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Assessment of Non-Fluorinated Firefighting Foams : Foam Performance and Ecotoxicity

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Table of Contents

Table of Contents.....	i
List of Figures	iii
List of Tables	iv
Executive Summary	v
1 Introduction	1
1.1 AFFF and F3	1
1.2 Objectives.....	3
2 Foam Properties	4
2.1 Foam Chemical and Physical Properties.....	4
2.1.1 Refractive index	4
2.1.2 Viscosity	4
2.1.3 pH.....	4
2.2 Foam Performance Properties	4
2.2.1 Spreading coefficient	4
2.2.2 Film formation and sealability.....	5
2.2.3 Foamability	5
2.2.4 Foam drainage	5
2.3 Foam Fire Suppression Performance	5
2.3.1 Standard test methods.....	5
2.3.2 Fire extinguishment	6
2.3.3 Torch tests for fuel shedding.....	7
2.3.4 Burnback flame resistance test	7
3 Alternatives to AFFF	9
3.1 Fluorine-free foams and their properties	9
3.2 Performance of alternative foams	12
3.2.1 Film forming and sealability of alternative foams.....	12
3.2.2 Foam drainage of alternative foams.....	13
3.2.3 F3 Fire performance of alternative foams	13
4 Eco-Toxicity of Alternative Foams.....	14
4.1 Methodology	14

4.2 Discussion	16
5 Conclusions and Recommendations	17
Acknowledgments	18
References	19
Supplement A	21

List of Figures

Figure 1 Function of firefighting foams	1
Figure 2 Structures of PFOS and PFOA.....	2
Figure 3 Alternative non-fluorinated chemicals.....	9
Figure 4 Surface tensions of various fuels (red bars) and foam surfactants (Blue line) [5], [14] (F: Polyfluorinated, S: siloxane, A: alkyl, W: water, ES: Ethoxy-Siloxane, B, K, KA, RH: non-fluorinated surfactants).....	12

List of Tables

Table 1 Foam properties	4
Table 2 Summary of test protocols of major standards.....	8
Table 3 List of selected products.....	10
Table 4 Chemical and physical properties of selected products	11
Table 5 Test results of film formation and fire extinguishment times of three commercial products [11]	12
Table 6 GHS hazard category, code, and statement [16].....	15
Table 7 GHS Summation Method for Category Classification of Mixtures (UN, 2019).	16
Table 8 Hazard category ranking of fluorine free and fluorinated foams (NAT = No acute toxicity, NCT = No chronic toxicity).	16

Assessment of Non-Fluorinated Firefighting Foams: Foam Performance and Ecotoxicity

Rokib Hassan, Nour Elsagan and Yoon Ko

Executive Summary

Aqueous Film-Forming Foam (AFFFs) are high performance firefighting foams suitable for rapid knockdown of flammable liquid fires with the outstanding film-forming capability owing to their key ingredient of fluorinated surfactants. However, the fluorinated surfactants used in AFFFs have negative impacts on the environment and health due to their low biodegradability and ecotoxicity. As such, a range of fluorine free foams (F3s) have been commercially developed using other chemicals including synthetic fluorine free ether based surfactants. The F3s were studied as an alternative to AFFFs in this study by reviewing the performance of commercially available F3s and assessing their ecotoxicity in comparison to AFFFs.

Generally, the fire suppression performance of foams can be estimated from foam properties, such as spreading coefficient, foamability and foam drainage, yet the fire suppression performance is examined by carrying out standard fire tests mainly examining fire extinguishment time, foam blanket sealability and burnback resistance time.

Only AFFFs with polyfluorinated surfactants have passed the most stringent fire extinguishment time requirement since the rapid fire control of pool fires depends strongly on the film forming ability of the foams rather than foam flows. It is also reported that F3 products did not fully seal the fuel surface by forming film over the surface of the fuel allowing fuel vapour re-ignition. Overall, the performance varies from product to product, but AFFFs demonstrated better performance than F3s.

An ecotoxicity analysis was conducted for twelve fluorine free foams and three AFFFs selected through the market survey conducted in the present study. Overall, the ecotoxicity of the F3s was not found to be better than the AFFFs. This is because the ecotoxicity depends on the chemical ingredients used in F3 products, which could be also equally or more toxic than the fluorinated surfactants used in AFFFs. In fact, many of the F3 products were found to have high concentrations of hazardous ingredients, which resulted in rankings between Acute 1 (very toxic) and Acute 3 (harmful) when analysed with the highest concentration values in their safety data sheets (SDS). Fluorinated foams have a more prominent chronic impact to aquatic life, yet the results from some of the F3s also indicated not only acute but also chronic impact to aquatic life.

1 Introduction

Firefighting foams are extensively used as a fire extinguishing medium for flammable and combustible liquids. The density of firefighting foam solutions is lower than oil, gasoline or water as they contain stable mass of small air-filled bubbles. These foams are mainly composed of water with a foaming agent, known as a surfactant. When these foams are applied to extinguish a fire, they cool off the fire, and some foams are designed to form a thin layer of water/surfactant film (see Figure 1). This thin film limits fuel vapour coming through the fuel surface, providing extra protection in addition to the foam blanket. The thin film and foam blanket serve as a barrier between the fuel and oxygen (air) resulting in suppression of the fuel combustion. In contrast, if water was used to extinguish a hydrocarbon fire, it will sink at the bottom of the fuel due to higher density [1]. Hence, firefighting foams are effective suppression system complementing limitation of water (i.e. higher density than fuels, potential boil over (i.e. fuel throwing out of the container) when heated above 100 °C).

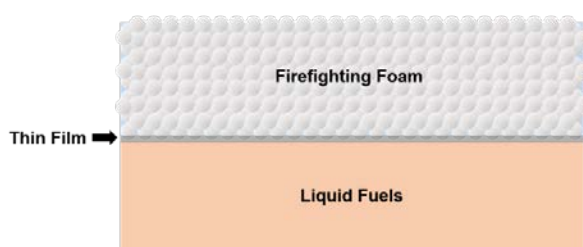


Figure 1 Function of firefighting foams

AFFF (Aqueous Film-Forming Foam) is used to extinguish high-hazard flammable liquid fires (Class B fires). This applies to chemical plants; flammable liquid storage and processing facilities; merchant operations (oil tankers, offshore platforms); municipal services (fire departments, firefighting training centers); oil refineries, terminals, and bulk fuel storage farms; aviation operations (aircraft rescue and firefighting, hangars); and military facilities. Currently, it is used in the U.S. military as well as in many countries around the world for most civilian applications. A large quantity of AFFF is currently in stock or service in the U. S., and the products are tested and certified by in conformance to the Military Specification [1]. Most of AFFF product being used are Underwriters Laboratory (UL) listed and conform to UL 162, "Foam Equipment and Liquid Concentrates".

1.1 AFFF and F3

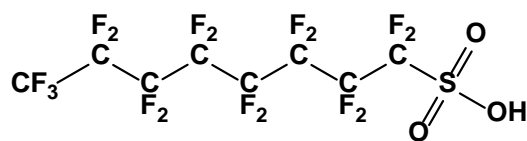
There are different types of foams for class B fires as follows;

- **Aqueous film-forming foam concentrates (AFFF)** based on mixtures of hydrocarbon surfactants and fluorinated surfactants with the ability to form an aqueous film on the surface of some hydrocarbon fuels;
- **Film-forming fluoroprotein foam concentrates (FFFP)** with added fluorinated surfactants and ability to form an aqueous film on the surface of some hydrocarbon fuels;
- **Fluoroprotein foam concentrates (FP)** with added fluorinated surfactants;
- **Protein foam concentrates (P)** derived from hydrolysed protein materials;
- **Synthetic foam concentrates (S)** based upon mixtures of hydrocarbon surfactants other than a fluorinated surfactant or hydrolyzed protein
- **Fluorine free foam concentrates (F3)** without using fluoroorganic compounds and based upon mixtures of hydrocarbon surfactants and non-fluorine containing stabilizers

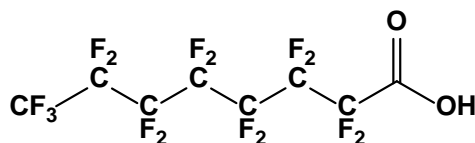
AFFF, FFFP and FP contain fluorinated surfactants, while P, S and F3 are fluorine free.

Each type of foams can be formulated to be Alcohol resistant foam concentrates (AR), which are suitable for both polar and non-polar liquid fuels by adding resistance to breakdown when applied to the surface of water-miscible liquid fuels. Among class B foams, AFFF has been widely used across the globe to extinguish fires caused by both polar and non-polar combustible liquids [2]–[5]. AFFF is composed of fluorinated surfactants, solvents, hydrocarbon surfactants and a low proportion of halide ions in slightly alkaline solution. These fluorinated surfactants are per- and polyfluoroalkyl substances. One of the most used fluorinated surfactants in foams is perfluorooctylsulfonate (PFOS) (Figure 2). In addition, there are two other fluorinated surfactants used including perfluorooctanoic acid (PFOA) (Figure 2) and perfluorocarboxylic acids (PFCA).

The use of AFFF has caused a significant backlash due to the negative impact of the fluorinated surfactants on the environment, ecology and health. Because of the chemical inertness, fluorinated surfactants have a very low biodegradability. Therefore upon leaching, they accumulate in the environment especially the ground soil and surface water [2]. In 2006, the European Union banned the use of PFOS. In the same year, the U.S. Environmental Protection Agency (EPA) reported PFOS as “likely to be carcinogenic to humans”. In 2009, PFOS was internationally classified as a persistent organic pollutant. Later, the U.S. EPA defined the concentration limits of PFOS and PFOA in drinking water, which are 0.2 µg/L and 0.4 µg/L, respectively [6]. Due to the low biodegradability, post-cleaning and disposing of fire extinguishing water containing AFFF are expensive and complex due to the environmental and toxicological regulation [5]. Thus, most of the fluorinated surfactants have been gradually phasing out of the market since 2009.



Perfluorooctanesulfonic acid (PFOS)



Perfluorooctanoic acid (PFOA)

Figure 2 Structures of PFOS and PFOA

In recent years, there have been several research initiatives to develop more environmentally benign fluorine free foams (F3) as alternatives to AFFF. The goal of these research initiatives is to develop foams using environmentally-friendly and non-hazardous ingredients, while offering similar fire suppression performance as AFFF. To date, there are a range of products available in the market including synthetic fluorine free ether based surfactants [4]. However, the performance of F3s has not been thoroughly reviewed. More importantly, the detailed environmental impact and the ecotoxicity of F3 are not well documented in peer reviewed literature. Hence, there is a need for a non-bias third party environmental impact and ecotoxicity assessment.

This report provides literature review of the chemical and physical properties of firefighting foams and fire performance testing and requirements. Also, a market survey was conducted to review the relative foam performance of several F3 and AFFF. This study also conducted ecotoxicity analyses of selected F3 products to understand the environmental benefits of fluorine free products.

1.2 Objectives

This report assesses the environmentally benign alternatives to the fluorinated class B firefighting foams, such as AFFFs. Hence, the focus of this study will be on AFFF class B firefighting foams and their alternative F3s. The objectives of this literature review are to;

1. review the chemical and physical properties of foams
2. compare fire performance testing methods and requirements in different standards
3. survey F3s with regard to the foam performance
4. conduct ecotoxicity analyses of selected F3s.

The findings from this literature review will help develop a future research plan to find green firefighting solutions.

2 Foam Properties

Firefighting foams are characterized by chemical and physical properties. Table 1 shows the different foam indications and their properties. Foams are required to be tested for a number of these properties by many standards and specifications, such as ICAO [7], IMO 1312 [8], EN 1568 [9] and UL 162. For example, approximately 20 foam properties are required for testing by the US military specification [1]. This section describes some of foam chemical/physical properties and foam performance properties as well as fire performance.

Table 1 Foam properties

Indications	Properties
General properties	Refractive Index, Viscosity, pH value, Corrosion
Foam performance properties	Foamability, Spreading Coefficient, Stability
Compatibility to other fire suppressants	Compatibility to dry chemicals and other foam products
Environment impact	Toxicity, Total halides, Fluorine content
Aging	Resistance to freezing and thawing, Sedimentation

2.1 Foam Chemical and Physical Properties

2.1.1 Refractive index

Refractive index (RI) is the measurement of speed of a light beam passing through a solution, which is proportional to the amount of solvent in the sample. Thus, RI is an indicator of the quality of a firefighting foam or premixed solution, and a lower RI value represents improper dilution by water or inadvertent dilution by system failures such as bladder rip. Hence, the MilSpec [1] has minimum requirements for specific concentrates (1.3630 for 3% foam solution and 1.3580 for 6% foam solution).

2.1.2 Viscosity

Foam viscosity; higher or lower than the anticipated value; provides insight into potential storage problems, such as dilution or polymer separation (i.e. caused by freezing and thawing of non-freeze protected foams). Also, typical alcohol resistant foams have high viscosities due to the large polymer ingredients used to achieve the alcohol resistance. High viscosity foams require attentions for extreme conditions of storage or foam ageing. In addition, high viscosity foams require a special proportioning orifice.

2.1.3 pH

A pH outside of 6.0 - 9.5 can be resulted from corrosion, contamination within the tank or degradation of the foam concentrate.

2.2 Foam Performance Properties

2.2.1 Spreading coefficient

Spreading coefficient indicates whether or not the foam has ability to spontaneously spread on the fuel surface and form a thin aqueous film on the surface of hydrocarbon liquid fuels. The film plays as an extra layer of protection on top of the foam blanket. The spreading coefficient (S) is the difference between the fuel surface

tension (δ_F) and the sum of the surface tension of the extinguishing agent (δ_A) and the interfacial tension between the fuel and the aqueous phase (δ_I).

$$S = \delta_F - (\delta_A + \delta_I)$$

If the foam has a positive spreading coefficient, it will spontaneously spread on the fuel surface and form a film. In contrast, a foam with a negative spreading coefficient will not form a film. IMO 1312 [8] and NFPA 11 [10] require a positive spreading coefficient, and the MilSpec [1] requires a minimum spreading coefficient of 3 dynes/cm when tested on cyclohexane.

2.2.2 Film formation and sealability

A small scale test is required by MilSpec [1] to evaluate the ability to form an extra film in addition to the foam blanket. No sustained ignition is required when a pilot flame is passed over the surface of a fuel (cyclohexane).

2.2.3 Foamability

Foamability or the foam expansion is another important physical property requirement of firefighting foams [5], [11]. Foams are thermodynamically unstable. Hence, they are stabilized by using surfactants, which prevent bubble collapse. Foamability increases with increasing surfactant concentration up to the critical concentration level, after which surfactant concentration has little impact on the foamability. Foamability also depends on the nozzle type and pressure used for making the foam. The foam expansion ratio is the coefficient of the volume of foam relative to the volume of the foam solution. The minimum foam expansion requirement of a firefighting foam, defined by the MilSpec, is 5.0 for both 3% and 6% solutions. International Maritime Organization IMCO 1312 [8] has no requirement, yet International Civil Aviation Organization [7] requires 6-10 and 8-12 for film-forming/fluorinated synthetic foams and for protein based foams, respectively.

2.2.4 Foam drainage

Foam drainage is the flow of liquid foam solution, which can occur while foam collapses. In general, the rate of drainage decreases when using cold water and increases with hard or saline water. This important property is assessed by measuring the foam drainage time, which is defined as the time to drain out the solution (specific percentages of 25% or 50%) from the foam bubbles. Drainage time gives indication on how fast the foam solution is released from the bubble mass. Thus, the longer the drainage time is, the greater is the ability of the foam to retain water and to maintain coverage over the fuel surface until the fire is being extinguished. MilSpec [1] requires minimum 2.5 minutes for 25% drainage time, and ICAO [7] requires drainage times in excess of 3 minutes for film-forming foams and synthetic foams, and in excess of 5 minutes for protein-based foams. NFPA 11 [10] describes the drainage time test in Annex D, but it does not specify required times.

2.3 Foam Fire Suppression Performance

The fire suppression performance criteria are the most important and critical properties of the foams. Fire suppression performance of foams can be estimated from foam properties, such as spreading coefficient, foamability and foam drainage, yet the fire suppression performance is examined by carrying out standard fire tests. Several standard fire test methods are available, each having different objectives and testing scope. This section discusses the standard test methods and compares the protocols of different standards.

2.3.1 Standard test methods

This section reviews the fire suppression test methods to evaluate Class B foams specified by the following standards and guidelines;

- MIL-PRF-24385 Performance specification - Fire extinguishing agent, aqueous film-forming foam (AFFF) liquid concentrate for fresh and sea water [1]
- ICAO Airport Services Manual Doc 9137-AN/898 Part1-Rescue and Firefighting Fourth Edition, 2015 [7]
- IMO1312 (new versions of IMO 582) Revised guidelines for the performance of foam concentrates [8]
- BS EN 1568-3 Fire extinguishing media – Foam concentrates, Part 3: Specification for low expansion foam concentrates for surface application to water-immiscible liquids [9]
- UL 162 Standard for Foam Equipment and Liquid Concentrates [12]
- NFPA 11 Standard for Low-, Medium-, and High-Expansion Foam [10]

These standards specify requirements for foam concentrate and foam, and provide testing protocols for evaluating the performance of low expansion (i.e. expansion ratio less than 20) foam system. NFPA 11 covers additionally the design, installation, operation, testing and maintenance of foam systems that applies to flammable liquid protection systems within buildings, for storage tanks and processing areas. ICAO (International Civil Aviation Organization) specifies requirements and testing protocols concerning aircraft fires. In addition, all foams used in civilian airports must be approved to ICAO Level A, B or C standard. IMO (International Maritime Organization) applies to fixed deck foam fire-extinguishing systems/portable foam applicators required for tankers and chemical tankers; and in machinery spaces. MIL-PRF-24385 covers military uses/aviation and is designed specifically for AFFF. BS EN 1568-3, which is a British and European standard, covers chemical, physical properties, and minimum performance requirements for low expansion foams suitable for surface application to liquid fuels. Covering not only foam concentrate/foam but also sprinklers/spray nozzles and equipment, UL 162 applies to petroleum industry, heavy industry and ware house.

As the scope and objectives of the standards vary, their test details and the performance criteria are different. Table 2 provides a summary of test protocols of the standards and compares the required performance criteria of the standards.

Each standard requires to test the foam against a circular or rectangular pool fire and evaluate the fire suppression performance based on the following criteria;

- Fire extinguishment time
- Foam blanket sealability test (Torch test)
- Burnback resistance time

2.3.2 Fire extinguishment

The fire suppression performance of foam is assessed mainly by measuring the fire extinguishment time of a pool fire. There are several factors, which directly impact the fire performance of the foams. These include air temperature, wind velocity, nozzle type; application density, discharge rate and its duration, pan size and its features; fuel type and preburn time [13]. Table 2 compares some of these factors for different standards.

While heptane is used as fuel for pool fire for IMO 1312, EN 1568 and UL 162, gasoline and Jet-A fuel are required by MIL-PRF2485 and ICAO, respectively. Since these fuels with the low boiling and flash points are susceptible to ignite and reignite, successful fire extinguishment requires foams to seal the fuel surface and to prevent fuel vapor transport through the foam layers.

Nozzles and application methods (forceful or gentle application) have direct impact on the fire suppression performance. While UNI 86 type nozzle is widely accepted by many standards, the MilSpec requires smaller NFS type nozzle with a relatively low flow rate. Some standards require gentle application of foams by applying to the vertical backboard (i.e. fitted to the wall of the base pool pan) rather than directly to the fuel surface.

The required extinguishment time varies with the objectives of each standard. The MIL-PRF2485 requires extremely rapid knockdown of fire because the objectives are to minimize thermal damage to costly weapons and maximize the rescue opportunities for the occupants, especially from the flight deck of an aircraft carrier. The extinguishment times required by the MIL-PRF2485 are within 30 seconds for a 2.6 m² pool and 50 seconds for a 4.6 m² pool at a relatively low application rate of 7.57 l/min, which are the most stringent time requirements compared to other standards. Since the rapid fire control of pool fires depends on the film forming ability of the foams rather than foam flows, only AFFFs with polyfluorinated surfactants have passed this stringent extinguishment time requirement [13].

Concerning airport fires where fast responses are critical, ICAO requires fire suppression with minute flame within 60 seconds and complete extinguishment within 120 seconds for a Jet-A pool fire. ICAO requires pan areas of 2.5, 4.8 and 7.32 m² for Level A, B and C, respectively. Among the pan sizes required by the standards, the largest pan size is 9 m² required by NFPA 11 (i.e. a pan size of 4.5 -4.8 m² is typical in the standards).

For scenarios of large fuel tank and ship fires, relatively long extinguishment times are allowed since foams' ability to spread and seal the fuel surface becomes important rather than rapid knockdown by film-formation. IMO 1312 uses a criterion of 300 seconds for fire extinguishment time for the heptane pool (4.5 m²), and EN uses a classification system allowing extinguishment times of 1.5, 3, 4 and 5 minutes for different types of foams. Typical film-forming foams (AFFF and FFFP) show the extinguishment performance of class I (3 minutes) whereas nonfilm-forming foams (FP, P and S) demonstrate the class II (4 minutes) or III (5 minutes) extinguishment performance.

2.3.3 Torch tests for fuel shedding

The fuel shedding ability is another important factor defining the fire performance of the foams, and it is determined by torch test. In this test, fuel diffusion through the foam blanket and the extent of fuel pick up by the foam on the fuel surface are evaluated by passing a lighted torch above the foam blanket over the entire pool surface as indicated by the standards. Generally, AFFFs show good fuel shedding ability as they have small interfacial tension between the fuel and foam solution.

2.3.4 Burnback flame resistance test

Another important test to evaluate the fire performance of foams is burnback resistance test. This test is required to be performed after some time (drainage time), from the foam application, during which the foam can undergo drainage or collapse. The drainage time required by MIL-PRF2485, ICAO, IMO and EN are 60, 120, 300 and 300 seconds, respectively. In general, prolonged delay time affords more drainage resulting in making the foam more susceptible to burnback [9]. The test is carried out by placing a burnback pot or pipe in the base pan so that the burnback flame can affect the surrounding foam and fuel in the base pan. While the height of the burnback pot or pipe is typically higher than the foam surface in the base pan, the height required by MIL-PRF2485 is low so that it could be more challenging to the foam in resisting the burnback. The burnback resistance is assessed by measuring the time required for a burnback flame to spread and cover 20% or 25% of the pan size. The burnback delay time requirements vary for different standards. The longest burnback time requirement is 15 min in IMO 1312 and EN 1568 (for burnback Level B).

Table 2 Summary of test protocols of major standards

	MIL-PRF-24385	ICAO	IMO 1312	EN 1568-3	UL162	NFPA 11 Annex F
Pool fire test						
Fuel	Gasoline	Jet A, Kerosene	Heptane	Heptane	Heptane	Gasoline
Test pan area [m²]	Circular 2.6, 4.6	Circular 2.5, 4.8, 7.32	Square, 4.5	Circular, 4.5	Square 4.6	Square 9
Vertical Back Board (BB)	no	no	1 m high	no or 1 m high	no	no
Substrate	water	water	sea water	water	water	water
Preburn time (sec)	10 sec	60 sec	60 ± 5 sec	60 ± 2 sec	60 sec	60 sec
Foam application	Forceful @6.89 bar	Forceful @7 bar	Gentle with BB @6.3 bar	Gentle with BB for P, S @6.3 bar	N/A	Gentle @6.89 bar
				Forceful for AFFF, FFFP, FP, F3 @6.3 bar		
Nozzle	NFS	UNI 86	UNI 86	UNI 86	Hose	
Flow rate [l/min]	7.57 l/min	11.4 l/min	11.4 l/min	11.4 l/min	18.6 or 11.6	22.7
application density[l/minm²]	1.65 or 2.91	1.56, 2.38 or 4.56	2.53	2.53	4 or 2.4	
Spray Duration	90 sec	120 sec	300 sec	300 sec for gentle	180 sec	300 sec
				180 sec for forceful		
Extinguish time	≤30 sec for 2.6 m²	≤ 60 sec suppression with minute flames ≤ 120 sec total extinguishment	≤300 sec	≤300 sec for gentle Class III	≤180 sec	≤300 sec
				≤90 sec for forceful Class I+		
	≤50 sec for 4.6 m²			≤180 sec for forceful Class I ≤240 sec for forceful Class II		
Torch Test						
Torch Test	No	No	No	No	yes	yes
Burnback test						
Burnback test fuel	Gasoline	gasoline or Kerosene	same fuel	same fuel	same fuel	same fuel
Pot size [m]	0.3 dia 0.05 high	0.3 dia 0.2 high	0.3 dia 0.15 high	0.3 dia 0.25 high	0.3 dia pipe	0.3 dia pipe
Drainage time (sec)	60 sec	120 sec	300 sec	300 s	540 sec	15 min
Measurement	Visual determination of 25% by area	Visual determination of 25% by area	visually or by thermal radiation measurements	visually or by thermal radiation measurements	Visual determination of 20% by area	
25% burnback time	360 sec	300 sec	900 sec	for Class I, II, III for gentle 900 sec for Level B 600 sec for Level C 300 sec for Level D	20% burnback time 300 sec	5 min burback area ≤ 0..25 m²
				for Class I, II forceful 600 sec for Level A		

3 Alternatives to AFFF

3.1 Fluorine-free foams and their properties

Despite the outstanding performance of AFFF in rapid attack of fires, alternatives have been sought since AFFF possesses adverse effects on our health and the environment. The growing stringency of environmental regulations for the fluorinated compounds used in AFFF has driven the development of environmentally benign foams to replace AFFF. As a result, the firefighting foam manufacturers were involved in developing new Fluorine-Free Foams (F3). This study conducted a market survey and identified 25 companies around the world currently offering F3 for both class A and class B fires. Through the market survey, six companies (Table 3) were selected for further analyses including ecotoxicity. The six companies manufacture synthetic Fluorine-Free Foams (F3) in different concentrations for class B fires. According to the SDS (Safety Data Sheet), the main ingredients of the products are different ether derivatives (Figure 3), which are mixed with other chemicals in different compositions. The proprietary mixtures consist of hydrocarbon surfactants, complex carbohydrates, inorganic salts, solvent and water.

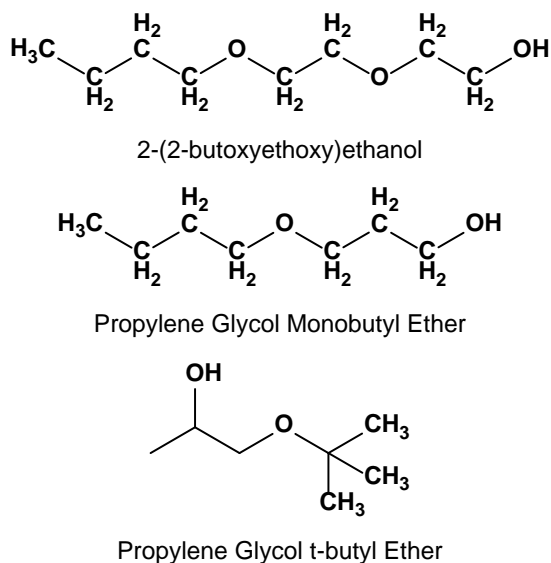


Figure 3 Alternative non-fluorinated chemicals

Table 3 summarizes the general product information offered by the six companies. All the products are either certified in accordance to UL 162 or EN1568. However, none of them are certified in accordance to Mil-F-24385F. While all the products are suitable for hydrocarbon fires, some of them are also applicable to polar solvent fires. Most of the products can be used with fresh, salt and brackish water except E1, which can be used only with fresh water.

The pH of all the selected products meets the Mil-F-24385F requirements of 7.0-8.5 (Table 4). However due to the lack of available information, the valid comparison of other chemical and physical properties with respect to the standard requirements was not possible.

Table 3 List of selected products

No.	Company	Brand	Fire Type	Water	Compatibility	Certifications	Hazardous Component
1	A	A1 (3%) A2 (6%)	Hydrocarbon fuel - Yes Polar solvent fuels - No	Fresh, salt and brackish	Dry powder agents	UL 162, ULC S564	2-(2-butoxyethoxy)ethanol ²
2	B	B1 ¹ (3%) B2 ¹ (6%)	Hydrocarbon fuel - Yes Polar solvent fuels - Yes	Fresh, salt and brackish	-	EN1568 3-4	Propylene Glycol Monobutyl Ether
3	C	C1 (2-6%)	Hydrocarbon fuel - Yes Polar solvent fuels - No	Fresh, salt and brackish	-	EN1568 2	2-(2-butoxyethoxy)ethanol ²
		C2 (3%) C3 (6%)	Hydrocarbon fuel - Yes Polar solvent fuels - Yes	Fresh, salt and brackish	-	European standards: EN 1568 1-2-3-4; Oil industry: GESIP-LASTFIRE; Marine: VERITAS; High expansion: APSAD R12; Aviation: ICAO level B.	2-(2-butoxyethoxy)ethanol ²
4	D	D1 ¹ (3%)	Hydrocarbon fuel - Yes Polar solvent fuels - Yes	Fresh (soft or hard), salt and brackish	Dry powder agents	EN1568 3-4	Propylene Glycol Monobutyl Ether
5	E	E1 (2%)	Hydrocarbon fuel - Yes Polar solvent fuels - No	Fresh water	-	UL Listed	2-(2-butoxyethoxy)ethanol ²
		E2 (6%)	Hydrocarbon fuel - Yes Polar solvent fuels - No	Fresh, salt and brackish	Dry powder agents	EN1568	
		E3 (2%)	Hydrocarbon fuel - Yes Polar solvent fuels - Yes	Fresh, salt and brackish	-	EN 1568: 2008 Part 2; ISO 7203 Part 2; IMO Msc 670; IMO Msc 1384 inside air test MED B	
6	F	F1 (3%) F2 (6%)	Hydrocarbon fuel - Yes Polar solvent fuels - No	Fresh, salt and brackish	-	UL Listed; GB15308-94; EN1568	Propylene Glycol t-butyl Ether

¹Alcohol resistant

²Alternate chemical names: Diethylene Glycol Monobutyl Ether (used by companies A and B); ButylDiGlycol Ether (used by company C); ButylCarbitol (used by company C)

Table 4 Chemical and physical properties of selected products

No.	Company	Brand	Refractive index	Viscosity	pH	Foam expansion	25% Drainage time
1	A	A1 (3%)	1.3865-1.3869	4900-5300 ² cP	7.0-8.0	-	-
		A2 (6%)	1.3800-1.3900	4500-5500 ² cP	7.0-8.5	-	-
2	B	B1 ¹ (3%)	-	1700 ^{3,4} cP	7.0-8.0	-	-
		B2 ¹ (6%)	-	Non-Newtonian Variable viscosity	7.0-8.0	-	-
3	C	C1 (2-6%)	-	-	7.0±1.0 ⁴	-	-
		C2 (3%)	-	5±2 ⁴ cSt	7.0±1.0 ⁴	2% – Low (>8), medium (>120) and high (>500) expansion. ⁶ 6% – Low (>9), medium (>150) and high (>700) expansion. ⁶	>6 mins (2%) >7 mins (6%)
		C3 (6%)	-	1300 ^{3,4} mPa.s 1600 ^{3,5} mPa.s	7.0±1.0 ⁴	3% – Low (8), medium (60) and high (800) expansion. ⁶ 6% – Low (9) and medium (>130) expansion. ⁶	15 mins (3%) 30 mins (6%)
4	D	D1 ¹ 3%	-	1700 ^{3,4} cP	7.0-8.0 ⁴	-	-
5	E	E1 = 2%	1.350 ± 0.015	185±25 cP	6.0-7.0	Medium and high expansion	
		E2 = 6%	-	5.0±2.0 ⁴ mm ² /s	7.0±0.5 ⁴	Low, medium and high expansion	≥6 mins (20 °C)
		E3 = 2%	-	17.0±4.0 ⁴ mm ² /s	7.5±0.5	Low, medium and high expansion	≥8 mins (20 °C)
6	F	F1 (3%) F2 (6%)	1.392	22 cP	8.2	-	-

¹Alcohol resistant; ²Brookfield Viscometer Spindle #4, Speed 30 rpm; ³Brookfield Viscometer Spindle #4, Speed 60 rpm; ⁴20 °C; ⁵-10 °C; ⁶Foam expansion value depends on the equipment

3.2 Performance of alternative foams

The main difference between AFFFs and their alternatives (F3s) is the presence of the polyfluorinated surfactants. This section reports some major properties of F3s in comparison with AFFFs.

3.2.1 Film forming and sealability of alternative foams

Film forming foams provide extra protection by forming a thin film on the fuel surface in addition to the foam blanket. The film forming ability is assessed by measuring spreading coefficient as described in Section 2.2.1. A positive spreading coefficient is required for film forming foams; however, it should be noted that positive values of spreading coefficient do not guarantee the film formation over various types of fuels since the spreading coefficients are evaluated by the standard test methods, which require the use of cyclohexane as a fuel. The surface tension of cyclohexane is 25 dynes/cm at 20°C, and that of gasoline is 20.8 dynes/cm at 24°C [5]. To achieve a positive spreading coefficient for film forming over a fuel, the sum of the surface tension of the foam and the interfacial tension requires to be significantly lower than 20-25 dynes/cm.

The excellent film forming performance of AFFFs is mainly due to the low surface tension (approximately 15 dynes/cm) of Polyfluorinated surfactants used in AFFFs. Alternative foams without fluorine are reported to have higher surface tensions than AFFFs, and significant research efforts are targeted to develop F3 with film forming ability using surfactants having low surface tensions. Hetzer et.al [5] measured the surface tensions of siloxane surfactants and alkyl surfactants, both of which have higher surface tensions than Polyfluorinated surfactants, resulting in negative spreading coefficients. As shown in Figure 4, which compares the surface tensions of various fuels and foam surfactants, the surface tensions of many alternative surfactants are higher than 20 dynes/cm, which make the alternatives not suitable to replace Polyfluorinated surfactants (marked as F in Figure 4).

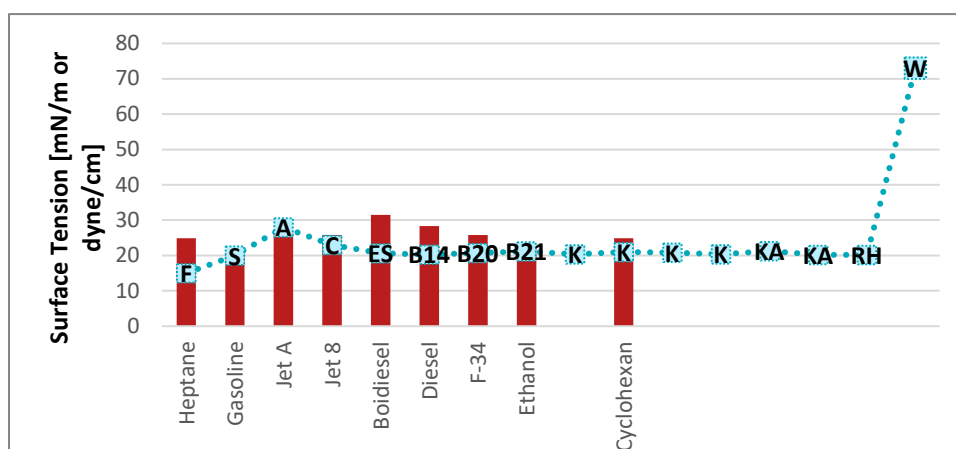


Figure 4 Surface tensions of various fuels (red bars) and foam surfactants (Blue line) [5], [14] (F: Polyfluorinated, S: siloxane, A: alkyl, W: water, ES: Ethoxy-Siloxane, B, K, KA, RH: non-fluorinated surfactants)

Following the sealability tests described in Section 2.2.2, Williams et. al [11] tested products of AFFF and F3 for film formation and found mixed results for different fuels (i.e. Gasoline, Iso-octane, Methylcyclohexane and Heptane), as shown in Table 5. The test results showed that the F3 product did not fully seal the fuel surface by forming film when tested on most of the fuels (gasoline, Iso-octane, Methylcyclohexane and Heptane).

Table 5 Test results of film formation and fire extinguishment times of three commercial products [11]

Fuel	AFFF-National Type 6	AFFF-Buckeye Type 3	F3-RF-6 (Type 6)
Gasoline	Film, 22 sec,	Film, 21 sec,	No Film, 35 sec, 41 sec,
Iso-octane	No film, 32 sec, 33 sec	Marginal ¹ , 32 sec, 33 sec	No film, 29 sec, 30 sec
Methylcyclohexane	Film, 22 sec, 23sec,	Film, 19 sec, 20 sec	No film, 33 sec, 46 sec
Heptane	Marginal ² 23 sec, 28 sec	Film 25 sec	No film 43 sec

¹Fuel was ignited on some attempts.

²Ignition occurred after 5 seconds of waiting time. No ignition occurred after waiting for 60 seconds of film formation.

3.2.2 Foam drainage of alternative foams

As discussed in Section 2.2.4, foam drainage is an indicative of foam collapse and flows, so for the quality of the foam, the minimum time requirements are imposed for foam drainage (usually 25% foam solution from the foam bubbles) measured using standard test methods. While relatively short drainage times are required for AFFF or film forming foams (e.g. 2.5 min by MilSpec [1] and 3 minutes by ICAO [7]), non-film forming foams are required to have longer drainage times (e.g. 5 minutes by ICAO [7]). The short drainage time of AFFF is in part caused by the surfactants present in AFFF that make the foam less viscous than other non-film forming foams. For this reason, alternative foams reported in Table 4 also show longer drainage times of 6- 30 min.

3.2.3 F3 Fire performance of alternative foams

Similar to the film forming test results, the F3 tested in Williams et al [11] also demonstrated poor fire performance with the extinguishment times being over the 30 second requirement by MilSpec. In contrast, the fire suppression tests showed that AFFFs met the MilSpec requirement of 30 seconds against Methylcyclohexane, Heptane and Gasoline.

The burnback tests were also carried out following the test protocols of MilSpec. The test results showed much longer burnback times than the MilSpec requirement of 360 seconds for both AFFF and F3 products. They have found that the burnback time is not directly related to either fuel flash points or foam film formation ability. The study suggested that more studies are necessary to find properties influencing the rate of vapor penetration through the foam. The test results reported in Hetzer et.al [5] of a F3 (Class B-foam) were also 80% longer for the fire extinguishment and 50% shorter for the burnback time than those of a AFFF product.

Hubert et. al [15] reported that the fluorine free commercial products, which were tested for Jet-A, heptane and IPA fires according to ICAO level B and EN 1568 fire tests, failed to extinguish the fire at all or showed considerable difficulty in extinguishing the fire. Very recently, Fire Protection Research Foundation assessed the fire performance of Class B fluorine free firefighting foams against hydrocarbon and alcohol based fuels. 165 tests were conducted in accordance to the UL 162 standard. The results showed that the firefighting capabilities of F3 varied from manufacturer to manufacturer while the baseline alcohol resistant AFFF demonstrated consistent/superior firefighting capabilities. In general, the F3 required 1.5 to 3 times higher application rates to produce comparable fire performance to that of the baseline AFFF.

Recently, Fire Safety Unit at NRC conducted a series of full-scale pan fire tests [13] in accordance to FM-5130 "Standard for Foam Equipment and Liquid Concentrates". The goal of these tests was to assess the feasibility of a CAF (Compressed Air Foam) system as a delivery system for fluorine free foams [13]. The study compared the application of four F3s at various concentrations with AFFFs. The burnback tests were conducted against Heptane, Isopropyl Alcohol and Acetone for different grid orientations of the fixed CAF systems tested. Both F3s and AFFFs showed variable performances from manufacturer to manufacturer.

4 Eco-Toxicity of Alternative Foams

A chemical can have an ecotoxic impact on both aquatic and terrestrial life. However, the ecotoxicity of a chemical is often reported in its safety data sheet (SDS) in terms of aquatic hazard (i.e. to fish, crustacea, and algae). While the evaluation of only aquatic hazards is limited in scope (because aquatic organisms are only one part of the ecosystem), the UN states the following rationale for their approach of considering aquatic hazards: “it is widely accepted that this compartment is both vulnerable, in that it is the final receiving environment for many harmful substances, and the organisms that live there are sensitive” [16]. In this regard, aquatic toxicity data is commonly reported, whereas terrestrial ecotoxicity data is rarely available.

Following the same approach, this study evaluated the ecological hazards (**ecotoxicity**, **degradability** and **bioaccumulation**) of some of the fluorinated and the fluorine free foams from the six companies (selected from the market survey presented in Section 3), using their available SDS and aquatic toxicity data. The **ecotoxicity** for fish are reported as Lethal Concentration 50 (LC₅₀)¹ values, for crustacea as Effective Concentration 50 (EC₅₀)² values, and for algae as either EC₅₀ or Effective Concentration Reduction 50 (ErC₅₀) values.

The **degradability** of a substance is a measure of its persistence in the environment. The biodegradability of a chemical is usually quantified as biochemical oxygen demand (BOD)³ and chemical oxygen demand (COD)⁴, both of which are derived from standard tests.

Finally, the potential for a substance to **bioaccumulate** is evaluated using its bioconcentration, which is defined as “the net result of uptake, transformation, and elimination of a substance in an organism due to waterborne exposure...”[16]. Two values are typically used to represent bioconcentrations: the octanol/water partition coefficient (Log K_{ow}) and the Bioconcentration Factor (BCF). The Log K_{ow} value is a measure of a substance’s lipophilicity, and the BCF is a ratio of the chemical concentration in the organism to chemical concentration in the surrounding water.

The following sections briefly describe the methodology adopted in evaluating the eco-toxicity of 12 fluorine free foams and 3 fluorinated foams, followed by the results and analysis. More details can be found in Supplement A

4.1 Methodology

Although the ecotoxicity of the foams is reported in their SDS, the reported values are inconsistent and can’t be used to compare the foams. Thus, a systematic methodology was followed to calculate the ecotoxicity of each foam, which enables comparisons between the foams. First, the ingredients (CAS No. and % concentration) of each foam were obtained from its SDS. Table 2 in Supplement A shows the ingredients of each of the investigated foams.

¹ LC₅₀ value represents the concentration of the chemical substance in water which results in death in 50% of the exposed fish.

² EC₅₀ value is the concentration of a substance that results in crustacea immobilization or a 50% reduction in algae growth rate

³ BOD is the amount of dissolved oxygen required by an aerobic organism to disintegrate an organic pollutant, commonly performed for 5 days (e.g. BOD₅).

⁴ COD is the amount of oxygen needed to oxidize organic and soluble matter.

Then, acute and chronic ecotoxicity data (LC_{50} , EC_{50} , ErC_{50} , ChV^5 , $NOEC^6$) and bioaccumulation data (Log Kow) for each ingredient were gathered utilizing the Environmental Protection Agency (EPA) Ecological Structure Activity Relationships (ECOSAR) Database [17].

In some cases the acute and chronic ecotoxicity and bioaccumulation data weren't available in ECOSAR, so the data were either gathered from the SDS of the foam (if available) or chemistry databases like PubChem or similar. Table 3 in Supplement A shows the ecotoxicity data of each of the ingredients of the studied foams.

Then, the Globally Harmonized System (GHS) of Classification and Labeling of Chemicals was used to classify the hazards of each individual ingredient within each foam, based on the collected ecotoxicity and bioaccumulation Data. The GHS includes three acute hazard categories and four chronic hazard categories [16], as summarized in Table 6.

Table 6 GHS hazard category, code, and statement [16]

Category	Hazard Code	Hazard Statement
Acute 1	H400	"Very toxic to aquatic life"
Acute 2	H401	"Toxic to aquatic life"
Acute 3	H402	"Harmful to aquatic life"
Chronic 1	H410	"Very toxic to aquatic life with long lasting effects"
Chronic 2	H411	"Toxic to aquatic life with long lasting effects"
Chronic 3	H412	"Harmful to aquatic life with long lasting effects"
Chronic 4	H413	"May cause long lasting harmful effects to aquatic life"

The GHS acute hazard category of a chemical or mixture is determined using its LC_{50} , EC_{50} and/or ErC_{50} value(s). The GHS chronic hazard category of a chemical or mixture is determined using its $NOEC$, $LOEC^7$, or ChV value.

Although the acute and chronic data for the 3 species (fish, crustacea and algae) were collected, only the lowest value of them was used in this classification in order to place each ingredient within the most conservative GHS hazard category. More details about the classification methodology can be found in Supplement A, and the results can be found in Table 5 in the Supplement A.

After classifying the hazard level of each ingredient, the GHS summation method was used to provide a hazard level for each of the investigated foams. The GHS summation method considers the hazard categories and percent (%) concentrations of "relevant ingredients" within the mixture to calculate the hazard category for the mixture. GHS defines the "relevant ingredients" as "those which are present in a concentration equal to or greater than 0.1% (w/w) for ingredients classified as Acute and/or Chronic 1 and equal to or greater than 1% (w/w) for other ingredients, unless there is a presumption (e.g. in the case of highly toxic ingredients) that an ingredient present at a concentration less than 0.1% can still be relevant for classifying the mixture for aquatic environmental hazards." [16]. Table 7 outlines the GHS summation method. A multiplication factor (M) is assigned as per the values suggested by the GHS[16].

⁵ ChV is Chronic Value, which is the geometric mean of the $NOEC$ and $LOEC$.

⁶ $NOEC$ is the No Observed Effect Concentration ($NOEC$), which represents the highest concentration, immediately below the $LOEC$, showing no statistically significant adverse impact when compared to the control.

⁷ $LOEC$ is the Lowest Observed Effect Concentration tested that results in a statistically significant adverse impact when compared to the control.

Table 7 GHS Summation Method for Category Classification of Mixtures (UN, 2019).

Category	Summation of Ingredients
Acute 1	If Acute 1 % x M \geq 25%
Acute 2	If (M x 10 x Acute 1 %) + Acute 2% \geq 25%
Acute 3	If (M x 100 x Acute 1 %) + (10 x Acute 2 %) + Acute 3 % \geq 25%
Chronic 1	If Chronic 1 % x M \geq 25%
Chronic 2	If (M x 10 x Chronic 1 %) + Chronic 2% \geq 25%
Chronic 3	If (M x 100 x Chronic 1 %) + (10 x Chronic 2 %) + Chronic 3 % \geq 25%
Chronic 4	If Chronic 1 % + Chronic 2 % + Chronic 3 % + Chronic 4 % \geq 25%

Usually the SDS of a foam states a range of concentrations for each ingredient. Both the maximum and minimum concentration of a relevant ingredient were used to determine the worst- and best-case scenarios. If a concentration range started at “0”, then a minimum value of 0.1% was assumed for Acute 1 and/or Chronic 1 substances, and 1% was assumed for all other substances. The results of the analysis is presented in Table 8.

Table 8 Hazard category ranking of fluorine free and fluorinated foams (NAT = No acute toxicity, NCT = No chronic toxicity).

FLUORINE FREE FOAMS					
Company	Brand	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture-Chronic High %
E	E1	Acute 3	Acute 2	NCT	Chronic 2
	E2	Acute 3	Acute 1	NCT	Chronic 2
	E3	Acute 3	Acute 2	NCT	Chronic 2
B	B1	Acute 3	Acute 2	NCT	Chronic 3
	B2	Acute 3	Acute 2	NCT	Chronic 3
D	D1	Acute 3	Acute 2	NCT	Chronic 3
C	C1	Acute 3	Acute 3	NCT	NCT
F	F1, F2	NAT*	Acute 3*	NCT*	NCT*
A	A1	NAT	Acute 3	NCT	NCT
A	A2	NAT	NAT	NCT	NCT
C	C2	NAT	NAT	NCT	NCT
FLUORINATED FOAMS					
A	A3	NAT	Acute 3	NCT	Chronic 3
B	B3	NAT	NAT	NCT	Chronic 3
G	G1	NAT*	NAT*	NCT*	NCT*

* evaluated with some missing ecotoxicity data

4.2 Discussion

The mixtures are ranked in Table 8 based upon their acute hazard category which also aligned with their chronic hazard category. A detailed discussion of the results can be found in Supplement A, only a brief summary is presented herein.

No mixture was categorized above Acute 3 when considering the lowest % concentration of each relevant ingredient. The product E2 was found to have the least favorable ranking at all concentrations. The Products A2 and C2 were found to have the most favorable ranking at all concentrations. It should be noted that, the absence of ecotoxicity data for some of the ingredients; specifically CAS 1078151-67-3 in products F1 and F2, and polyfluorinated alkyl betaine in product G1; might be affecting the hazard ranking of their corresponding foams.

The three fluorinated foams evaluated in this study were found to have limited acute and chronic toxicity. The more favorable ranking of the fluorinated foams, when compared to most of the fluorine free foams, appears counterintuitive; however, there are plausible explanations for these results. Firstly, ecotoxicity varies between fluorinated compounds and not all fluorinated compounds are highly toxic. The fluorinated foams evaluated in this study were selected based upon their common use. Additionally, they were selected because their SDSs contained sufficient data related to their fluorinated ingredients; often, data for fluorinated components is not reported on the SDS, because it is considered proprietary. It was not the objective of this study to seek out highly toxic fluorinated foams for comparison with fluorine free foams; hence, the fluorinated foams selected in this study appear to be of a lesser toxicity when compared to some fluorine free foams.

The findings of our study agree with some of the work published in literature. Ashworth [2] evaluated the ecotoxic hazards of different fluorinated foams and one fluorine free foam and developed an impact score based upon their biodegradability, short- term and long-term aquatic toxicity, and per- and polyfluoroalkyl substances (PFAS) content. The study showed that alcohol resistant (AR) foams ranked least favorable of the fluorinated brands. This is consistent with the results in Table 8, which shows that the AR fluorine free foams also rank among the most ecotoxic.

In addition, Schaefer [18] presented the results of testing conducted by the Fire Fighting Foam Coalition, in which two fish species (rainbow trout and fathead minnows) were exposed to six fire extinguishing agents (one wetting agent, two fluorine free foams, and 3 fluorinated foams). The results of testing were reported using the US Fish and Wildlife Service (FWS) classification system. For comparison, the FWS acute toxicity classifications were converted into equivalent GHS classification categories and presented in Table 11 in Supplement A. The results are similar to those of the current study, where the acute toxicity of the fluorine free foams is more significant than the fluorinated foams. Also AR fluorinated foams were found more acutely toxic than non-AR foams which is consistent with the results in Table 8. Schaefer [18] pointed to the hydrocarbon surfactants in the Class B fluorine free foams as the source of the ecological hazards. While the fluorinated foams present greater chronic impact to the aquatic environment, Schaefer [18] concluded that the fluorine free foams present a greater acute impact to the aquatic environment. According to Schaefer [18], because fluorinated foams are highly stable and do not readily biodegrade, they persist in the environment for long periods of time. Conversely, fluorine free hydrocarbon surfactants biodegrade but utilize dissolved oxygen to do so, thereby reducing the available oxygen to aquatic species and resulting in higher acute toxicity. Hence, both fluorinated and fluorine free foams can result in adverse environmental impacts; however, these impacts are unique and different. While fluorine free foams may have a higher impact on aquatic life, the persistence of fluorinated foams results in a greater impact on human life due to long-term toxicant migration into water and food sources.

5 Conclusions and Recommendations

AFFFs are high performance firefighting foams suitable for rapid knockdown of flammable liquid fires with the outstanding film-forming capability owing to their key ingredients of fluorinated surfactants. However, the fluorinated surfactants used in AFFFs have negative impacts on the environment and health due to the low

biodegradability as well as ecotoxicity. The growing stringency of environmental regulations for the fluorinated surfactants used in AFFFs has driven the development of environmentally benign foams to replace them.

With recent research efforts, a range of F3s have been developed using other chemicals including synthetic fluorine free ether based surfactants. This study reviewed the performance of F3s and assessed their ecotoxicity in comparison to AFFFs.

Fire suppression performance of foams can be estimated from foam properties, such as spreading coefficient, foamability and foam drainage, yet the fire suppression performance is examined by carrying out standard fire tests mainly examining fire extinguishment time, foam blanket sealability and burnback resistance time.

The fire extinguishment time requirements vary depending on the objectives of each standard, and the most stringent extinguishment time is required Millspec. Only AFFFs with polyfluorinated surfactants have passed this requirement since the rapid fire control of pool fires depends strongly on the film forming ability of the foams rather than foam flows,. As such, the products surveyed in this study are either certified in accordance to UL 162 or EN1568 but not to Mil-F-24385F.

For film forming and sealability, it is reported that F3 products did not fully seal the fuel surface by forming film over the surface of the fuel, which prevent fuel vapor transport through the foam layers. AFFFs demonstrated better performance of burnback resistance than F3s, and F3s were required 1.5 to 3 times higher application rates to produce comparable fire performance to that of AFFF.

An ecotoxicity analysis was conducted with the 12 fluorine free foams and 3 AFFFs selected through the market survey conducted in the present study. Overall, the ecotoxicity of the F3s is not evaluated better than the AFFFs. This is because the ecotoxicity is depend on the chemical ingredients used in F3 products, which could be also equally or more toxic than the fluorinated surfactants used in AFFF. In fact, many of the F3 products are found to have high concentrations of hazardous substances, which resulted in rankings between Acute 1(very toxic) and Acute 3 (harmful) when analysed with the highest concentration values in their SDS. Fluorinated foams have a more prominent chronic impact to aquatic life, yet the results from some of the F3s also indicate not only acute but also chronic impact to aquatic life.

The fluorine free foams have potentials to provide environmentally benign alternates to AFFF since there is a continuous effort to develop a new product, which can meet the required fire performance by current test standards. This study suggests some potential research areas, which can be explored in the future, as follows;

- Toxicity of AFFF and F3 when used for firefighting: The disbursement of foam constituents into the air (either virgin or formed as products of combustion) could introduce health hazards.
- Toxicity and ecotoxicity issues during the course of AFFF phase-out activities
- Evaluating the fire performance of alternative foams
- Evaluating the impact of foam application systems on the fire performance of alternative foams

Acknowledgments

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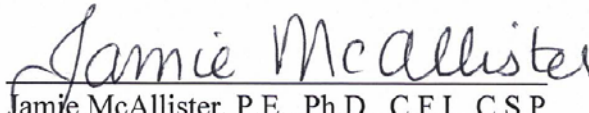
Supplement A



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ECOTOXICITY OF FLUORINE FREE FOAMS USED FOR FIRE EXTINGUISHMENT

by



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BACKGROUND

The purpose of this study was to review and compare ecological hazard data for twelve fluorine free foams and three fluorinated foams. The foams investigated in this study are presented in Table 1.

Table 1: List of foams evaluated in study.

Company	Brand
FLUORINE FREE FOAMS	
B	B1
	B2
C	C1
	C2
F	F1 and F2
D	D1
E	E3
	E1
	E2
A	A1
	A2
FLUORINATED FOAMS	
B	B3
G	G1
A	A3

The ecotoxicity, degradability, and bioaccumulation of a chemical are factors commonly used to quantify its ecological hazards. Although a chemical can have an ecotoxic impact on both aquatic and terrestrial life, often, safety data sheets (SDSs) only reported aquatic (e.g. fish, crustacea, and algae) hazards. The ecotoxicity for fish are reported as Lethal Concentration 50 (LC₅₀) values, for crustacea as Effective Concentration 50 (EC₅₀) values, and for algae as either EC₅₀ or Effective Concentration Reduction 50 (ErC₅₀) values. The LC₅₀ value represents the concentration of the chemical substance in water which results in death in 50% of the exposed fish. The EC₅₀ value is the concentration of a substance that results in crustacea immobilization or a 50% reduction in algae growth rate (Kendall et al, 2001). The LC₅₀ values are derived from acute (short-term) exposures, typically 96 hours in duration (Kendall et al, 2001). The EC₅₀ values for crustacea are commonly reported for 48- hour exposures, and EC(r)₅₀ values for algae are commonly reported for 72 to 96-hour exposures.

Chronic toxicity is reported as the Lowest Observed Effect Concentration (LOEC) or the No Observed Effect Concentration (NOEC). The LOEC is the lowest concentration tested that results in a statistically significant adverse impact when compared to the control. The NOEC represents the highest concentration, immediately below the LOEC, showing no statistically

significant adverse impact when compared to the control. In some cases, a Chronic Value (ChV) may be reported. The ChV is the geometric mean of the NOEC and LOEC.

The degradability of a substance is a measure of its persistence in the environment. Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are used to quantify biodegradability. The BOD is the amount of dissolved oxygen required by an aerobic organism to disintegrate an organic pollutant. The test is commonly performed for 5 days (e.g. BOD₅). The COD is the amount of oxygen needed to oxidize organic and soluble matter. The BOD and COD are derived from standardized tests. In some cases, a manufacturer may report a theoretical oxygen demand (ThOD) which is the amount of oxygen needed to oxidize a substance. The ThOD is a calculated value based on the substance's chemical structure. The ThOD can be used in place of the COD (UN, 2019).

The potential for a substance to bioaccumulate is evaluated using its bioconcentration criteria. Bioconcentration is “the net result of uptake, transformation, and elimination of a substance in an organism due to waterborne exposure...” (UN, 2019). Two values are typically used to represent bioconcentrations: the octanol/water partition coefficient (Log K_{ow}) and the Bioconcentration Factor (BCF). The Log K_{ow} value is a measure of a substance's lipophilicity, and the BCF is a ratio of the chemical concentration in the organism to chemical concentration in the surrounding water.

The ecological hazard data for a foam and/or its ingredients is reported in Section 12 of the material's SDS. As a first step, the SDSs for the twelve fluorine free and three fluorinated foams evaluated in this study were reviewed for ecotoxicity, degradability, and bioaccumulation data. The Analysis Section of this report discusses the findings from the SDSs and other sources, as well as the methodology utilized to compare the ecological hazards of the foams.

ANALYSIS

The ability to perform a comparative analysis of the foams evaluated in this study was challenged by inconsistencies in available data from the SDSs. Some manufacturers reported ecological hazard data for the foam mixture, whereas others reported ecological hazard data for the chemical components within the foam mixture. To overcome this issue, the following steps were taken:

Step 1: Section 3 of the SDS, *Composition/ information on ingredients*, was used to determine the ingredients of the foam. The CAS No. and % concentration for each foam ingredient was gathered and is shown in Table 2.

Step 2: Acute and chronic ecotoxicity data (LC₅₀, EC₅₀, ErC₅₀, ChV, NOEC) and bioaccumulation data (Log K_{ow}) for each ingredient was gathered utilizing the Environmental Protection Agency (EPA) Ecological Structure Activity Relationships (ECOSAR) Database (EPA, 2020). This data is reported in Table 3.

Step 3: If ECOSAR did not contain information on an ingredient, but information for the ingredient was included on the SDS, the SDS information was utilized (displayed in red in Table 3).

Step 4: If information was not available from ECOSAR or the SDS, data for the ingredient was gathered from PubChem or similar (displayed in blue in Table 3).

The ECOSAR database is used by the EPA to assess the hazards of chemicals undergoing pre-manufacturer evaluations. This database is maintained by the EPA and has been in existence for approximately 30 years. Comprehensive data sets exist for freshwater fish with limited data on saltwater fish. According to the EPA, the ECOSAR program focuses on freshwater fish “because most releases of industrial chemicals go to freshwater bodies.” As such, only freshwater fish were evaluated in this study.

Table 2: SDS chemical composition data

FLUORINE FREE FOAMS					
Company	Brand	Composition	CAS No.	%	Source for Chemical Composition
B	B1	1, 2-propanediol	57-55-6	4-10	From SDS dated 10/6/2019
		1-butoxy-2-propanol	5131-66-8	4-10	
		Sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts	85338-42-7	1-4	
		Sodium Laureth Sulfate	68891-38-3	1-4	
		1-Dodecanol	112-53-8	0.1-1.0	
		1-Tetradecanol	112-72-1	0.1-1.0	
Company	Brand	Composition	CAS No.	%	
B	B2	1, 2-propanediol	57-55-6	4-10	From SDS dated 10/6/2019
		1-butoxy-2-propanol	5131-66-8	4-10	
		Sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts	85338-42-7	1-4	
		Sodium Laureth Sulfate	68891-38-3	1-4	
		1-Dodecanol	112-53-8	0.1-1.0	
		1-Tetradecanol	112-72-1	0.1-1.0	
Company	Brand	Composition	CAS No.	%	
C	C1	ButylDiGlycol Ether	112-34-5	1-5	From SDS dated 7/28/2014
		Alkene Sulfonate	68439-57-6	5-10	
		Alkyl Sulfate	151-21-3	1-5	
Company	Brand	Composition	CAS No.	%	
C	C2	2-(2-Butoxyethoxy)Ethanol	112-34-5	10 <= x < 25	From SDS dated 9/15/2017
		Ethylene glycol	107-21-1	2.5 <= x < 10	
		Sodium Octyl Sulfate	142-31-4	0<= x < 2.5	
		Preservative		< 0.0015	

Company	Brand	Composition	CAS No.	%	
F	F1 and F2	2-Methyl-2,4-pentanediol	107-41-5	0-10	From SDS dated 5/24/2018
		D-Glucopyranoside, C9-C11 Oligomer	132778-08-6	0-10	
		Ammonium alcohol (C6-10) ether sulfate	68037-05-8	0-10	
		Dodecanamide-N-[2-[[2-[[2-((2-aminoethyl)amino)ethyl]amino]ethyl]amino]ethyl]-, Polymer with N-(2-aminoethyl)-N'-[2-[(2-aminoethyl)amino]ethyl]-1,2-ethandiamine and 2,5-furandione, Sodium Salt	1078151-67-3	0-10	
		Isopropanol	67-63-0	0-10	
		3-Butoxy-2-propanol	5131-66-8	0-10	
Company	Brand	Composition	CAS No.	%	
D	D1	Propylene Glycol Monobutyl Ether	5131-66-8	3-7	From SDS dated 4/1/2019
		Sodium Decyl Sulfate	142-87-0	1-5	
		Sodium Octyl Sulfate	142-31-4	1-5	
		Sodium laureth sulfate	68891-38-3	1-5	
		Butanedioic acid, 2-sulfo-, C-isodecyl ester, disodium salt	37294-49-8	0.5-1.5	
		1-Dodecanol	112-53-8	0.1-1.0	
		1-Tetradecanol	112-72-1	0.1-1.0	
Company	Brand	Composition	CAS No.	%	
E	E3	2-Butoxyethanol	111-76-2	10-20	From SDS dated 5/24/2018
		2-(2-Butoxyethoxy)ethanol	112-34-5	10-20	
		TEA lauryl ether sulfate	157627-94-6	0-10	
		Fatty Alcohol sulfate, TEA-salts	139-96-8	0-10	
		Sodium Octyl Sulfate	142-31-4	0-10	
		Lauryl Alcohol	112-53-8	0-10	
		Ethylene glycol	107-21-1	0-10	
		Sodium Alkene Sulphonate	68439-57-6	0-10	
		Cocoamidopropyl amine oxide	61792-31-2	0-10	
		TEA Sulfate	7376-31-0	0-10	

Company	Brand	Composition	CAS No.	%	
E	E1	Sulfuric acid, mono-C10-16 esters, ammonium salts	68081-96-9	10-20	From SDS dated 2/25/2020
		Ethylene glycol	107-21-1	10-20	
		2-(2-Butoxyethoxy)ethanol	112-34-5	0-10	
		Dodecan-1-ol ethoxylated, sulfates, ammonium salts	32612-48-9	0-10	
		Lauryl Alcohol	112-53-8	0-10	
		Ethanol	64-17-5	0-10	
Company	Brand	Composition	CAS No.	%	
E	E2	2-Butoxyethanol	111-76-2	10-20	From SDS dated 5/24/2018
		Ethylene Glycol	107-21-1	0-10	
		Fatty Alcohol sulfate, sodium salts	9004-82-4	0-10	
		Lauryl Alcohol	112-53-8	0-10	
		1-Tetradecanol	112-72-1	0-10	
Company	Brand	Composition	CAS No.	%	
A	A1	Diethylene Glycol Monobutyl Ether	112-34-5	<20	From SDS dated 10/20/2008
		starch	9005-25-8	>1	
		tris(2-hydroxyethyl)ammonium dodecylsulfate	139-96-8	<20	
		alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl)C9-11 alkyl ethers, sodium salts	96130-61-9	<5	
		1-propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts	61789-40-0	<20	
		1-propanaminium, N-(3-aminopropyl)-2-hydroxy-N,Ndimethyl-3-sulfo-, N-coco acyl derivs., hydroxides, inner salts	68139-30-0	<2.5	
		D-glucopyranose, oligomers, decyl octyl glycosides	68515-73-1	<5	
		sucrose	57-50-1	>1	
Company	Brand	Composition	CAS No.	%	
A	A2	Diethylene Glycol Monobutyl Ether	112-34-5	5-15	
		Cocoamidopropyl betaine	61789-40-0	1-10	

		N-Cocoamidopropyl-N, N-dimethyl-N-2-hydroxypropyl sulfobetaine	68139-30-0	1-10	From SDS Dated 8/23/2016
FLUORINATED FOAMS					
Company	Brand	Composition	CAS No.	%	
B	B3	2-(2-Butoxyethoxy)ethanol	112-34-5	25-50	From SDS dated 10/06/2019
		Ethane-1, 2-diol	107-21-1	10-25	
		Ethanol	64-17-5	1-4	
		Fluorosurfactant blend	Proprietary	1-4	
		Sodium Octyl Sulfate	142-31-4	1-4	
		2-Methyl-2,4-pentanediol	107-41-5	0.1-1	
		2-methyl-2-propanol	75-65-0	0.1-1	
Company	Brand	Composition	CAS No.	%	
G	G1	2-(2-Butoxyethoxy)ethanol	112-34-5	10-30	From SDS dated 1/13/2019
		D-Glucopyranoside, C9-C11 Oligomer	132778-08-6	1-5	
		Polyfluorinated alkyl betaine	Proprietary	1-5	
		Sodium Decyl Sulfate	142-87-0	1-5	
		Polyfluorinated alkyl polyamide	Proprietary	0.1-1	
Company	Brand	Composition	CAS No.	%	
A	A3	2-(2-Butoxyethoxy)ethanol	112-34-5	< 20	From SDS dated 01-2008
		Sodium Octyl Sulfate	142-31-4	< 5	
		Poly(1, 1, 2, 2, -tetrafluoro-1,2-ethanediyl),alpha-fluoro-omega-2-[3- ((carboxylatomethyl)dimethylammonio)propylaminosulfonyl]ethyl	161278-39-3	< 25	
		Ethanol	64-17-5	> 0.1	

Table 3: Ecotoxicity and Bioaccumulation Data for Fluorine Free and Fluorinated Foams. (Note: Foams with higher LC₅₀, EC₅₀, ErC₅₀, and NOEC/ChV values are less toxic than those with lower LC₅₀, EC₅₀, or ErC₅₀, and NOEC/ChV values.)

FLUORINE FREE FOAMS

Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
B – B1	1, 2-propanediol	1970	8650	2230	-0.782	329	
	1-butoxy-2-propanol	887	459	232	0.9842	34.5	
	sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts	No aquatic hazard code per reference					a
	sodium laureth sulfate	7.1	7.4	27.2	0.3	0.14	b
	1-dodecanol	0.498	0.365	0.783	4.7698	0.066	
	1-tetradecanol	0.075	0.06	0.188	5.752	0.011	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
B – B2	1, 2-propanediol	1970	8650	2230	-0.782	329	
	1-butoxy-2-propanol	887	459	232	0.9842	34.5	
	sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts	No aquatic hazard code per reference					a
	Sodium Laureth Sulfate	7.1	7.4	27.2	0.3	0.14	b
	1-dodecanol	0.498	0.365	0.783	4.7698	0.066	
	1-tetradecanol	0.075	0.06	0.188	5.752	0.011	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
C – C1	ButylDiGlycol Ether	4560	2210	857	0.2922	139	
	Alkene Sulfonate	13.8	9.89	19.1	4.4937	1.77	
	Alkyl Sulfate	91.5	54	47.3	2.4218	5.87	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
C – C2	2-(2-Butoxyethoxy)Ethanol	4560	2210	857	0.2922	139	
	Ethylene glycol	38100	16100	3540	-1.1996	480	
	Sodium Octyl Sulfate	4200	2070	854	0.4574	136	
	Preservative	0.19	0.16	0.027	H400/H410 per SDS		
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
F – F1, F2	2-Methyl-2,4-pentanediol	1830	911	395	0.5802	61.7	
	D-Glucopyranoside, C9-C11 Oligomer	No aquatic hazard code per reference					c
	Ammonium alcohol (C6-10) ether sulfate	> 1.5	5-37		H412 per reference		d

	Dodecanamide-N-[2-[[[2-[[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]amino]ethyl]-, Polymer with N-(2-aminoethyl)-N'-[2-[[2-[(2-aminoethyl)amino]ethyl]-1,2-ethandiamine and 2,5-furandione, Sodium Salt						
	Isopropanol	1740	844	326	0.2764	52.9	
	3-Butoxy-2-propanol	887	459	232	0.9842	34.5	
Brand	Composition						
D – D1	Propylene Glycol Monobutyl Ether	887	459	232	0.9842	34.5	
	Sodium Decyl Sulfate	624	336	202	1.4396	28.4	
	Sodium Octyl Sulfate	4200	2070	854	0.4574	136	
	Sodium laureth sulfate	7.1	7.4	27.2	0.3	0.14	b
	Butanedioic acid, 2-sulfo-, C-isodecyl ester, disodium salt	66.4	118	40.2	3.4272	3.70	
	1-Dodecanol	0.498	0.365	0.783	4.7698	0.066	
	1-Tetradecanol	0.075	0.06	0.188	5.752	0.011	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
E – E3	2-Butoxyethanol	1880	936	403	0.5666	63.1	
	2-(2-Butoxyethoxy)ethanol	4560	2210	857	0.2922	139	
	TEA lauryl ether sulfate	7.1	7.4	14	< 4	0.14	e
	Fatty Alcohol sulfate, TEA-salts	109	65.4	60	2.549	7.34	
	Sodium Octyl Sulfate	4200	2070	854	0.4574	136	
	Lauryl Alcohol	0.498	0.365	0.783	4.7698	0.066	
	Ethylene glycol	38100	16100	3540	-1.1996	480	
	Sodium Alkene Sulphonate	13.8	9.89	19.1	4.4937	1.77	
	Cocoamidopropyl amine oxide	4.86	0.701	0.397	3.6354	0.069	
	TEA Sulfate	>10000	>10000	>10000	-5.9938	> 10000	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
E – E1	Sulfuric acid, mono-C10-16 esters, ammonium salts	12.3	7.97	10.2	3.4218	1.12	
	Ethylene glycol	38100	16100	3540	-1.1996	480	
	2-(2-Butoxyethoxy)ethanol	4560	2210	857	0.2922	139	
	Dodecan-1-ol ethoxylated, sulfates, ammonium salts	No aquatic hazard code per reference					f
	Lauryl Alcohol	0.498	0.365	0.783	4.7698	0.066	

	Ethanol	3170	1480	486	-0.1412	81.9	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
E – E2	2-Butoxyethanol	1880	936	403	0.5666	63.1	
	Ethylene Glycol	38100	16100	3540	-1.1996	480	
	Fatty Alcohol sulfate, sodium salts	28.4	67.5	47.5	2.3496	1.52	
	Lauryl Alcohol	0.498	0.365	0.783	4.7698	0.066	
	1-Tetradecanol	0.075	0.06	0.188	5.752	0.011	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
A – A1	Diethylene Glycol Monobutyl Ether	4560	2210	857	0.2922	139	
	starch	No aquatic hazard code per reference					g
	tris(2-hydroxyethyl)ammonium dodecylsulfate	109	65.4	60	2.549	7.34	
	alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl)C9-11 alkyl ethers,sodium salts	No aquatic hazard code per reference					h
	1-propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts	279	245	43.6	2.687	4.93	
	1-propanaminium, N-(3-aminopropyl)-2-hydroxy-N,Ndimethyl-3-sulfo-, N-coco acyl derivs., hydroxides, inner salts	No aquatic hazard code per reference					i
	D-glucopyranose, oligomers, decyl octyl glycosides	81700	36600	10200	-0.5769	1570	
	sucrose	>10000	>10000	>10000	-4.2701	>10000	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
A – A2	Diethylene Glycol Monobutyl Ether	4560	2210	857	0.2922	139	
	Cocoamidopropyl betaine	279	245	43.6	2.687	4.93	
	N-Cocoamidopropyl-N, N-dimethyl-N-2-hydroxpropyl sulfobetaine	No aquatic hazard code per reference					i
FLUORINATED FOAMS							
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
B – B3	2-(2-Butoxyethoxy)ethanol	4560	2210	857	0.2922	139	
	Ethane-1, 2-diol	38100	16100	3540	-1.1996	480	
	Ethanol	3170	1480	486	-0.1412	81.9	
	Fluorosurfactant blend	H411 per SDS					

	Sodium Octyl Sulfate	4200	2070	854	0.4574	136	
	2-Methyl-2,4-pentanediol	1830	911	395	0.5802	61.7	
	2-methyl-2-propanol	842	425	195	0.7299	29.9	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
G – G1	2-(2-Butoxyethoxy)ethanol	4560	2210	857	0.2922	139	
	D-Glucopyranoside, C9-C11 Oligomer	No aquatic hazard code per reference					c
	Polyfluorinated alkyl betaine	No data found					
	Sodium Decyl Sulfate	624	336	202	1.4396	28.4	
	Polyfluorinated alkyl polyamide	> 14	> 20	> 15		14	
Company/ Brand	Composition	Fish LC50	Crustacea EC50	Algae ErC50	Log Kow	ChV or NOEC	Ref
A – A3	2-(2-Butoxyethoxy)ethanol	4560	2210	857	0.2922	139	
	Sodium Octyl Sulfate	4200	2070	854	0.4574	136	
	Poly(1, 1, 2, 2, -tetrafluoro-1,2-ethanediyl),alpha-fluoro-omega-2-[3- ((carboxylatomethyl)dimethylammonio)propylaminosulfonyl]ethyl	R52/53 per SDS					
	Ethanol	3170	1480	486	-0.1412	81.9	

References:

- <https://pubchem.ncbi.nlm.nih.gov/compound/129681407#section=GHS-Classification>
- <https://echa.europa.eu/registration-dossier/-/registered-dossier/15887>
- <https://angusfire.co.uk/wp-content/uploads/Trainol-3.pdf>
- <https://www.stepan.com/msds/00198600.pdf>
- <https://echa.europa.eu/registration-dossier/-/registered-dossier/26526>
- <https://pubchem.ncbi.nlm.nih.gov/compound/61913#section=GHS-Classification>
- https://www.chemicalbook.com/CASEN_9005-25-8.htm#SafetyData
- http://www.solbergfoam.com/getattachment/70da8f32-16aa-492d-a9d5-ee76d2209ff9/SDS_RF1_Safety_Data_ENG.aspx
- <https://pubchem.ncbi.nlm.nih.gov/compound/83841>

After compiling the data, the following steps were taken to perform a comparative analysis:

Step 5: The hazards of each individual ingredient within the foam were classified using the Globally Harmonized System (GHS) of Classification and Labeling of Chemicals.

Step 6: The hazards of the foam mixture was classified using the GHS Summation Method.

Foam Ingredient Classification- GHS Hazard Category

The hazard associated with each ingredient shown in Table 2 was classified using the ecological data from Table 3. To do so, the hazard classification methodology set forth in the 8th edition of the GHS was utilized (UN, 2019). The GHS was adopted by the United Nations in 2003 to unify the approach used across the world to classify the environmental, physical, and health hazards of chemicals (UNECE, 2020). The requirement to align the Canadian Workplace Hazardous Materials Information System (WHMIS) with GHS was adopted in 2015 (Canada Gazette, 2015; CCOHS, 2020, Health Canada, 2020). Final compliance was required by December 1, 2018 (Canada Gazette, 2015; CCOHS, 2020, Health Canada, 2020). While Canada only adopts the GHS requirements for physical and health hazards, the GHS methodology utilized to classify environmental hazards still provides a logical framework to assess the ecological hazards of chemicals and mixtures.

The GHS environmental hazard classification scheme focuses on the aquatic impact of chemicals (UN, 2019). While it is recognized that aquatic organisms are only one part of the ecosystem, and therefore the evaluation of only aquatic hazards is limited in scope, the UN states the following rationale for their approach: “it is widely accepted that this compartment is both vulnerable, in that it is the final receiving environment for many harmful substances, and the organisms that live there are sensitive.” (UN, 2019). Additionally, aquatic toxicity data is commonly the only ecotoxicity data available, whereas terrestrial ecotoxicity data is rarely reported.

The GHS includes three acute hazard categories and four chronic hazard categories (UN, 2019), as summarized in Table 4.

Table 4: GHS hazard category, code, and statement (UN, 2019).

Category	Hazard Code	Hazard Statement
Acute 1	H400	“Very toxic to aquatic life”
Acute 2	H401	“Toxic to aquatic life”
Acute 3	H402	“Harmful to aquatic life”
Chronic 1	H410	“Very toxic to aquatic life with long lasting effects”
Chronic 2	H411	“Toxic to aquatic life with long lasting effects”
Chronic 3	H412	“Harmful to aquatic life with long lasting effects”
Chronic 4	H413	“May cause long lasting harmful effects to aquatic life”

The GHS acute hazard category of a chemical or mixture is determined using its LC₅₀, EC₅₀ and/or ErC₅₀ value(s). The GHS chronic hazard category of a chemical or mixture is determined using its NOEC, LOEC, or ChV value. In the absence of chronic toxicity data, the

chronic hazard category of a chemical or mixture is determined using acute toxicity data as well as degradability and bioaccumulation data for the substance. Appendix A includes extracted content from the 8th edition of the GHS detailing the classification methodology (UN, 2019).

Acute data was reported in Table 3 for all three species for comparison and informational purposes, however, only the lowest acute LC₅₀, EC₅₀, or ErC₅₀ value was used for classification. Additionally, although the ECOSAR database included chronic values for all three species, for simplicity, only the lowest chronic value was reported in Table 3 given that this was the only value to be used in the analysis. As stated, an ingredient was placed within the most conservative GHS hazard category based on an evaluation of the acute and chronic fish, crustacea, and algae ecotoxicity data for that component. For example, if a component had an L(E₅₀) less than or equal to 1 mg/L for either fish, crustacea, or algae, it was classified as Acute 1, as outlined in Appendix A- Table 4.1.1 (a)- *Short-term (acute) aquatic hazard*. If a substance had an L(E₅₀) > 100 mg/L, it was considered to have no acute toxicity (NAT), as outlined in Appendix A- Table 4.1.1 (a)- *Short-term (acute) aquatic hazard*. If a component had an NOEC or ChV less than or equal to 0.1 mg/L for either fish, crustacea, or algae and it was not rapidly degradable, then it was classified as Chronic 1, as outlined in Appendix A Table 4.1.1 (b)(i)- *Non-rapidly degradable substances for which there are adequate chronic toxicity data available*. If a substance was rapidly degradable and had a NOEC or ChV less than or equal to 1 mg/L, it was classified as Chronic 3, as outlined in Appendix A Table 4.1.1 (b)(ii)- *Rapidly degradable substances for which there are adequate chronic toxicity data available*. The degradability of the substances was determined based upon information from its SDS as well as its potential to bioaccumulate (Log Kow ≥ 4).

A summary of the acute and chronic classifications for each ingredient is provided in Table 5. For ingredients that did not have a reported chronic value, such as sodium laureth sulfate, the methodology outlined in Appendix A- Table 4.1.1. (b) (iii)- *Substances for which adequate chronic toxicity data are not available* was utilized. For ingredients that had low chronic values but Log Kow < 4, such as the sulfuric acid, mono-C10-16 esters, ammonium salts in product E1, additional research was performed to establish their degradability (OECD, 2020). In some cases, a CAS was not provided in the SDS for the ingredient, but a GHS classification code was provided and used for classification, e.g. the preservative in product C2 and fluorosurfactant blend in product B3 (shown in red). A CAS of the fluorosurfactant used in product A3, however, a risk phrase (i.e. R-phrase or R-code) for this ingredient was provided on the SDS and was used for classification. Risk phrases are defined under the European Union Directive 67/548/EEC: *Nature of special risks attributed to dangerous substances and preparations*. As part of harmonization, R-phrases are being replaced by equivalent GHS classification codes. The R52/R53 classification is “harmful to aquatic organisms” and “may cause long-term adverse effects in the aquatic environment” is equivalent to Acute 3/Chronic 3 on the GHS classification scale (Waeterschoot, 2001). Lastly, alkene sulfonate, which was found in products C1 and E3 had a Log Kow > 4, however, its ChV was slightly greater than 1. Additional research showed that it was readily biodegradable and has a BCF < 100, therefore, it was classified as NCT (ECHA, 2020).

Table 5: Ingredient hazard category for foams using GHS classification criteria (NAT = No acute toxicity, NCT = No chronic toxicity).

FLUORINE FREE FOAMS							
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
B – B1	1, 2-propanediol	1970	-0.782	329	NAT	NCT	
	1-butoxy-2-propanol	232	0.9842	34.5	NAT	NCT	
	sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts	No aquatic hazard code per reference			NAT	NCT	a
	sodium laureth sulfate	7.1	0.3	0.14	2	3	b
	1-dodecanol	0.365	4.7698	0.066	1	1	
	1-tetradecanol	0.06	5.752	0.011	1	1	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
B – B2	1, 2-propanediol	1970	-0.782	329	NAT	NCT	
	1-butoxy-2-propanol	232	0.9842	34.5	NAT	NCT	
	sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts	No aquatic hazard code per reference			NAT	NCT	a
	Sodium Laureth Sulfate	7.1	0.3	0.14	2	3	b
	1-dodecanol	0.365	4.7698	0.066	1	1	
	1-tetradecanol	0.06	5.752	0.011	1	1	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
C – C1	ButylDiGlycol Ether	857	0.2922	139	NAT	NCT	
	Alkene Sulfonate	9.89	4.4937	1.77	2	NCT	
	Alkyl Sulfate	47.3	2.4218	5.87	3	NCT	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
C – C2	2-(2-Butoxyethoxy)Ethanol	857	0.2922	139	NAT	NCT	
	Ethylene glycol	3540	-1.1996	480	NAT	NCT	

	Sodium Octyl Sulfate	854	0.4574	136	NAT	NCT	
	Preservative	0.027	H400/H410 per SDS		1	1	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
F – F1, F2	2-Methyl-2,4-pentanediol	395	0.5802	61.7	NAT	NCT	
	-Glucopyranoside, C9-C11 Oligomer	No aquatic hazard code per reference			NAT	NCT	c
	Ammonium alcohol (C6-10) ether sulfate	> 1.5	H412 per reference		2	3	d
	Dodecanamide-N-[2-[[2-[[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]amino]ethyl]-, Polymer with N-(2-aminoethyl)-N'-[2-[(2-aminoethyl)amino]ethyl]-1,2-ethandiamine and 2,5-furandione, Sodium Salt	No data found					
	Isopropanol	326	0.2764	52.9	NAT	NCT	
	3-Butoxy-2-propanol	232	0.9842	34.5	NAT	NCT	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
D – D1	Propylene Glycol Monobutyl Ether	232	0.9842	34.5	NAT	NCT	
	Sodium Decyl Sulfate	202	1.4396	28.4	NAT	NCT	
	Sodium Octyl Sulfate	854	0.4574	136	NAT	NCT	
	Sodium laureth sulfate	7.1	0.3	0.14	2	3	b
	Butanedioic acid, 2-sulfo-, C-isodecyl ester, disodium salt	40.2	3.4272	3.70	3	NCT	
	1-Dodecanol	0.365	4.7698	0.066	1	1	
	1-Tetradecanol	0.06	5.752	0.011	1	1	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
E – E3	2-Butoxyethanol	403	0.5666	63.1	NAT	NCT	
	2-(2-Butoxyethoxy)ethanol	857	0.2922	139	NAT	NCT	
	TEA lauryl ether sulfate	7.1	< 4	0.14	2	3	e
	Fatty Alcohol sulfate, TEA-salts	60	2.549	7.34	3	NCT	
	Sodium Octyl Sulfate	854	0.4574	136	NAT	NCT	

	Lauryl Alcohol	0.365	4.7698	0.066	1	1	
	Ethylene glycol	3540	-1.1996	480	NAT	NCT	
	Sodium Alkene Sulphonate	9.89	4.4937	1.77	2	NCT	
	Cocoamidopropyl amine oxide	0.397	3.6354	0.069	1	1	
	TEA Sulfate	>10000	-5.9938	> 10000	NAT	NCT	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
E – E1	Sulfuric acid, mono-C10-16 esters, ammonium salts	7.97	3.4218	1.12	2	NCT	
	Ethylene glycol	3540	-1.1996	480	NAT	NCT	
	2-(2-Butoxyethoxy)ethanol	857	0.2922	139	NAT	NCT	
	Dodecan-1-ol ethoxylated, sulfates, ammonium salts	No aquatic hazard code per reference			NAT	NCT	f
	Lauryl Alcohol	0.365	4.7698	0.066	1	1	
	Ethanol	486	-0.1412	81.9	NAT	NCT	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
E – E2	2-Butoxyethanol	403	0.5666	63.1	NAT	NCT	
	Ethylene Glycol	3540	-1.1996	480	NAT	NCT	
	Fatty Alcohol sulfate, sodium salts	28.4	2.3496	1.52	3	NCT	
	Lauryl Alcohol	0.365	4.7698	0.066	1	1	
	1-Tetradecanol	0.06	5.752	0.011	1	1	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
A – A1	Diethylene Glycol Monobutyl Ether	857	0.2922	139	NAT	NCT	
	starch	No aquatic hazard code per reference			NAT	NCT	g
	tris(2-hydroxyethyl)ammonium dodecylsulfate	60	2.549	7.34	3	NCT	
	alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl)C9-11 alkyl ethers, sodium salts	No aquatic hazard code per reference			NAT	NCT	h
	1-propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts	43.6	2.687	4.93	3	NCT	

	1-propanaminium, N-(3-aminopropyl)-2-hydroxy-N,Ndimethyl-3-sulfo-, N-coco acyl derivs., hydroxides, inner salts	No aquatic hazard code per reference			NAT	NCT	i
	D-glucopyranose, oligomers, decyl octyl glycosides	10200	-0.5769	1570	NAT	NCT	
	sucrose	>10000	-4.2701	>10000	NAT	NCT	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
A – A2	Diethylene Glycol Monobutyl Ether	857	0.2922	139	NAT	NCT	
	Cocoamidopropyl betaine	43.6	2.687	4.93	3	NCT	
	N-Cocoamidopropyl-N, N-dimethyl-N-2-hydroxypropyl sulfobetaine	No aquatic hazard code per reference			NAT	NCT	i
FLUORINATED FOAMS							
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
B – B3	2-(2-Butoxyethoxy)ethanol	857	0.2922	139	NAT	NCT	
	Ethane-1, 2-diol	3540	-1.1996	480	NAT	NCT	
	Ethanol	486	-0.1412	81.9	NAT	NCT	
	Fluorosurfactant blend	H411 per SDS			NAT	2*	
	Sodium Octyl Sulfate	854	0.4574	136	NAT	NCT	
	2-Methyl-2,4-pentanediol	395	0.5802	61.7	NAT	NCT	
	2-methyl-2-propanol	195	0.7299	29.9	NAT	NCT	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref
G – G1	2-(2-Butoxyethoxy)ethanol	857	0.2922	139	NAT	NCT	
	D-Glucopyranoside, C9-C11 Oligomer	No aquatic hazard code per reference			NAT	NCT	c
	Polyfluorinated alkyl betaine	No data found					
	Sodium Decyl Sulfate	202	1.4396	28.4	NAT	NCT	
	Polyfluorinated alkyl polyamide	> 14		14	3	NCT	
Company/ Brand	Composition	Lowest Acute Value	Log Kow	Lowest Chronic Value	Acute Category	Chronic Category	Ref

A – A3	2-(2-Butoxyethoxy)ethanol	857	0.2922	139	NAT	NCT	
	Sodium Octyl Sulfate	854	0.4574	136	NAT	NCT	
	Poly(1, 1, 2, 2, -tetrafluoro-1,2-ethanediyl),alpha-fluoro-omega-2-[3-((carboxylatomethyl)dimethylammonio)propylaminosulfonyl]ethyl	R52/53 per SDS			3**	3**	
	Ethanol	486	-0.1412	81.9	NAT	NCT	

References:

- a. <https://pubchem.ncbi.nlm.nih.gov/compound/129681407#section=GHS-Classification>
- b. <https://echa.europa.eu/registration-dossier/-/registered-dossier/15887>
- c. <https://angusfire.co.uk/wp-content/uploads/Trainol-3.pdf>
- d. <https://www.stepan.com/msds/00198600.pdf>
- e. <https://echa.europa.eu/registration-dossier/-/registered-dossier/26526>
- f. <https://pubchem.ncbi.nlm.nih.gov/compound/61913#section=GHS-Classification>
- g. https://www.chemicalbook.com/CASEN_9005-25-8.htm#SafetyData
- h. http://www.solbergfoam.com/getattachment/70da8f32-16aa-492d-a9d5-ee76d2209ff9/SDS_RF1_Safety_Data_ENG.aspx
- i. <https://pubchem.ncbi.nlm.nih.gov/compound/83841>

Foam Mixture Classification- GHS Summation Method

The classification of a component (i.e. ingredient) within a foam mixture does not necessarily represent the hazard of the foam mixture itself; the percentage of an ingredient in the mixture and variability of ingredient hazard categories is relevant when classifying a mixture. The GHS summation method considers the hazard categories and percent (%) concentrations of “relevant ingredients” within the mixture to calculate the hazard category for the mixture. GHS defines the “relevant ingredients” as “those which are present in a concentration equal to or greater than 0.1% (w/w) for ingredients classified as Acute and/or Chronic 1 and equal to or greater than 1% (w/w) for other ingredients, unless there is a presumption (e.g. in the case of highly toxic ingredients) that an ingredient present at a concentration less than 0.1% can still be relevant for classifying the mixture for aquatic environmental hazards.” (UN, 2019).

The GHS summation methodology is outlined in Table 6. If an ingredient is categorized as Acute 1, a multiplication factor (M-factor) is assigned. The M-factor is determined utilizing Table 7, which was extracted from the GHS (UN, 2019). The criteria for being placed in a category is a calculated concentration equal to or greater than 25%.

Table 6: GHS Summation Method for Category Classification of Mixtures (UN, 2019).

Category	Summation of Ingredients
Acute 1	If Acute 1 % x M \geq 25%
Acute 2	If (M x 10 x Acute 1 %) + Acute 2% \geq 25%
Acute 3	If (M x 100 x Acute 1 %) + (10 x Acute 2 %) + Acute 3 % \geq 25%
Chronic 1	If Chronic 1 % x M \geq 25%
Chronic 2	If (M x 10 x Chronic 1 %) + Chronic 2% \geq 25%
Chronic 3	If (M x 100 x Chronic 1 %) + (10 x Chronic 2 %) + Chronic 3 % \geq 25%
Chronic 4	If Chronic 1 % + Chronic 2 % + Chronic 3 % + Chronic 4 % \geq 25%

Table 7: Multiplying factors for highly toxic ingredients (extracted from GHS (UN, 2019)) ^a Non-rapidly degradable, ^b Rapidly degradable.

Acute toxicity	M factor	Chronic toxicity	M factor	
L(E)C ₅₀ value		NOEC value	NRD ^a ingredients	RD ^b ingredients
0.1 < L(E)C ₅₀ ≤ 1	1	0.01 < NOEC ≤ 0.1	1	-
0.01 < L(E)C ₅₀ ≤ 0.1	10	0.001 < NOEC ≤ 0.01	10	1
0.001 < L(E)C ₅₀ ≤ 0.01	100	0.0001 < NOEC ≤ 0.001	100	10
0.0001 < L(E)C ₅₀ ≤ 0.001	1000	0.00001 < NOEC ≤ 0.0001	1000	100
0.00001 < L(E)C ₅₀ ≤ 0.0001	10000	0.000001 < NOEC ≤ 0.00001	10000	1000
(continue in factor 10 intervals)		(continue in factor 10 intervals)		

Most SDSs provided a concentration range for each foam ingredient (See Table 2). Worst- and best-case scenarios were evaluated by using the minimum and maximum concentrations of a substance based on the ranges provided in the SDS. If a concentration range started at “0”, then a minimum value of 0.1% was assumed for Acute 1 and/or Chronic 1 substances and 1% was assumed for all other substances to align with the GHS definition of a “relevant ingredient”. The results of the summation analysis are presented in Table 8.

Table 8: Mixture hazard category for foams using GHS Summation Method (NAT = No acute toxicity, NCT = No chronic toxicity).

FLUORINE FREE FOAMS									
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
B – B1	1, 2-propanediol					Acute 3	Acute 2	NCT	Chronic 3
	1-butoxy-2-propanol					Acute 1 (%) =	Acute 1 (%) =	Chronic 1 (%) =	Chronic 1 (%) =
	Sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts					1.1	11	0.2	2
	Sodium Laureth Sulfate			1	4	Acute 2 (%) =	Acute 2 (%) =	Chronic 2 (%) =	Chronic 2 (%) =
	1-Dodecanol	1	1	0.1	1	12	114	2	20
	1-Tetradecanol	10	1	0.1	1	Acute 3 (%) =		Chronic 3 (%) =	Chronic 3 (%) =
						120		21	204
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
B – B2	1, 2-propanediol					Acute 3	Acute 2	NCT	Chronic 3
	1-butoxy-2-propanol					Acute 1 (%) =	Acute 1 (%) =	Chronic 1 (%) =	Chronic 1 (%) =
	Sulfuric acid, mono-C8-10 (even numbered)-alkyl esters, sodium salts					1.1	11	0.2	2
	Sodium Laureth Sulfate			1	4	Acute 2 (%) =	Acute 2 (%) =	Chronic 2 (%) =	Chronic 2 (%) =
	1-Dodecanol	1	1	0.1	1	12	114	2	20
	1-Tetradecanol	10	1	0.1	1	Acute 3 (%) =		Chronic 3 (%) =	Chronic 3 (%) =
						120		21	204
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %

C – C1	ButylDiGlycol Ether					Acute 3	Acute 3	NCT	NCT
	Alkene Sulfonate			5	10	Acute 2 (%) =	Acute 2 (%) =		
	Alkyl Sulfate			1	5	5	10		
						Acute 3 (%) =	Acute 3 (%) =		
						51	105		
	Alkene Sulfonate			5	10	Acute 2 (%) =	Acute 2 (%) =		
	Alkyl Sulfate			1	5	5	10		
						Acute 3 (%) =	Acute 3 (%) =		
						51	105		
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
C – C2	2-(2-Butoxyethoxy)Ethanol					NAT	NAT	NCT	NCT
	Ethylene glycol					Acute 1 (%) =	Acute 1 (%) =	Chronic 1 (%) =	Chronic 1 (%) =
	Sodium Octyl Sulfate					0.015	0.015	0.015	0.015
	Preservative	10	10	0.001 5	0.001 5	Acute 2 (%) =	Acute 2 (%) =	Chronic 2 (%) =	Chronic 2 (%) =
						0.15	0.15	0.15	0.15
						Acute 3 (%) =	Acute 3 (%) =	Chronic 3 (%) =	Chronic 3 (%) =
						1.5	1.5	1.5	1.5
								Chronic 4 (%) =	Chronic 4 (%) =
								0.0015	0.0015
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
F – F1, F2	2-Methyl-2,4-pentanediol					NAT	Acute 3	NCT	NCT
	D-Glucopyranoside, C9-C11 Oligomer								

	Ammonium alcohol (C6-10) ether sulfate			1	10	Acute 2 (%) =	Acute 2 (%) =	Chronic 3 (%) =	Chronic 3 (%) =
	Dodecanamide-N-[2-[[2-[[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]amino]ethyl]-, Polymer with N-(2-aminoethyl)-N'-[2-[(2-aminoethyl)amino]ethyl]-1,2-ethandiamine and 2,5-furandione, Sodium Salt					1	10	1	10
	Isopropanol					Acute 3 (%) =	Acute 3 (%) =	Chronic 4 (%) =	Chronic 4 (%) =
	3-Butoxy-2-propanol					10	100	1	10
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture-Acute Low %	Mixture-Acute High %	Mixture-Chronic Low %	Mixture-Chronic High %
D – D1	Propylene Glycol Monobutyl Ether					Acute 3	Acute 2	NCT	Chronic 3
	Sodium Decyl Sulfate					Acute 1 (%) =	Acute 1 (%) =	Chronic 1 (%) =	Chronic 1 (%) =
	Sodium Octyl Sulfate					1.1	11	0.2	2
	Sodium laureth sulfate			1	5	Acute 2 (%) =	Acute 2 (%) =	Chronic 2 (%) =	Chronic 2 (%) =
	Butanedioic acid, 2-sulfo-, C-isodecyl ester, disodium salt			0.5	1.5	12	115	2	20
	1-Dodecanol	1	1	0.1	1	Acute 3 (%) =		Chronic 3 (%) =	Chronic 3 (%) =
	1-Tetradecanol	10	1	0.1	1	120.5		21	205
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture-Acute Low %	Mixture-Acute High %	Mixture-Chronic Low %	Mixture-Chronic High %
E – E3	2-Butoxyethanol					Acute 3	Acute 2	NCT	Chronic 2
	2-(2-Butoxyethoxy)ethanol								
	TEA lauryl ether sulfate			1	10	Acute 1 (%) =	Acute 1 (%) =	Chronic 1 (%) =	Chronic 1 (%) =
	Fatty Alcohol sulfate, TEA-salts			1	10	0.2	20	0.20	20
	Sodium Octyl Sulfate					Acute 2 (%) =	Acute 2 (%) =	Chronic 2 (%) =	Chronic 2 (%) =

	Lauryl Alcohol	1	1	0.1	10	4	120	2	200
	Ethylene glycol					Acute 3 (%) =		Chronic 3 (%) =	
	Sodium Alkene Sulphonate			1	10	41		21	
	Cocoamidopropyl amine oxide	1	-	0.1	10				
	TEA Sulfate								
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
E – E1	Sulfuric acid, mono-C10-16 esters, ammonium salts			10	20	Acute 3	Acute 2	NCT	Chronic 2
	Ethylene glycol					Acute 1 (%) =	Acute 1 (%) =	Chronic 1 (%) =	Chronic 1 (%) =
	2-(2-Butoxyethoxy)ethanol					0.1	10	0.1	10
	Dodecan-1-ol ethoxylated, sulfates, ammonium salts					Acute 2 (%) =	Acute 2 (%) =	Chronic 2 (%) =	Chronic 2 (%) =
	Lauryl Alcohol	1	1	0.1	10	11	120	1	100
	Ethanol					Acute 3 (%) =		Chronic 3 (%) =	
						110		10	
								Chronic 4 (%) =	
								0.1	
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
E – E2	2-Butoxyethanol					Acute 3	Acute 1	NCT	Chronic 2
	Ethylene Glycol					Acute 1 (%) =	Acute 1 (%) =	Chronic 1 (%) =	Chronic 1 (%) =
	Fatty Alcohol sulfate, sodium salts			1	10	1.1	110	0.2	20
	Lauryl Alcohol	1	1	0.1	10	Acute 2 (%) =		Chronic 2 (%) =	Chronic 2 (%) =
	1-Tetradecanol	10	1	0.1	10	11		2	200
						Acute 3 (%) =		Chronic 3 (%) =	

						111		20	
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
A – A1	Diethylene Glycol Monobutyl Ether					NAT	Acute 3	NCT	NCT
	starch								
	tris(2-hydroxyethyl)ammonium dodecylsulfate			1	20				
	alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl)C9-11 alkyl ethers, sodium salts								
	1-propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts			1	20				
	1-propanaminium, N-(3-aminopropyl)-2-hydroxy-N,Ndimethyl-3-sulfo-, N-coco acyl derivs., hydroxides, inner salts					Acute 3 (%) =	Acute 3 (%) =		
	D-glucopyranose, oligomers, decyl octyl glycosides					2	40		
	sucrose								
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
A – A2	Diethylene Glycol Monobutyl Ether					NAT	NAT	NCT	NCT
	Cocoamidopropyl betaine			1	10	Acute 3 (%) =	Acute 3 (%) =		
	N-Cocoamidopropyl-N, N-dimethyl-N-2-hydroxpropyl sulfobetaine					1	10		
FLUORINATED FOAMS									
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
B – B3	2-(2-Butoxyethoxy)ethanol					NAT	NAT	NCT	Chronic 3
	Ethane-1, 2-diol							Chronic 2 (%) =	
	Ethanol							1	

	Fluorosurfactant blend			1	4			Chronic 3 (%) =	Chronic 2 (%) =
	Sodium Octyl Sulfate							10	4
	2-Methyl-2,4-pentanediol							Chronic 4 (%) =	Chronic 3 (%) =
	2-methyl-2-propanol							1	40
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
G – G1								NCT	NCT
	2-(2-Butoxyethoxy)ethanol					NAT	NAT		
	D-Glucopyranoside, C9-C11 Oligomer								
	Polyfluorinated alkyl betaine								
	Sodium Decyl Sulfate					Acute 3 (%) =	Acute 3 (%) =		
	Polyfluorinated alkyl polyamide			0.1	1	0.1	1		
Company/ Brand	Composition	Acute M	Chronic M	Low %	High %	Mixture- Acute Low %	Mixture- Acute High %	Mixture- Chronic Low %	Mixture- Chronic High %
A – A3	2-(2-Butoxyethoxy)ethanol					NAT	Acute 3	NCT	Chronic 3
	Sodium Octyl Sulfate					Acute 3 (%) =	Acute 3 (%) =	Chronic 3 (%) =	Chronic 3 (%) =
	Poly(1, 1, 2, 2, -tetrafluoro-1,2-ethanediyl),alpha-fluoro-omega-2-[3-((carboxylatomethyl)dimethylammonio)propylaminosulfonyl]ethyl			1	25	1	25	1	25
	Ethanol							Chronic 4 (%) =	
								1	

Table 9 provides a consolidated ranking of the fluorine free and fluorinated foams from most aquatically toxic to least aquatically toxic.

Table 9: Hazard category ranking of fluorine free and fluorinated foams (NAT = No acute toxicity, NCT = No chronic toxicity).

FLUORINE FREE FOAMS					
Company	Brand	Mixture-Acute Low %	Mixture-Acute High %	Mixture-Chronic Low %	Mixture-Chronic High %
E	E2	Acute 3	Acute 1	NCT	Chronic 2
	E3	Acute 3	Acute 2	NCT	Chronic 2
	E1	Acute 3	Acute 2	NCT	Chronic 2
B	B1	Acute 3	Acute 2	NCT	Chronic 3
	B2	Acute 3	Acute 2	NCT	Chronic 3
D	D1	Acute 3	Acute 2	NCT	Chronic 3
C	C1	Acute 3	Acute 3	NCT	NCT
F	F1 and F2	NAT	Acute 3	NCT	NCT
A	A1	NAT	Acute 3	NCT	NCT
	A2	NAT	NAT	NCT	NCT
C	C2	NAT	NAT	NCT	NCT
FLUORINATED FOAMS					
A	A3	NAT	Acute 3	NCT	Chronic 3
B	B3	NAT	NAT	NCT	Chronic 3
G	G1	NAT	NAT	NCT	NCT

The mixtures were ranked based upon their acute hazard category which also aligned with their chronic hazard category. No mixture was categorized above Acute 3 when considering the lowest % concentration of each relevant ingredient. The product E2 was found to have the least favorable ranking at all concentrations. The products A2 and C2 were found to have the most favorable ranking at all concentrations. It should be noted that the most comprehensive SDS for A1 was from October 2008, whereas the SDS for A2 was from August 2016. It would be expected that these two foams have similar ingredients, however their ingredients differed which resulted in a slightly different ranking. Additionally, with regards to the products F1 and F2, ecotoxicity data for one ingredient (CAS 1078151-67-3) could not be found. Limited information available for this substance indicates that it is exempt from reporting requirements, however, the specific reason is unclear. It is possible that inclusion of this ingredient in the hazard analysis could alter the foam hazard category ranking.

The three fluorinated foams evaluated in this study were found to have limited acute and chronic toxicity. The product A3 ranked least favorable of the fluorinated foams but was less ecotoxic than most of the fluorine free foams. It should be noted that data for the fluorinated components was provided in the SDSs with the exception of polyfluorinated alkyl betaine, one of two

fluorinated components in G1. As such, it is possible that the hazard ranking of G1 could be underrepresented.

The more favorable ranking of the fluorinated foams, when compared to most of the fluorine free foams, appears counterintuitive; however, there are plausible explanations for these results. Firstly, ecotoxicity varies between fluorinated compounds and not all fluorinated compounds are highly toxic. The fluorinated foams evaluated in this study were selected based upon their common use. Additionally, they were selected because their SDSs contained sufficient data related to their fluorinated ingredients; often, data for fluorinated components is not reported on the SDS, because it is considered proprietary. It was not the objective of this study to seek out highly toxic fluorinated foams for comparison with fluorine free foams; hence, the fluorinated foams selected in this study appear to be of a lesser toxicity when compared to some fluorine free foams.

Further to this point, data from Ashworth (2017) shows the differences in ecotoxicity of various fluorinated foams. Ashworth (2017) evaluated the ecotoxic hazards of different fluorinated foams and one fluorine free foam and developed an impact score based upon their biodegradability, short- term and long-term aquatic toxicity, and per- and polyfluoroalkyl substances (PFAS) content. The results of Ashworth's (2017) evaluation are shown in Table 10.

Table 10: Extracted Data from New Zealand Fire Service Commission Report (Ashworth, 2017).

Company/Brand	Foam Type	Impact Score
Solberg Fire Brake	Class A	5.4
Solberg RF 3X6 ATC	Class B- Fluorine Free	12
Angus Tridol S6	Class B	20
Angus FP-70	Class B- FP	24
Kerr A836 AR	Class B- AR AFFF	30
Angus Alcoseal	Class B- AR FFFP	60

Table 10 depicts the differences between brands of Class B fluorinated foams (and non-fluorinated and Class A foams). Additionally, Table 10 shows that alcohol resistant (AR) foams ranked least favorable of the fluorinated brands. This is consistent with the results in Table 9, which shows that the AR fluorine free foams also rank among the most ecotoxic.

In his whitepaper, Schaefer (2013) provides additional context regarding the hazards of fluorinated and fluorine free foams. Schaefer (2013) presented the results of testing conducted by the Fire Fighting Foam Coalition, in which two fish species (rainbow trout and fathead minnows) were exposed to six fire extinguishing agents (one wetting agent, two fluorine free foams, and 3 fluorinated foams). The results of testing were reported using the US Fish and Wildlife Service (FWS) classification system. For comparison, the FWS acute toxicity classifications were converted into equivalent GHS classification categories and presented in Table 11.

Table 11: Extracted Data from Fire Fighting Foam Coalition Study (Schaefer, 2013)

Agent	Rainbow Trout LC50	GHS Code	Fathead Minnow LC50	GHS Code
Wetting Agent	1.06	Acute 2	0.887	Acute 1
Fluorine-Free Foam A	65	Acute 3	171	NAT
Fluorine-Free Foam B	71	Acute 3	171	NAT
US Mil Spec AFFF	2176	NAT	884	NAT
AR-AFFF	3536	NAT	1487	NAT
UL ARFF	5657	NAT	1726	NAT

The results in Table 11 show a similar trend to those found in Table 9; the acute toxicity of the fluorine free foams is more significant than the fluorinated foams. Additionally, Table 11 shows that AR fluorinated foams are more acutely toxic than non-AR foams which is consistent with the results from Tables 9 and 10. Schaefer (2013) pointed to the hydrocarbon surfactants in the Class B fluorine free foams as the source of the ecological hazards. While the fluorinated foams present greater chronic impact to the aquatic environment, Schaefer (2013) concluded that the fluorine free foams present a greater acute impact to the aquatic environment. According to Schaefer (2013), because fluorinated foams are highly stable and do not readily biodegrade, they persist in the environment for long periods of time. Conversely, fluorine free hydrocarbon surfactants biodegrade but utilize dissolved oxygen to do so, thereby reducing the available oxygen to aquatic species and resulting in higher acute toxicity. Hence, both fluorinated and fluorine free foams can result in adverse environmental impacts; however, these impacts are unique and different. While fluorine free foams may have a higher impact on aquatic life, the persistence of fluorinated foams results in a greater impact on human life due to long-term toxicant migration into water and food sources.

CONSIDERATIONS

The standardized tests used to derive ecotoxicity data allow the user to define the type of fish, invertebrates, and algae to be tested. For example, tested fish species may include bluegill sunfish, common carp, fathead minnow, guppy, rainbow trout, red killifish, zebrafish, etc. The ECOSAR system is used without consideration for the specific type of fish species. The EPA states the following with regards to the species data: "the equations in ECOSAR are derived from surrogate species of fish, zooplankton, and phytoplankton. While these surrogate species can comprise several genera as well as families, the equations are not intended to assess toxicity to only those species, but rather to the general trophic levels they represent (fish, aquatic invertebrates, and aquatic plants)." Certain species can be more susceptible to chemical exposure, and this specific susceptibility may not be captured within the ECOSAR database. As such, variations in test results are possible such that the ecotoxicity of a chemical could change based upon the data set being evaluated.

Lastly, while the summation method does account for the % composition of the ingredient in the mixture, the hazard classification is based upon the undiluted mixture's composition. In

use, firefighting foams are commonly diluted into 3 parts concentrate and 97 parts water or 6 parts concentrate and 94 parts water. The hazard assessment presented in this report assumes the potential for contamination of ecological system by undiluted foam mixtures due to misapplication, misuse, or accidental release.

RECOMMENDATIONS FOR FUTURE WORK

This study focused on the aquatic hazards of fluorine free and fluorinated foams which is one component of an environmental hazard assessment. In the case of firefighting foams, disbursement of foam constituents into the air via the fire plume is another route for environmental contaminations. The disbursement of foam constituents into the air (either virgin or formed as products of combustion) could potentially introduce health hazards that are worse than those already present from the fire itself. In addition to their impact on the environment, certain types of PFAS found in fluorinated foams are carcinogenic and mutagenic or have other negative health effects. The adverse environmental and health hazards associated with certain types of PFAS was the impetus for banning their use in firefighting foams. It was outside the scope of this study to evaluate or compare the physical and health hazards associated with the ingredients in fluorine free foams; however, it is recommended that a comprehensive assessment be performed to include not only environmental impacts of fluorine free foams but physical and health hazards as well.

CONCLUSIONS

The following is a summary of conclusions based upon the findings of this study:

- When considering the lowest concentration of hazardous substances in the fluorine free foams, no foam ranked higher than Acute 3 and most fluorine free foams were Acute 3 (8 out of 12).
- When considering the highest concentration of hazardous substances in the fluorine free foams, most foams ranked between Acute 1 and Acute 3 with the largest percentage of fluorine free foams falling into Acute 2 (5 out of 12).
- When considering the lowest concentration of hazardous substances in the fluorine free foams, all fluorine free foams were found to have NCT (12 out of 12).
- When considering the highest concentration of hazardous substances in the fluorine free foams, most fluorine free foams were found to have NCT (6 out of 12).
- The product E2 was found to have the least favorable ranking (most aquatically toxic) when considering all ingredients and concentrations within the mixture.
- The products A2 and C2 were found to have the most favorable ranking (no aquatic toxicity) when considering all ingredients and concentrations within the mixture.
- The Products B1, B2, C1, D1, E1, E2 and E3 all contained ingredients that have the potential to bioaccumulate (Log Kow > 4).
- Data on fluorinated and fluorine free AR foams shows that they are more ecotoxic when compared to non-AR foams.
- Fluorine free foams have a more prominent acute impact to aquatic life whereas fluorinated foams have a more prominent chronic impact to aquatic life.

- Because of their persistence, fluorinated foams present both an environmental hazard as well as a health hazard.
- The hazard classification and comparative analyses in this study is based upon the undiluted foam mixture. Dilution of the foam mixture could decrease the hazards associated with the foam and could result in different rankings.
- Future research should investigate the air pollution impact of firefighting foams, as well as, the physical and health hazards of the ingredients in various fluorine free foams.

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Appendix A: Extracted GHS Classification Tables (UN, 2019)

Table 4.1.1: Categories for substances hazardous to the aquatic environment *(Note 1)*

(a) Short-term (acute) aquatic hazard

Category Acute 1: *(Note 2)*

96 hr LC ₅₀ (for fish)	≤ 1 mg/l and/or
48 hr EC ₅₀ (for crustacea)	≤ 1 mg/l and/or
72 or 96hr ErC ₅₀ (for algae or other aquatic plants)	≤ 1 mg/l <i>(Note 3)</i>
Category Acute 1 may be subdivided for some regulatory systems to include a lower band at L(E)C ₅₀ ≤ 0.1 mg/l	

Category Acute 2:

96 hr LC ₅₀ (for fish)	>1 but ≤ 10 mg/l and/or
48 hr EC ₅₀ (for crustacea)	>1 but ≤ 10 mg/l and/or
72 or 96hr ErC ₅₀ (for algae or other aquatic plants)	>1 but ≤ 10 mg/l <i>(Note 3)</i>

Category Acute 3:

96 hr LC ₅₀ (for fish)	>10 but ≤ 100 mg/l and/or
48 hr EC ₅₀ (for crustacea)	>10 but ≤ 100 mg/l and/or
72 or 96hr ErC ₅₀ (for algae or other aquatic plants)	>10 but ≤ 100 mg/l <i>(Note 3)</i>

Some regulatory systems may extend this range beyond an L(E)C₅₀ of 100 mg/l through the introduction of another category.

Table 4.1.1: Categories for substances hazardous to the aquatic environment (Note 1) (cont'd)

(b) Long-term (chronic) aquatic hazard (see also figure 4.1.1)

(i) Non-rapidly degradable substances (Note 4) for which there are adequate chronic toxicity data available

Category Chronic 1: (Note 2)	
Chronic NOEC or EC _x (for fish)	≤ 0.1 mg/l and/or
Chronic NOEC or EC _x (for crustacea)	≤ 0.1 mg/l and/or
Chronic NOEC or EC _x (for algae or other aquatic plants)	≤ 0.1 mg/l
Category Chronic 2:	
Chronic NOEC or EC _x (for fish)	≤ 1 mg/l and/or
Chronic NOEC or EC _x (for crustacea)	≤ 1 mg/l and/or
Chronic NOEC or EC _x (for algae or other aquatic plants)	≤ 1 mg/l

(ii) Rapidly degradable substances for which there are adequate chronic toxicity data available

Category Chronic 1: (Note 2)	
Chronic NOEC or EC _x (for fish)	≤ 0.01 mg/l and/or
Chronic NOEC or EC _x (for crustacea)	≤ 0.01 mg/l and/or
Chronic NOEC or EC _x (for algae or other aquatic plants)	≤ 0.01 mg/l
Category Chronic 2:	
Chronic NOEC or EC _x (for fish)	≤ 0.1 mg/l and/or
Chronic NOEC or EC _x (for crustacea)	≤ 0.1 mg/l and/or
Chronic NOEC or EC _x (for algae or other aquatic plants)	≤ 0.1 mg/l
Category Chronic 3:	
Chronic NOEC or EC _x (for fish)	≤ 1 mg/l and/or
Chronic NOEC or EC _x (for crustacea)	≤ 1 mg/l and/or
Chronic NOEC or EC _x (for algae or other aquatic plants)	≤ 1 mg/l

(iii) Substances for which adequate chronic toxicity data are not available

Category Chronic 1: (Note 2)	
96 hr LC ₅₀ (for fish)	≤ 1 mg/l and/or
48 hr EC ₅₀ (for crustacea)	≤ 1 mg/l and/or
72 or 96hr ErC ₅₀ (for algae or other aquatic plants)	≤ 1 mg/l (Note 3)
and the substance is not rapidly degradable and/or the experimentally determined BCF is ≥ 500 (or, if absent, the log K _{ow} ≥ 4). (Notes 4 and 5)	
Category Chronic 2:	
96 hr LC ₅₀ (for fish)	> 1 but ≤ 10 mg/l and/or
48 hr EC ₅₀ (for crustacea)	> 1 but ≤ 10 mg/l and/or
72 or 96hr ErC ₅₀ (for algae or other aquatic plants)	> 1 but ≤ 10 mg/l (Note 3)
and the substance is not rapidly degradable and/or the experimentally determined BCF is ≥ 500 (or, if absent, the log K _{ow} ≥ 4). (Notes 4 and 5)	
Category Chronic 3:	
96 hr LC ₅₀ (for fish)	> 10 but ≤ 100 mg/l and/or
48 hr EC ₅₀ (for crustacea)	> 10 but ≤ 100 mg/l and/or
72 or 96hr ErC ₅₀ (for algae or other aquatic plants)	> 10 but ≤ 100 mg/l (Note 3)
and the substance is not rapidly degradable and/or the experimentally determined BCF is ≥ 500 (or, if absent, the log K _{ow} ≥ 4). (Notes 4 and 5).	

(c) "Safety net" classification

Category Chronic 4:	
Poorly soluble substances for which no acute toxicity is recorded at levels up to the water solubility, and which are not rapidly degradable and have a log K _{ow} ≥ 4, indicating a potential to bioaccumulate, will be classified in this category unless other scientific evidence exists showing classification to be unnecessary. Such evidence would include an experimentally determined BCF < 500, or a chronic toxicity NOECs > 1 mg/l, or evidence of rapid degradation in the environment.	

Table 4.1.2: Classification scheme for substances hazardous to the aquatic environment

Classification categories			
Short-term (acute) hazard (Note 1)	Long-term (chronic) hazard (Note 2)		
	Adequate chronic toxicity data available		Adequate chronic toxicity data not available (Note 1)
	Non-rapidly degradable substances (Note 3)	Rapidly degradable substances (Note 3)	
Category: Acute 1 $L(E)C_{50} \leq 1.00$	Category: Chronic 1 $NOEC \text{ or } EC_x \leq 0.1$	Category: Chronic 1 $NOEC \text{ or } EC_x \leq 0.01$	Category: Chronic 1 $L(E)C_{50} \leq 1.00$ and lack of rapid degradability and/or $BCF \geq 500$ or, if absent $\log K_{ow} \geq 4$
Category: Acute 2 $1.00 < L(E)C_{50} \leq 10.0$	Category: Chronic 2 $0.1 < NOEC \text{ or } EC_x \leq 1$	Category: Chronic 2 $0.01 < NOEC \text{ or } EC_x \leq 0.1$	Category: Chronic 2 $1.00 < L(E)C_{50} \leq 10.0$ and lack of rapid degradability and/or $BCF \geq 500$ or, if absent $\log K_{ow} \geq 4$
Category: Acute 3 $10.0 < L(E)C_{50} \leq 100$		Category: Chronic 3 $0.1 < NOEC \text{ or } EC_x \leq 1$	Category: Chronic 3 $10.0 < L(E)C_{50} \leq 100$ and lack of rapid degradability and/or $BCF \geq 500$ or, if absent $\log K_{ow} \geq 4$
	Category: Chronic 4 (Note 4) Example: (Note 5) No acute toxicity and lack of rapid degradability and $BCF \geq 500$ or, if absent $\log K_{ow} \geq 4$, unless $NOECs > 1 \text{ mg/l}$		

NOTE 1: Acute toxicity band based on $L(E)C_{50}$ values in mg/l for fish, crustacea and/or algae or other aquatic plants (or QSAR estimation if no experimental data).

NOTE 2: Substances are classified in the various chronic categories unless there are adequate chronic toxicity data available for all three trophic levels above the water solubility or above 1 mg/l. ("Adequate" means that the data sufficiently cover the endpoint of concern. Generally this would mean measured test data, but in order to avoid unnecessary testing it can, on a case-by-case basis, also be estimated data, e.g. (Q)SAR, or for obvious cases expert judgment).

NOTE 3: Chronic toxicity band based on $NOEC$ or equivalent EC_x values in mg/l for fish or crustacea or other recognized measures for chronic toxicity.

NOTE 4: The system also introduces a "safety net" classification (referred to as category Chronic 4) for use when the data available do not allow classification under the formal criteria but there are nevertheless some grounds for concern.

NOTE 5: For poorly soluble substances for which no acute toxicity has been demonstrated at the solubility limit, and are both not rapidly degraded and have a potential to bioaccumulate, this category should apply unless it can be demonstrated that the substance does not require classification for aquatic long-term (chronic) hazards.