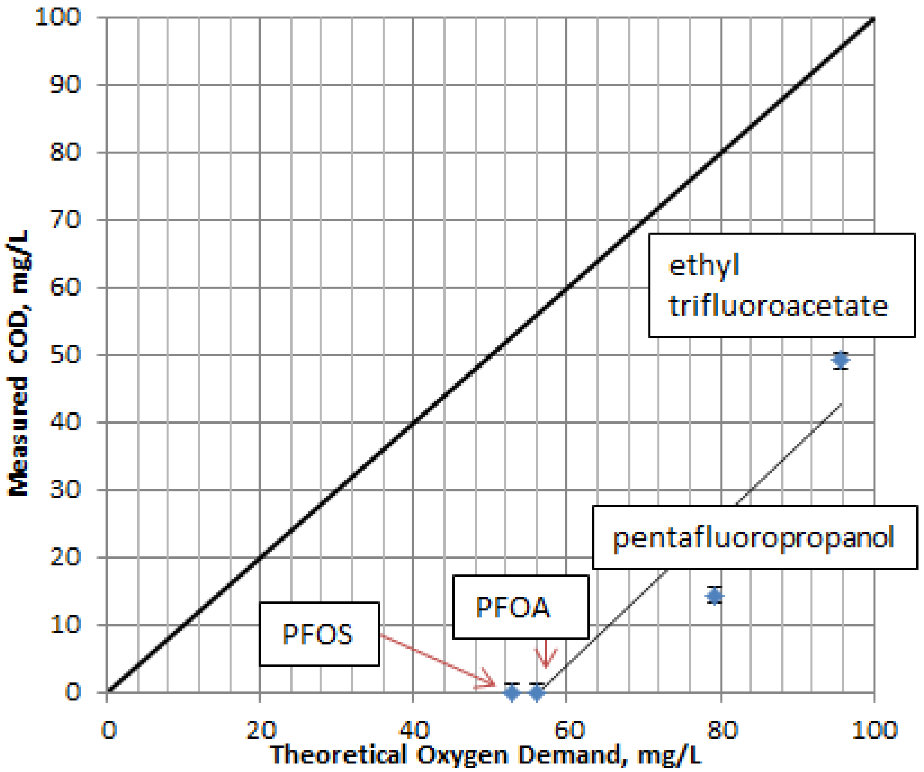

Figure 6: Theoretical and measured chemical oxygen demands for known fluorocompounds

Standard Methods for the Examination of Water and Wastewater states that "volatile organic compounds are oxidized [by COD test methods] only to the extent that they remain in contact with the oxidant" [69]. If volatile straight-chain aliphatic compounds proportion into the vapor phase, they may not be in sufficient contact with the oxidizing liquid. Silver sulfate may be added as a catalyst to increase oxidation of aliphatic compounds, however, silver sulfate reacts with halides to form precipitates that are not fully oxidized. Mercuric sulfate may be added instead [69]. COD testing in this study did not investigate use of metal catalysts. Since ethyl trifluoroacetate is the most volatile of the four compounds measured and COD was able to measure 49% of its ThOD while measuring zero COD for negligibly volatile PFOA and PFOS, it is concluded that volatility is not responsible for dichromate COD test ineffectiveness for fluorinated compounds.

Sample adsorption to glassware may have contributed to low or zero COD values. For example, PFOS is known to irreversibly adsorb to glassware [110]. Further investigation of this is recommended with the use of polypropylene plasticware. However, based on the relative effectiveness of TOC compared to COD, it seems that the potassium dichromate COD reagents provided insufficient oxidative potential to measure COD of the fluorinated compounds, particularly PFOS and PFOA with perfluorinated chains. TOC proved more effective (91% average detected compared to calculated organic carbon) than COD (16% of ThOD detected, or

32% excluding PFOS and PFOA zero values) at providing a quantification or fluorinated compounds' organic content.

5.2 Organic Content of Ansul Fire Fighting Foams

TOC and COD of Ansul fire fighting foam solutions are shown in Table 15, all for 100 mg foam concentrate/L, though based on the preceding results it is clear that these values are not likely to be completely accurate if fluorinated compounds are present in the foams. If fluorinated compounds in these foams are assumed to be the most difficult to accurately measure with TOC analysis and are assumed to behave similarly to the known fluorocompounds used in this study, these foam TOC results may be expected to represent a minimum of 91% of the carbon in solution. No conclusions can be drawn regarding the true COD values except that these measured values are likely to be falsely lower than theoretical oxygen demand. All solution concentrations were 100 mg/L in water. This concentration represents approximately 0.33% of a typical 3% foam solution as prepared for use on fires; a foam solution use for fire application would have a TOC or COD of 300 times these values.

Table 15: Total organic carbon and chemical oxygen demand of Ansul AFFF, AR-AFFF, and fluoroprotein foams

Solution	TOC, mg/L	COD, mg/L
AFFF	7.12	28.24
AR-AFFF	4.47	18.24
Fluoroprotein	10.70	39.26

Expected components of fire fighting foam concentrates include more readily degradable materials in addition to fluorinated components, and it is these more readily biodegradable materials that are reflected predominantly in COD measured for these foams. Water is the primary ingredient when diluted to 100 mg concentrate/L. Ansul reports the following compositions of these foams (Table 16), retaining secrecy of these compositions due to their proprietary classification.

Table 16: Listed composition of Ansul foams [78-80]

Composition	Ansulite 3% AFFF	Ansulite ARC 3x6 (AR-AFFF)	Ansul 3% Fluoroprotein
Butyl carbitol	2.5-10%	2.5-10%	N/A
Polyethylene glycol	N/A	N/A	2.5-10%
Other components below reportable levels	>90%	>90%	>90%

5.3 Oxidation and Defluorination Using Fenton's Oxidation

Since dichromate used in COD testing proved to be an insufficiently strong oxidant to break C-F bonds and allow organic content measurement, oxidation with stronger oxidants was also conducted. Table 17 lists relative oxidative strengths of four strong oxidants at 298K (E°, in V). Fenton's oxidation using the hydroxyl radical and ozonation were conducted.

Table 17: Oxidation potential of strong oxidants [111]

Oxidant	E° (V)
Hydroxyl Radical	2.80
Ozone	2.07
Permanganate	1.68
Dichromate	1.33

Solutions of PFOA and pentafluoropropanol, one perfluorinated fluorochemical and one partially fluorinated, were subjected to Fenton's oxidation and ozonation. The initial TOC was measured, and then remeasured after oxidation experiments. Successful oxidation was expected to result in C-F bond breakage, CO_2 formation, and lower TOC values. Successful oxidation would also be accompanied by fluorine liberation and the detection of fluoride ions in solution using ion chromatography. Table 18 reports the reduction in TOC and liberation of fluoride in terms of defluorination, given by Equation 7 where $C_{Fl,initial}$ is the calculated fluorine content of the base compound and $C_{Fl\text{- } liberated}$ as measured by the IC. TOC after ozonation is not reported due to the interference of residual ozone in solution, exact quantification of which was not attempted since ozonation proved ineffective at significant defluorination.

$$Defluorination, \% = \frac{C_{Fl,initial} - C_{Fl^{-}liberated}}{C_{Fl,initial}} * 100 \qquad \text{(Equation 7)}$$

Table 18: Defluorination and TOC decrease observed after oxidation of known fluorocarbons

Fluoro-chemical Solution	Oxidation	Calculated Fluorine Content, mg/L	Fluoride Concentration After Oxidation, mg/L	Defluorination, %	TOC Decrease, %
PFOA (100 mg/L)	Fenton's, 100:5:1, pH 2.5	15.97	0	0	-4
	Fenton's, 200:10:1, pH 2.5		0	0	-3
	Ozonation, pH 10		0.01	0.1	N/A
Pentafluoro-propanol (100 mg/L)	Fenton's, 100:5:1, pH 2.5	15.20	10.4	68	34
	Fenton's, 200:10:1, pH 2.5		8.5	56	33
	Ozonation, pH 10		1.7	11	N/A

For both PFOA and pentafluoropropanol, the degree of oxidation (i.e. TOC reduction) accomplished with Fenton's reagent was the same using molar ratios of ferrous sulfate:hydrogen peroxide:fluorinated organic of 200:10:1 and 100:5:1. The reagents can be assumed to be in sufficient excess to have achieved the maximum oxidation possible. The 48-hour reaction time is also assumed to have allowed for equilibrium to be reached. PFOA was not degraded by Fenton's reagent or ozonation, although literature reports of successful PFOA degradation with a UV/Fenton process exist [112]. Pentafluoropropanol experienced 34% TOC reduction and an average 62% defluorination with Fenton's oxidation, and 11% defluorination with ozonation. The 2-hour ozonation period used for this testing did lead to minor fluoride release from PFOA and for further investigation of ozone effectiveness, longer duration tests would be recommended along with reaction rate analysis to determine reaction completion. Lin et al. were able to degrade PFOA and PFOS by 85-100% with a combination of pretreatment and longer duration (4 hour) ozonation with pH adjustment [113]. Based on these results, Fenton's oxidation was regarded as more rapidly effective for fluorocompound degradation.

These results for pentafluoropropanol oxidation is consistent with the oxidation potentials given in Table 17, where the hydroxyl radical used in Fenton's oxidation achieved the greatest degradation based on TOC reduction, followed by ozone (based on defluorination observed). During the COD test, dichromate was able to measure 14% of ThOD. These TOC and COD values are not directly comparable, and end products of the COD test were not measured under TOC due to the presence of other compounds in solution, but this does provide a relative ranking of the successful oxidation of pentalfuoropropanol observed during this test: hydroxyl radical > ozone > dichromate—consistent with oxidant strength. For PFOA, the lack of TOC reduction observed with Fenton's oxidation and lack of significant defluorination with Fenton's oxidation or ozonation indicates neither are able to oxidize perfluorinated PFOA as performed in this study. This is consistent with this study's previous results proving ineffectiveness of the COD test for perfluorinated PFOA and PFOS since the COD test uses weaker oxidants. Perfluorinated compounds were not oxidized successfully in this study.

AFFF, AR-AFFF, and FP fire fighting foam solutions were also reacted with Fenton's reagent, the strongest oxidant of methods used in this study, in attempts to determine fluorine content. Since complete defluorination and TOC reduction were not observed with the known fluorocompounds using Fenton's reagent, this was not anticipated with the foam solutions either. Significant TOC reduction, 64-76%, was achieved during Fenton's oxidation of the three types of foams, but no fluoride was liberated (Table 19). This confirms the hypothesis that though some mineralization of carbon content did occur, carbon-fluorine bonds remained resistant to Fenton's oxidation similar to PFOA. Specifically, PFOA existence in these foams measured is not likely based on the use of fluorotelomers in the foam industry in recent decades rather than fully perfluorinated compounds from the electrochemical fluorination process.

Table 19: Defluorination and TOC decrease observed after oxidation of fire fighting foams

Fluorochemical Solution	Oxidation	Esimated Fluorine Content*, mg/L	Fluoride Concentration After Oxidation, mg/L	Defluorin-ation, %	TOC Decrease, %
AFFF	**Fenton's**	0.5-10 or lower	0	0	74
AR-AFFF	**Fenton's**	0.5-10 or lower	0	0	75
Fluoroprotein foam	**Fenton's**	0.5-10 or lower	0	0	64

*Based on foam MSDS available from Chemguard, National Foam, Ansul, and Angus manufacturers [26-30, 34-42, 76-80]

Fluoride liberation, had it occurred during foam oxidation, would have been detected by the ion chromatograph. The instrument has adequate sensitivity for concentrations down to 10 µg/L. The 0.5-10% range of reported concentrations of fluorinated surfactants in foam concentrates (by weight from MSDS) corresponds to 600-1500 mg fluorine/L in a 3% solution. For 100 mg/L solutions during this testing, this 0.5-10 wt% would correspond to 0.5-10 mg/L fluorinated surfactant. This is an overestimation since MSDSs list these percentages for fluorinated surfactants which would result in lower elemental fluorine concentrations. A possible value for fluorine concentration alone may be 30% or greater of the fluorinated surfactant, resulting in a calculated 0.15-3 wt% of the foam concentrate, or higher. As a reference, the 6:2 fluorotelomer thioether amido sulfonate which has been identified in some AFFF formulations, molecular formula $C_{15}H_{17}O_4NS_2F_{13}^{-1}$, is 42% fluorine by weight. With these assumptions, 100 mg foam concentrate/L solutions used in current testing represents a minimum of 150 µg/L fluorine which would be well within detection limits. Therefore, no fluoride was liberated with Fenton's oxidation of these fire fighting foams. Since ozonation was less successful than Fenton's oxidation for PFOA and pentafluoropropanol, ozonation of these foams was not attempted.

5.4 DOC Die-Away of Foam Solutions

Initial testing for inhibitory effects of AFFF foam upon biodegradation of the easily biodegradable reference compound sodium benzoate did not indicate signs of inhibition. Sodium benzoate underwent 96% DOC reduction in 7-days while a 50-50 mixture of sodium benzoate and AFFF foam concentrate with the same overall organic loading underwent 94% DOC reduction (Table 20). Slightly lower DOC reduction of the mixture is due to the AFFF component's lower biodegradability and/or testing variability between bottles. AFFF foam was not found to be inhibitory for the DOC Die-Away test method using activated sludge inoculum from a domestic wastewater treatment facility.

Table 20: DOC reduction of sodium benzoate with AFFF during initial biodegradation test

Solution	Initial DOC (mg/L)	DOC After 7 days (mg/L)	% Reduction in DOC
100 mg/L AFFF	7.0	2.0	72
100 mg/L sodium benzoate	58.5	2.5	96
50-50 mixture (100 mg/L total organics)	30.9	1.8	94

DOC degradation during 28-day DOC Die-Away tests for the three foam solutions is presented in Table 21 and Figure 7. Initial DOC concentrations of AFFF, AR-AFFF, and FP solutions in nutrient media were 14.5 mg C/L, 20.0 mg C/L, and 19.8 mg C/L. The nutrient media contained no carbon and therefore did not contribute to this TOC value. Degradation levels at the end of each test were 89%, 96%, ad 77% calculated using Equation 5. Values in Table 21 are average DOC values for duplicate flasks with the contribution to DOC from procedural blanks removed.

Table 21: Foam degradation values throughout DOC Die-Away testing

Time (days)	Avg AFFF DOC (mg/L)	AFFF Degradation (%)	Avg AR-AFFF DOC (mg/L)	AR-AFFF Degradation (%)	Avg FP DOC (mg/L)	FP Degradation (%)
0	14.5	0	20.0	0	19.8	0
3	4.9	66	13.3	33	9.7	51
7	1.6	89				
8			1.9	91	5.8	71
14	1.2	91	1.4	93	5.0	75
21	1.6	89	1.3	94	4.4	78
28	**1.5 ± 0.4**	**89 ± 2**	**0.9 ± 0.4**	**96 ± 2**	**4.6 ± 0.4**	**77 ± 2**

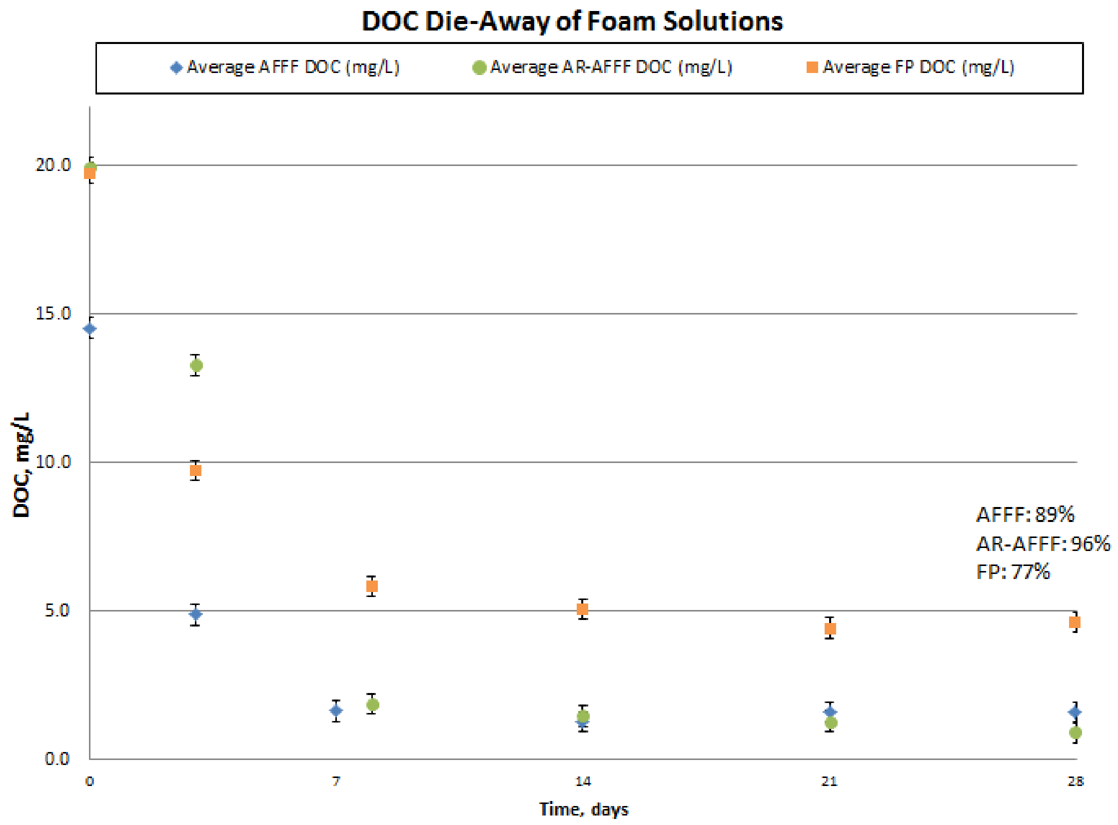

Figure 7: Foam degradation throughout DOC Die-Away testing

When using the DOC Die-Away Test Method, ready biodegradability is defined as 70% DOC removal during a 10-day window beginning when 10% DOC biodegradation is reached. The frequency of DOC testing dates limited the determination of the start of this 10-day period but since Ansul AFFF, AR-AFFF, and FP solutions surpassed 10% biodegradation by day 3, this window was conservatively assumed to begin on day 0. All three then did surpass 70% DOC reduction by day 7 or 8, meeting the standard for “ready biodegradability” within 10 days.

Error reported in Table 21 was calculated based on the TOC of KHP standards measured throughout the course of this study. Deviation between duplicate bottles at the end of each foam degradation test is presented in Table 22. The deviation between AFFF duplicate bottles at day 7, 8, or 28 did not exceed the 20% limit set by OECD 301 for test validity.

Table 22: Percentage deviation of DOC between duplicate bottles at start and end of testing

Time (days)	AFFF Duplicates	AR-AFFF Duplicates	FP Duplicates
0	4.5	3.8	3.4
7 or 8	7.8	9.9	4.3
28	16.4	2.1	8.4

Ansul does not report BOD, COD, or other biodegradability information online. AFFF foams from Chemguard, National Foam, and Angus which are not formulated to meet military specifications report some biodegradability values calculated as the ratio of BOD to COD in the range of 35-60% (Table 5) (not all-inclusive for these manufacturers), and AR-AFFF values in the range of 32-80% [26-30, 34-42, 76-80]. These are based on either 5 or 20-day BOD tests. As such, biodegradability values from the current study that use DOC Die-Away over a 28-day test period are not directly comparable but do show greater biodegradation than these reported values for other manufacturers in the fire fighting foam industry. Values at day 21 of the current study may be more comparable—89%, 94%, and 78% DOC reduction of AFFF, AR-AFFF, and FP foams. These are not significantly different than values measured at day 28. If COD can be anticipated to produce falsely low values for fluorinated substances based on results from the current study, reported BOD/COD calculations from foam manufacturers are likely falsely high.

Measured Ansul biodegradation rates are greater than values reported by Król et al. for the AFFF, AR-AFFF, and FP foams in that study. Their order of biodegradation susceptibility for these three types was established as AFFF > AR-AFFF > FP. The current study has found Ansul AFFF and AR-AFFF biodegradability roughly equal, and both greater than FP. Again, values from Król et al. are based on either 5 or 20-day BOD tests and results from day 21 of the current study may be used for comparison although these did not differ significantly from final degradation at the end of the current 28-day test. Figure 8 provides a comparison of the current study's measured biodegradability values against these reported values from Król et al. and manufacturers (either BOD_{20}/COD or BOD_5/COD, see Table 5).

NFPA recommended test method for biodegradability evaluation is based on CO_2 evolution. The calculation for biodegradability for this uses theoretical carbon dioxide production, or if the test substance's identity is not known, a calculation involving TOC. This is more appropriate for fluorinated substances than COD. However, manufacturers and other studies report biodegradability using COD values. These must be evaluated for their validity since the present study has demonstrated that use of COD in biodegradability determinations for fluorinated compounds can lead to inaccuracies stemming from the insufficient oxidative potential of dichromate. Consistency among test methods would increase reported measures' validity.

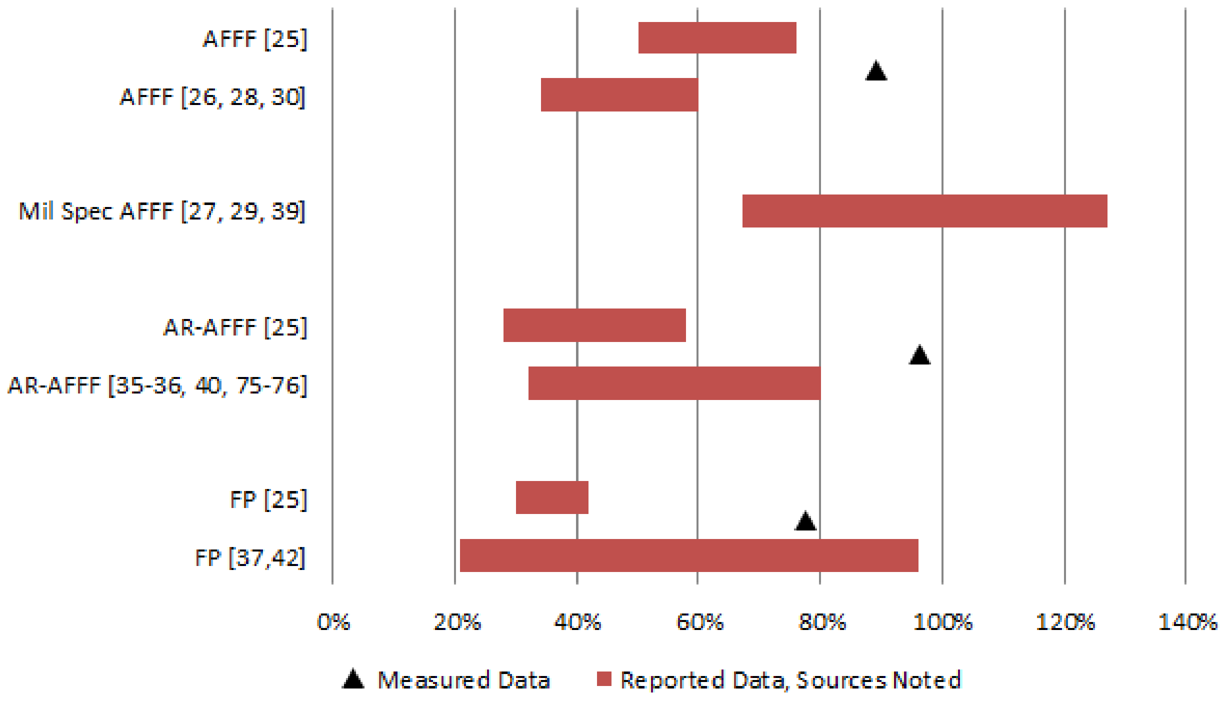

Figure 8: Comparison of measured Ansul biodegradation to other reported foam values

Król et al. note metal salts, hexylene glycol, preservatives, and any protein hydrolysis products as possible causes for reduced biodegradation of FP foams in their study. Stabilizer and inhibitors, particularly microbial inhibitors used to extend product life, could limit biodegradability of fluoroprotein foams. Ansul FP MSDS reports only the freeze point depressant polyethylene glycol (2.5-10%) under ingredients listed [80]. Zgola-Grzeskowiak et al. report nearly 99% biodegradation of a polyethylene glycol mixture of average molecular weight of 300 in 24 days using river water [114]. However, biodegradability of polyethylene glycols with increasing molecular weights may vary [115]. Without more information from the manufacturer regarding FP composition, it is difficult to comment on the reduced biodegradation of Ansul FP as compared to AFFF and AR-AFFF.

Fluoride liberated during AR-AFFF and FP 28-day biodegradation testing is reported in Table 23. No fluoride was detected in AFFF samples. Based on the presence of fluoride in both other foam solutions at the end of the 28 days, it is suspected that greater AFFF sample dilution than was later used for AR-AFFF and FP samples resulted in possible fluoride levels below the ion chromatography detection limit. Initial fluorine concentration in foams is unknown. Mass of fluoride liberated after 28-day tests is presented as a percentage of the initial mass of foam concentrate in solution.

Table 23: Fluoride liberated during foam biodegradation testing

Solution	Fluoride Concentration (µg/L)	Weight % of Fluoride Compared to Initial Foam Concentrate
AFFF	N/A	N/A
AR-AFFF	40.4	0.009
FP	19.5	0.010

A conservative low-range fluorine content estimate of 0.15-3% (by weight) in a foam concentrate was developed earlier based on MSDS from three foam manufacturers. Fluoride levels detected after biodegradation of Ansul AR-AFFF and FP foams are one to two orders of magnitude lower than this estimation. It is possible that Ansul foams possess lower fluorine content to begin with (not reported by manufacturer), however, from this study it is concluded that biodegradation of AR-AFFF and FP foams according to the DOC Die-Away test method has likely not led to complete defluorination despite all three meeting criteria for "ready biodegradability." A similar conclusion can be made for the AFFF foam since fluoride was either not present or below detection limits.

6. Conclusions

In the current study, TOC measured as non-purgeable organic carbon was able to detect an average of 91% of organic carbon content in four fluorinated test substances: PFOA, PFOS, ethyl trifluoroacetate, and pentafluoropropanol—two of which were perfluorinated. COD failed to measure any oxygen demand for PFOA and PFOS and measured an average of 32% of the stoichiometric theoretical oxygen demand of the remaining two compounds. Since TOC was largely successful at quantifying organic content for these compounds, low COD values are not likely due to sample volatility or adsorption to glassware which would have affected both test methods. High carbon-fluorine bond strength and chain rigidity led to test substances' resistance to the dichromate COD test, particularly for perfluorinated PFOA and PFOS.

Since biodegradability is often evaluated based on ratios between BOD and COD, these results raises the significant concern that falsely low COD values for fluorinated compounds have led to falsely high biodegradability reports for fluorinated compounds, particularly fluorinated fire fighting foams which have had variable reports in literature and product MSDSs [23-30]. Although NFPA standards 18, 18A, and 1150 recommend carbon dioxide evolution as the analytical parameter for evaluating fire fighting foams' biodegradability [71-72], manufacturers and researchers may report biodegradability using other analytical parameters which may involve COD measurements. Based on this study, measures involving COD must be critically evaluated since dichromate has proved to be an insufficiently strong oxidant for fluorinated substances. A test that uses TOC is instead recommended, such as the carbon dioxide evolution test which uses a calculation involving TOC to determine theoretical carbon dioxide production.

In this study, Ansul AFFF, AR-AFFF, and FP foams demonstrated 89, 96, and 77% DOC reduction in 28-days, respectively. Within an 8-day window, these met OECD and NFPA standards for classification as readily biodegradable based on >70% DOC reduction within a 10-day window (time frame difference due to sampling frequency). Ansul AFFF and AR-AFFF were more completely degraded than FP which has been reported in a previous study [25]. Due to the proprietary nature of foam formulations, specific solvents, surfactants, and additives in foams are unknown and further work into components used in each foam would be required to determine causes for this difference in biodegradability. Ansul foam biodegradability levels based on DOC die-away in the current test are higher than those reported by peers Chemguard, National Foam, and Angus on MSDS's available online for similar 3% formulations for non-military use, although it must be noted that these manufacturers report BOD:COD ratios for which 60% biodegradability is comparable to 70% when using a DOC Die-Away Test. Still, Ansul biodegradability measured in this study surpasses levels reported on other manufacturers' MSDSs.

Based on the fluoride detected in solutions at the end of 28-day AR-AFFF and FP tests, it is apparent that some defluorination due to microbial activity occurs. However, it is unclear to what level successful defluorination has occurred since initial fluorine content was not measured in this study. An estimate was made that fluorine content in foam concentrations may be in the range of 0.15-0.3% (or higher) by weight based on three manufacturers' disclosure of ingredients on MSDSs. Compared to this estimate, final fluoride content yielded from defluorination of Ansul AR-AFFF and FP foams in the 28-day test may be 1-2 orders of magnitude lower than overall fluorine content (estimated) in foam concentrates. AFFF defluorination was not measurable in this study due to excess dilution of samples. The identity and concentration of fluorinated compounds in these foams is unknown.

In conclusion, the present study has shown that a significant portion of the Ansul 3% AFFF, AR-AFFF, and FP foam concentrates used are ready biodegradable. However, complete defluorination did not occur. This is the first biodegradability study of fire fighting foams to report observed defluorination. While there has been research into defluorination of perfluoroalkyls or fluorotelomers, microbial defluorination of foam formulations with a comparison to their total fluorine content has not been studied, in part due to their proprietary status. With long-term health effects and persistence of many fluorinated compounds relevant to foam formulations unknown—and the identity of others unknown—a greater understanding of biodegradability of foams' fluorinated surfactants in particular is needed.

Secondly, a standard dichromate COD test has demonstrated failure to accurately measure organic content of four fluorinated substances. This, along with the wide range of reported biodegradability measurements from studies or reported by manufacturers, including values exceeding 100% based on a BOD:COD ratio, demands further research to identify a suitable and accurate measure of biodegradability of fluorine-containing fire fighting foams that does not involve COD. Validity of test methods becomes crucial when many analytical parameters are accepted for biodegradability testing. DOC die-away is recommended as one method to quantify foam biodegradability that could provide consistency among researchers due to its extensive use.

Appendices

Appendix A: MSDS for Ansul AFFF Foam Tested [78]

MATERIAL SAFETY DATA SHEET
ANSULITE 3% AFFF (AFC-3-A)
Product Code: 1010-2-016 ANa Issue Date: 01-08-2014

1. Product and Company Identification

Material name ANSULITE 3% AFFF (AFC-3-A)
Version #
Revision date
CAS #
Product Code
Product use
02
01-08-2014
Mixture
1010-2-016 ANa
Fire extinguishing agent
CHEMTREC 800-424-9300 or 703-527-3887
http://www.ansul.com
Marinette, WI 54143-2542
One Stanton Street
Tyco Fire Protection Products
Emergency Phone Number
Internet
Phone
Address
Name
Supplier
Manufacturer / Importer /
715-735-7411

2. Hazards Identification

Emergency overview WARNING! Causes skin and eye irritation.

OSHA regulatory status This product is considered hazardous under 29 CFR 1910.1200 (Hazard Communication).

Potential health effects

Routes of exposure Eye contact. Skin contact. Inhalation. Ingestion.

Eyes Do not get this material in contact with eyes.

Skin Avoid contact with the skin. Frequent or prolonged contact may defat and dry the skin, leading to
discomfort and dermatitis.

Inhalation Do not breathe vapor. May be irritating.

Ingestion Not a likely route of entry. Do not ingest.

Target organs Eyes. RESPIRATORY SYSTEM. Skin. Central nervous system.

Chronic effects Frequent or prolonged contact may defat and dry the skin, leading to discomfort and dermatitis.

Signs and symptoms Irritation of nose and throat. Irritation of eyes and mucous membranes. Defatting of the skin.

Rash. Skin irritation.

Components CAS # Percent

3. Composition / Information on Ingredients

Butyl Carbitol 112-34-5 2.5 - 10

Other components below reportable levels > 90

4. First Aid Measures

First aid procedures

Eye contact Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if

present and easy to do. Continue rinsing. Get medical attention if irritation persists after washing.

Skin contact Wash off with warm water and soap. Get medical attention if irritation develops and persists.

Inhalation Move to fresh air. For breathing difficulties, oxygen may be necessary. Get medical attention, if

needed.

Ingestion Rinse mouth. Do not induce vomiting without advice from poison control center. IF SWALLOWED:

Immediately call a POISON CENTER or doctor/physician. If vomiting occurs, keep head low so that stomach content doesn't get into the lungs.

Notes to physician Symptoms may be delayed.

Material name: ANSULITE 3% AFFF (AFC-3-A)

1521 Version #: 02 Revision date: 01-08-2014

MSDS US

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General advice If you feel unwell, seek medical advice (show the label where possible). Ensure that medical

personnel are aware of the material(s) involved, and take precautions to protect themselves.

Show this safety data sheet to the doctor in attendance.

5. Fire Fighting Measures

Flammable properties No unusual fire or explosion hazards noted.

Extinguishing media

Suitable extinguishing media

This product is not flammable. Use extinguishing agent suitable for type of surrounding fire.

Protection of firefighters

Specific hazards arising from the chemical

None known.

Specific methods None known.

Hazardous combustion products

May include oxides of nitrogen.

6. Accidental Release Measures

Personal precautions Local authorities should be advised if significant spillages cannot be contained. Surfaces may
become slippery after spillage.

Environmental precautions Prevent further leakage or spillage if safe to do so. Avoid discharge into drains, water courses or
onto the ground.

Methods for containment Stop the flow of material, if this is without risk. Dike the spilled material, where this is possible.
Prevent entry into waterways, sewer, basements or confined areas.

Methods for cleaning up Should not be released into the environment.
Large Spills: Dike far ahead of spill for later disposal. Use a non-combustible material like vermiculite, sand or earth to soak up the product and place into a container for later disposal.
Small Spills: Wipe up with absorbent material (e.g. cloth, fleece).
Never return spills in original containers for re-use. Following product recovery, flush area with water. Clean surface thoroughly to remove residual contamination.

7. Handling and Storage

Handling Do not get this material in contact with eyes. Avoid contact with skin. Avoid prolonged exposure.
Handle and open container with care.

Storage Store in cool place. Store in a well-ventilated place. Keep container tightly closed. Keep out of the
reach of children. Use care in handling/storage.

8. Exposure Controls / Personal Protection

Personal protective equipment

Eye / face protection Do not get in eyes. Wear approved chemical safety glasses or goggles where eye exposure is
reasonably probable.

Skin protection Wear appropriate chemical resistant clothing. Chemical resistant gloves.

Respiratory protection When workers are facing concentrations above the exposure limit they must use appropriate
certified respirators.

General hygiene considerations

Handle in accordance with good industrial hygiene and safety practice. When using, do not eat, drink or smoke. Avoid contact with skin.

9. Physical & Chemical Properties

Appearance

Form Liquid.

Color Light yellow. Clear.

Odor Mild. Sweet.

Physical state Liquid.

pH 6.5 - 8.5

Melting point Not available.

Freezing point Not available.
Boiling point 206.6 °F (97 °C)
Material name: ANSULITE 3% AFFF (AFC-3-A)
1521 Version #: 02 Revision date: 01-08-2014
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Flash point > 212 °F (> 100 °C)
Evaporation rate Not available.
Flammability limits in air, upper, % by volume
Not available.
Flammability limits in air, lower, % by volume
Not available.
Vapor pressure Not available.
Vapor density Not available.
Specific gravity 1.02
Relative density Not available.
Solubility (water) Not available.
Partition coefficient (n-octanol/water)
Not available
Auto-ignition temperature Not available.
Decomposition temperature Not available.
VOC Not available.

10. Chemical Stability & Reactivity Information

Chemical stability Material is stable under normal conditions.
Conditions to avoid None known.
Incompatible materials Alkaline metals. Strong acids, alkalies and oxidizing agents.
Hazardous decomposition products
Nitrogen oxides (NOx). Sulfur oxides. Carbon oxides.

11. Toxicological Information

Toxicological information The toxicity of this product has not been tested.
Toxicological data
Components Test Results
Butyl Carbitol (112-34-5) Acute Dermal LD50 Rabbit: 2700 mg/kg
Acute Oral LD50 Guinea pig: 2000 mg/kg
Acute Oral LD50 Rabbit: 2200 mg/kg
Acute Oral LD50 Rat: 6560 mg/kg
Acute Other LD50 Mouse: 850 mg/kg
Acute Other LD50 Rat: 500 mg/kg
Local effects Components of the product may be absorbed into the body through the skin. Contact may irritate
or burn eyes.

Carcinogenicity This product is not considered to be a carcinogen by IARC, ACGIH, NTP, or OSHA.

Ecotoxicological data

12. Ecological Information

Components Test Results

Butyl Carbitol (112-34-5) EC50 Algae: > 100 mg/l 96.00 Hours
EC50 Water flea (Daphnia magna): 3184 mg/l 24.00 hours
LC50 Bluegill (Lepomis macrochirus): 1300 mg/l 96.00 hours

Ecotoxicity Not expected to be harmful to aquatic organisms.

Environmental effects An environmental hazard cannot be excluded in the event of unprofessional handling or disposal.

Persistence and degradability Not available.

Material name: ANSULITE 3% AFFF (AFC-3-A)
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13. Disposal Considerations

Disposal instructions This product, in its present state, when discarded or disposed of, is not a hazardous waste according to Federal regulations (40 CFR 261.4 (b)(4)). Under RCRA, it is the responsibility of the user of the product to determine, at the time of disposal, whether the product meets RCRA criteria for hazardous waste. Dispose of waste material according to Local, State, Federal, and Provincial Environmental Regulations.

Waste from residues / unused products

Dispose of in accordance with local regulations.

14. Transport Information

DOT

Not regulated as dangerous goods.

15. Regulatory Information

US federal regulations This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication Standard, 29 CFR 1910.1200.

All components are on the U.S. EPA TSCA Inventory List.

US EPCRA (SARA Title III) Section 313 - Toxic Chemical: De minimis concentration

Butyl Carbitol (CAS 112-34-5) 1.0 % N230

US EPCRA (SARA Title III) Section 313 - Toxic Chemical: Listed substance

Butyl Carbitol (CAS 112-34-5) Listed. N230

CERCLA (Superfund) reportable quantity

None

Superfund Amendments and Reauthorization Act of 1986 (SARA)

Hazard categories Acute Health - Yes
Chronic Health - No
Fire Hazard - No
Pressure Hazard - No

Reactivity Hazard - No

Section 302 extremely hazardous substance

No

Section 311 hazardous chemical

No

Inventory status

Country(s) or region Inventory name On inventory (yes/no)*

Australia Australian Inventory of Chemical Substances (AICS) Yes
Canada Domestic Substances List (DSL) No
Canada Non-Domestic Substances List (NDSL) No
China Inventory of Existing Chemical Substances in China (IECSC) No
Europe European Inventory of Existing Commercial Chemical Yes
Substances (EINECS)
Europe European List of Notified Chemical Substances (ELINCS) No
Japan Inventory of Existing and New Chemical Substances (ENCS) No
Korea Existing Chemicals List (ECL) Yes
New Zealand New Zealand Inventory Yes
Philippines Philippine Inventory of Chemicals and Chemical Substances No
(PICCS)
United States & Puerto Rico Toxic Substances Control Act (TSCA) Inventory Yes

*A "Yes" indicates that all components of this product comply with the inventory requirements administered by the governing country(s)

State regulations This product does not contain a chemical known to the State of California to cause cancer, birth defects or other reproductive harm.

US - New Jersey Community RTK (EHS Survey): Reportable threshold

Butyl Carbitol (CAS 112-34-5) 500 LBS

US - Pennsylvania RTK - Hazardous Substances: Listed substance

Butyl Carbitol (CAS 112-34-5) Listed.

Material name: ANSULITE 3% AFFF (AFC-3-A)
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16. Other Information

Further information HMIS® is a registered trade and service mark of the NPCA.

HMIS® ratings Health: 1
Flammability: 0
Physical hazard: 0

NFPA ratings Health: 1
Flammability: 0
Instability: 0

Disclaimer The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

Issue date 01-08-2014
Material name: ANSULITE 3% AFFF (AFC-3-A)
1521 Version #: 02 Revision date: 01-08-2014
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Appendix B: MSDS for Ansul AFFF Foam Tested [79]

MATERIAL SAFETY DATA SHEET
ANSULITE ARC 3x6
Product Code: 1011-2-068 ANa Issue Date: 12-17-2013

1. Product and Company Identification

Material name ANSULITE ARC 3x6
Version #
Revision date
CAS #
Product Code
Product use
02
12-17-2013
Mixture
1011-2-032 ANa
Fire extinguishing agent
Tyco Fire Protection Products
One Stanton Street
Marinette, WI 54143-2542
715-735-7411
http://www.ansul.com
Emergency Phone Number CHEMTREC 800-424-9300 or 703-527-3887
Internet
Phone
Address
Name
Supplier
Manufacturer / Importer /

2. Hazards Identification

Emergency overview WARNING! Causes skin and eye irritation.

OSHA regulatory status This product is considered hazardous under 29 CFR 1910.1200 (Hazard Communication).

Potential health effects

Routes of exposure Eye contact. Skin contact. Inhalation. Ingestion.

Eyes Do not get this material in contact with eyes.
Skin Avoid contact with the skin. Frequent or prolonged contact may defat and dry the skin, leading to
discomfort and dermatitis.
Inhalation Do not breathe vapor. May be irritating.
Ingestion Not a likely route of entry. Do not ingest.
Target organs Eyes. RESPIRATORY SYSTEM. Skin. Central nervous system.
Chronic effects Frequent or prolonged contact may defat and dry the skin, leading to discomfort and dermatitis.
Signs and symptoms Irritation of nose and throat. Irritation of eyes and mucous membranes. Defatting of the skin.
Rash. Skin irritation.
Components CAS # Percent

3. Composition / Information on Ingredients

Butyl Carbitol 112-34-5 2.5 - 10
Other components below reportable levels > 90

4. First Aid Measures

First aid procedures
Eye contact Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if
present and easy to do. Continue rinsing. Get medical attention if irritation persists after washing.
Skin contact Wash off with warm water and soap. Get medical attention if irritation develops and persists.
Inhalation Move to fresh air. For breathing difficulties, oxygen may be necessary. Get medical attention, if
needed.
Ingestion Rinse mouth. Do not induce vomiting without advice from poison control center. IF SWALLOWED:
Immediately call a POISON CENTER or doctor/physician. If vomiting occurs, keep head low so that stomach content doesn't get into the lungs.
Notes to physician Symptoms may be delayed.
Material name: ANSULITE ARC 3x6
1522 Version #: 02 Revision date: 12-17-2013
MSDS US
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General advice If you feel unwell, seek medical advice (show the label where possible). Ensure that medical
personnel are aware of the material(s) involved, and take precautions to protect themselves.
Show this safety data sheet to the doctor in attendance.

5. Fire Fighting Measures

Flammable properties No unusual fire or explosion hazards noted.
Extinguishing media
Suitable extinguishing media
This product is not flammable. Use extinguishing agent suitable for type of surrounding fire.

Protection of firefighters

Specific hazards arising from the chemical

None known.

Specific methods In the event of fire, cool tanks with water spray.

Hazardous combustion products

May include oxides of nitrogen.

6. Accidental Release Measures

Personal precautions Local authorities should be advised if significant spillages cannot be contained. Surfaces may become slippery after spillage.

Environmental precautions Prevent further leakage or spillage if safe to do so. Avoid discharge into drains, water courses or onto the ground.

Methods for containment Stop the flow of material, if this is without risk. Dike the spilled material, where this is possible.

Prevent entry into waterways, sewer, basements or confined areas.

Methods for cleaning up Should not be released into the environment.

Large Spills: Dike far ahead of spill for later disposal. Use a non-combustible material like vermiculite, sand or earth to soak up the product and place into a container for later disposal.

Small Spills: Wipe up with absorbent material (e.g. cloth, fleece).

Never return spills in original containers for re-use. Following product recovery, flush area with water. Clean surface thoroughly to remove residual contamination.

7. Handling and Storage

Handling Do not get this material in contact with eyes. Avoid contact with skin. Avoid prolonged exposure.

Handle and open container with care.

Storage Store in cool place. Store in a well-ventilated place. Keep container tightly closed. Keep out of the reach of children. Use care in handling/storage.

8. Exposure Controls / Personal Protection

Personal protective equipment

Eye / face protection Do not get in eyes. Wear approved chemical safety glasses or goggles where eye exposure is reasonably probable.

Skin protection Wear appropriate chemical resistant clothing. Chemical resistant gloves.

Respiratory protection When workers are facing concentrations above the exposure limit they must use appropriate certified respirators.

General hygiene considerations

When using do not smoke. Avoid contact with skin. Keep away from food and drink. Handle in accordance with good industrial hygiene and safety practice.

9. Physical & Chemical Properties

Appearance
Form Liquid. Gel.
Color Light yellow.
Odor Mild. Sweet.
Physical state Liquid.
pH 6.5 - 8.5
Melting point Not available.
Freezing point Not available.
Boiling point > 212 °F (> 100 °C)
Material name: ANSULITE ARC 3x6
1522 Version #: 02 Revision date: 12-17-2013
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Flash point Not available.
Evaporation rate Not available.
Flammability limits in air, upper, % by volume
Not available.
Flammability limits in air, lower, % by volume
Not available.
Vapor pressure Not available.
Vapor density Not available.
Specific gravity 1
Relative density Not available.
Solubility (water) Not available.
Partition coefficient (n-octanol/water)
Not available
Auto-ignition temperature Not available.
Decomposition temperature Not available.
VOC Not available.

10. Chemical Stability & Reactivity Information

Chemical stability Material is stable under normal conditions.
Conditions to avoid None known.
Incompatible materials Alkaline metals. Strong acids, alkalies and oxidizing agents.
Hazardous decomposition products
Nitrogen oxides (NOx). Sulfur oxides. Carbon oxides.

11. Toxicological Information

Toxicological information The toxicity of this product has not been tested.
Toxicological data
Components Test Results
Butyl Carbitol (112-34-5) Acute Dermal LD50 Rabbit: 2700 mg/kg
Acute Oral LD50 Guinea pig: 2000 mg/kg

Acute Oral LD50 Rabbit: 2200 mg/kg
Acute Oral LD50 Rat: 6560 mg/kg
Acute Other LD50 Mouse: 850 mg/kg
Acute Other LD50 Rat: 500 mg/kg

Local effects Components of the product may be absorbed into the body through the skin. Contact may irritate
or burn eyes.

Carcinogenicity This product is not considered to be a carcinogen by IARC, ACGIH, NTP, or OSHA.

Ecotoxicological data

12. Ecological Information

Components Test Results

Butyl Carbitol (112-34-5) EC50 Algae: > 100 mg/l 96.00 Hours
EC50 Water flea (Daphnia magna): 3184 mg/l 24.00 hours
LC50 Bluegill (Lepomis macrochirus): 1300 mg/l 96.00 hours

Ecotoxicity Contains a substance which causes risk of hazardous effects to the environment.

Environmental effects An environmental hazard cannot be excluded in the event of unprofessional handling or disposal.

Persistence and degradability Not available.

Material name: ANSULITE ARC 3x6
1522 Version #: 02 Revision date: 12-17-2013
MSDS US
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13. Disposal Considerations

Disposal instructions This product, in its present state, when discarded or disposed of, is not a hazardous waste
according to Federal regulations (40 CFR 261.4 (b)(4)). Under RCRA, it is the responsibility of the user of the product to determine, at the time of disposal, whether the product meets RCRA criteria for hazardous waste. Dispose of waste material according to Local, State, Federal, and Provincial Environmental Regulations.

Waste from residues / unused products

Dispose of in accordance with local regulations.

14. Transport Information

DOT

Not regulated as dangerous goods.

15. Regulatory Information

US federal regulations This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication
Standard, 29 CFR 1910.1200.

All components are on the U.S. EPA TSCA Inventory List.

US EPCRA (SARA Title III) Section 313 - Toxic Chemical: De minimis concentration

Butyl Carbitol (CAS 112-34-5) 1.0 % N230

US EPCRA (SARA Title III) Section 313 - Toxic Chemical: Listed substance

Butyl Carbitol (CAS 112-34-5) Listed. N230

CERCLA (Superfund) reportable quantity
None
Superfund Amendments and Reauthorization Act of 1986 (SARA)
Hazard categories Acute Health - Yes
Chronic Health - No
Fire Hazard - No
Pressure Hazard - No
Reactivity Hazard - No
Section 302 extremely hazardous substance
No
Section 311 hazardous chemical
No
Inventory status
Country(s) or region Inventory name On inventory (yes/no)*
Australia Australian Inventory of Chemical Substances (AICS) Yes
Canada Domestic Substances List (DSL) No
Canada Non-Domestic Substances List (NDSL) No
China Inventory of Existing Chemical Substances in China (IECSC) No
Europe European Inventory of Existing Commercial Chemical Yes
Substances (EINECS)
Europe European List of Notified Chemical Substances (ELINCS) No
Japan Inventory of Existing and New Chemical Substances (ENCS) No
Korea Existing Chemicals List (ECL) No
New Zealand New Zealand Inventory No
Philippines Philippine Inventory of Chemicals and Chemical Substances No
(PICCS)
United States & Puerto Rico Toxic Substances Control Act (TSCA) Inventory Yes
*A "Yes" indicates that all components of this product comply with the inventory requirements administered by the governing country(s)
State regulations WARNING: This product contains a chemical known to the State of California to cause cancer.
US - New Jersey Community RTK (EHS Survey): Reportable threshold
Butyl Carbitol (CAS 112-34-5) 500 LBS
US - Pennsylvania RTK - Hazardous Substances: Listed substance
Butyl Carbitol (CAS 112-34-5) Listed.
Material name: ANSULITE ARC 3x6
1522 Version #: 02 Revision date: 12-17-2013
MSDS US
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16. Other Information

Further information HMIS® is a registered trade and service mark of the NPCA.
HMIS® ratings Health: 1
Flammability: 0

Physical hazard: 0
NFPA ratings Health: 1
Flammability: 0
Instability: 0

Disclaimer The information provided in this Safety Data Sheet is correct to the best of our knowledge,
information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

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Appendix C: MSDS for Ansul AFFF Foam Tested [80]

MATERIAL SAFETY DATA SHEET
ANSUL 3% FLUOROPROTEIN FOAM CONCENTRATE
Product Code: 1050-3-001 SBg Issue Date: 11-12-2013
1. Product and Company Identification
Material name ANSUL 3% FLUOROPROTEIN FOAM CONCENTRATE
Version #
Revision date
CAS #
Product Code
Product use
05
11-12-2013
Mixture
1050-3-001 SBg
Fire extinguishing agent
CHEMTREC 800-424-9300 or 703-527-3887
http://www.ansul.com
Marinette, WI 54143-2542
One Stanton Street
Tyco Fire Protection Products
Emergency Phone Number
Internet
Phone
Address
Name
Supplier
Manufacturer / Importer /

715-735-7411

2. Hazards Identification

Emergency overview Causes skin and eye irritation.

OSHA regulatory status NON-HAZARDOUS SUBSTANCE. NON-DANGEROUS GOODS.

Potential health effects

Routes of exposure Eye contact. Skin contact.

Skin Avoid contact with the skin. Frequent or prolonged contact may defat and dry the skin, leading to
discomfort and dermatitis.

Inhalation May be irritating.

Ingestion Not a likely route of entry.

Target organs Eyes. Skin.

Chronic effects Frequent or prolonged contact may defat and dry the skin, leading to discomfort and dermatitis.

Signs and symptoms Defatting of the skin. Skin irritation.

Components CAS # Percent

3. Composition / Information on Ingredients

POLYETHYLENE GLYCOL 25322-68-3 2.5 - 10

Other components below reportable levels > 90

4. First Aid Measures

First aid procedures

Eye contact Rinse with water.

Skin contact Get medical attention if irritation develops and persists.

Inhalation Move to fresh air. Get medical attention, if needed.

Ingestion Rinse mouth.

Notes to physician Symptoms may be delayed.

General advice If you feel unwell, seek medical advice (show the label where possible). Show this safety data
sheet to the doctor in attendance.

5. Fire Fighting Measures

Flammable properties This product is not flammable.

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Extinguishing media

Suitable extinguishing media

This product is not flammable. Use extinguishing agent suitable for type of surrounding fire.

Protection of firefighters

Specific hazards arising from the chemical

None known.

Specific methods None known.

Hazardous combustion

products
May include oxides of nitrogen.

6. Accidental Release Measures

Personal precautions Surfaces may become slippery after spillage.
Environmental precautions Prevent further leakage or spillage if safe to do so. Avoid discharge into drains, water courses or
onto the ground.
Methods for containment Dike the spilled material, where this is possible.
Methods for cleaning up Large Spills: Use a non-combustible material like vermiculite, sand or earth to soak up the product
and place into a container for later disposal.
Small Spills: Wipe up with absorbent material (e.g. cloth, fleece).
Never return spills in original containers for re-use.

7. Handling and Storage

Handling Avoid contact with skin.
Storage Keep container tightly closed.

8. Exposure Controls / Personal Protection

Engineering controls None known.
Personal protective equipment
Respiratory protection Not normally needed.
General hygiene considerations
Handle in accordance with good industrial hygiene and safety practice. Avoid contact with skin.

9. Physical & Chemical Properties

Appearance
Form Liquid.
Color Brown.
Odor Not available.
Physical state Liquid.
pH 6.5 - 7.5
Melting point Not available.
Freezing point Not available.
Boiling point 212 °F (100 °C)
Flash point Not available.
Evaporation rate Not available.
Flammability limits in air, upper, % by volume
Not available.
Flammability limits in air, lower, % by volume
Not available.
Vapor pressure Not available.
Vapor density Not available.
Specific gravity Not available.
Relative density Not available.

Solubility (water) completely soluble
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Partition coefficient (n-octanol/water)
Not available

Auto-ignition temperature Not available.

Decomposition temperature Not available.

VOC Not available.

Pour point < 10.4 °F (< -12 °C)

10. Chemical Stability & Reactivity Information

Chemical stability This is a stable material.

Conditions to avoid None known.

Incompatible materials Alkaline metals.

Hazardous decomposition products
Nitrogen oxides (NOx). Sulfur oxides. Carbon oxides.

11. Toxicological Information

Toxicological information The toxicity of this product has not been tested.

Local effects Irritating to eyes. Mild skin irritation

Carcinogenicity This product is not considered to be a carcinogen by IARC, ACGIH, NTP, or OSHA.

Ecotoxicological data

12. Ecological Information

Components Test Results
POLYETHYLENE GLYCOL (25322-68-3) LC50 Atlantic salmon (Salmo salar): > 1000 mg/l 96.00 hours

Ecotoxicity Not expected to be harmful to aquatic organisms.

Environmental effects An environmental hazard cannot be excluded in the event of unprofessional handling or disposal.

Aquatic toxicity Not known.

Persistence and degradability Not available.

13. Disposal Considerations

Waste from residues / unused products
Dispose of in accordance with local regulations.

14. Transport Information

DOT
Not regulated as dangerous goods.

15. Regulatory Information

US federal regulations Not regulated.
All components are on the U.S. EPA TSCA Inventory List.

CERCLA (Superfund) reportable quantity

None

Superfund Amendments and Reauthorization Act of 1986 (SARA)

Hazard categories Acute Health - No
Chronic Health - No
Fire Hazard - No
Pressure Hazard - No
Reactivity Hazard - No

Section 302 extremely hazardous substance
No

Section 311 hazardous chemical
No

Inventory status

Country(s) or region Inventory name On inventory (yes/no)*
Australia Australian Inventory of Chemical Substances (AICS) Yes
Canada Domestic Substances List (DSL) Yes
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Country(s) or region Inventory name On inventory (yes/no)*
Canada Non-Domestic Substances List (NDSL) No
China Inventory of Existing Chemical Substances in China (IECSC) No
Europe European Inventory of Existing Commercial Chemical Yes
Substances (EINECS)
Europe European List of Notified Chemical Substances (ELINCS) No
Japan Inventory of Existing and New Chemical Substances (ENCS) No
Korea Existing Chemicals List (ECL) Yes
New Zealand New Zealand Inventory Yes
Philippines Philippine Inventory of Chemicals and Chemical Substances No
(PICCS)
United States & Puerto Rico Toxic Substances Control Act (TSCA) Inventory Yes

*A "Yes" indicates that all components of this product comply with the inventory requirements administered by the governing country(s)

State regulations This product does not contain a chemical known to the State of California to cause cancer, birth defects or other reproductive harm.

16. Other Information

Further information HMIS® is a registered trade and service mark of the NPCA.

HMIS® ratings Health: 1
Flammability: 0
Physical hazard: 0

NFPA ratings Health: 1
Flammability: 0

Instability: 0

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Issue date 11-12-2013

Material name: ANSUL 3% FLUOROPROTEIN FOAM CONCENTRATE
1648 Version #: 05 Revision date: 11-12-2013
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