

## New Zealand Fire Service Research Report

#### ENVIRONMENTAL ASSESSMENT OF EXISTING FIRE-FIGHTING FOAMS IN USE BY NEW ZEALAND FIRE SERVICE

#### INSTITUTE OF ENVIRONMENTAL SCIENCE AND RESEARCH

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Fire-fighting foam is an additive product that is mixed with water to increase the efficiency and speed of extinguishing a fire. The growing recognition of the opportunity to reduce the impact of fire-fighting on receiving environments and the regulatory requirement to minimise harm means that the impact of foam additives has come under scrutiny in the last decade. The recognition was initially prompted by the high visibility withdrawal of PFOS from the US market in 2001 and its inclusion under the Stockholm convention in 2009. The scrutiny has become greater as the suite of compounds used as fire-fighting additives has been more widely investigated and the potential for negative environmental outcomes identified. This report provides a brief overview of the reasoning behind the environmental concerns about the long-term effects and immediate environmental impacts of fire-fighting foam.

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Environmental Assessment of Existing Fire-fighting Foams in use by New Zealand Fire Service



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## 1. EXECUTIVE SUMMARY

Fire-fighting foam is an additive product that is mixed with water to increase the efficiency and speed of extinguishing a fire. The growing recognition of the opportunity to reduce the impact of fire-fighting on receiving environments and the regulatory requirement to minimise harm means that the impact of foam additives has come under scrutiny in the last decade. The recognition was initially prompted by the high visibility withdrawal of PFOS from the US market in 2001 and it's inclusion under the Stockholm convention in 2009. The scrutiny has become greater as the suite of compounds used as fire-fighting additives has been more widely investigated and the potential for negative environmental outcomes identified.

This report has given a brief overview of the some of the reasoning behind the environmental concerns with regard to:

- 1. Persistence, bioaccumulation and toxicity of compounds (long-term effects); and
- 2. Immediate environmental impacts caused by increased oxygen requirements on receiving environments as represented by biological and chemical oxygen demand.

To allow consideration of these aspects of environmental impact an assessment framework has been developed. The framework uses data provided by manufacturers in material safety data sheets (MSDS). Data taken from the MSDS are:

- 1. The chemical compounds and their percentage composition used in formulation of the product;
- 2. Any environmental hazard statement associated with individual compounds.

These data are required for products to be compliant with the HSNO Act Firefighting chemicals group standard (2006). However, in the absence of sufficient data being provided in MSDS provision is made for inclusion of data derived from chemical analysis of samples by appropriately accredited laboratories.

The framework has addressed the question of how fire-fighting foam products can be assessed with regard to their potential for negative environmental impact in both the shortand long-term. A systematic approach to ranking the potential long-term and short-term environmental impact of a product has been created, thereby allowing end-users to factor this aspect of foam performance into their considerations. The framework is developed to provide a reproducible means of assessment that allows current and future foam products to be assessed against the same criteria. Therefore, environmental impact can become part of the assessment criteria for future procurement and be directly compared to environmental performance of existing stocks.

The fire-fighting foam products assessed in this report were identified in consultation with the New Zealand Fire Service national foam procurement team and consist of five Class B foams and one Class A foam. The selection was made based on the volume held in stock through the fire regions, priority was given to products held in high volumes as these have



highest probability being used operationally and also represent the greatest legacy risk in the event of their removal from service.

All Class B foams were analysed at an as-used concentration of 3%, representative of induction rate for operational use. The single Class A foam was also analysed at the 3% concentration level, but a correction factor was applied to produce data consistent with the operational induction rate of 0.3%. this correction factor should be used whenever comparing Class A foams.

The foam products tested and ranked are shown in the table below. The ranking is such that the lowest score represents the lowest environmental impact risk according to the framework. The score assigned to a product is only of relevance when being used to compare against other products assessed using the same framework.

Product	Framework score
Solberg Fire Brake	5.4
Solberg RF 3x6 ATC	12
Angus Tridol S 6	20
Angus FP70	24
Kerr A836	30
Alcoseal	60

Additionally the importance of the short-term impact of fire-fighting foam on the receiving environment is represented using the BOD5 and COD values. These parameters give an indication of the metabolic or chemical rate of use of oxygen in the aquatic environment and show the level of oxygen depletion that might be expected through release to a body of water. A standardised approach was taken, which applied a 100-fold dilution of the foam product as-used (a total of 3300-fold dilution of the concentrated product). This assumes that for each cubic metre of produced foam entering the environment and Conservation Council have identified recommended guidelines for both BOD5 and COD of water used for aquaculture, as <15 mg  $O_2/L$  and <40 mg  $O_2/L$  respectively (ANZECC, 2000). These values represent a level that was considered to be acceptable for long-term farming of fish. In the context of this report the ANZECC values are used as a baseline level for comparison of foam BOD5 and COD results for diluted foam products as shown in the following table.



Product	BOD5 (mg O₂/L)	COD (mg O <sub>2</sub> /L)
Solberg Firebrake	6	11
Angus FP70	40	186
Kerr A836	64	127
Alcoseal	27	139
Solberg RF 3x6 ATC	34	110
Angus Tridol S 6	36	32
Reagent blank (water)	<1	<15

The values for the BOD5 can be compared against the data in the following table which shows the indicative BOD for a range of products and effluents that may be deliberately or accidentally released into receiving waters.

	Indicative BOD (mg O <sub>2</sub> /I)
Natural rivers (uncontaminated)	0.5 – 5 (reference value)
Treated sewage	3 – 50
Paper mill effluent	100 - 400
Crude (untreated) Sewage	200 - 800
Silage Liquor	60,000
Orange juice	80,000
Milk	140,000

The report recognises the importance of awareness of environmental impact over the shortterm and the long-term. Hence this process may become a step in recognising the receiving environment in the context of operational decision making.



## 2. INTRODUCTION

Fire-fighting foam is an additive product that is mixed with water to increase the efficiency and speed of extinguishing a fire. There is a range of foam types (see Table 1) and manufacturers; the chemical composition of a foam determines the application to which it is best suited. Fire-fighting foams are considered to be an essential element in the operational resources of fire services around the world.

Fire-fighting foam types
Protein Foam
Fluoroprotein Foam (FP)
Film Forming Fluoroprotein Foam (FFFP)
Alcohol-resistant Film Forming Fluoroprotein Foam (AR-FFFP)
Aqueous Film-forming Foam (AFFF)
Alcohol-resistant Aqueous Film-forming Foam (AR-AFFF)
Synthetic Detergent Foam
Class A Foam
Fluorine-free Foam (F3)

The New Zealand Fire Service (NZFS) and National Rural Fire Authority (NRFA) use a number of different types of foams to improve the efficiency of knock-down and continued suppression when fighting fires. The additives used are generally described under one of two broad headings, Class A foams or Class B foams.

In New Zealand, fire-fighting chemicals including foams, are subject to the Hazardous Substances and New Organisms Act (1996). The Environmental Risk Management Authority (now the Environmental Protection Agency (EPA)) has issued the Fire Fighting Chemicals Group Standard (ERMA 2006), last amended 8 September 2010. The group standard lists details of chemicals that may be used and how they must be described by the manufacturer in safety data sheets for New Zealand use. The group standard also identifies prohibited compounds, and a classification of compounds and hazard groups.

## 2.1 FIRE-FIGHTING FOAM APPLICATIONS AND PRODUCTS IN USE IN NEW ZEALAND

During an incident the decision to use a foam additive to fight a fire may be taken and will be made based on the type of materials involved in the incident.

Class A foams are used when tackling fires involving solid, flammable products, such as timber, vegetation, paper and rubbish. Initially identified for use in wildfire scenarios, their



favourable performance characteristics have led to them being applied in other scenarios such as structural and furniture fires.

Class A foams act to reduce the surface tension of water used in fire-fighting through addition of a surfactant. This increases the ability of the water to penetrate into materials which allows for improved wetting and thus more rapid and complete end to combustion.

Class A foams used by the NZFS and NRFA are as shown in Table 2:

Manufacturer	Product
Solberg	FireBrake
Angus	Forexpans
Phoscheck	WD881
Chemguard	Class A
Ansul	SILV-EX

 Table 2 - Class A fire-fighting foam products used by NZFS and NRFA in New Zealand

Class B foams are used to deal with fires involving flammable liquids. Class B foams are formulated to form a thermally stable cap or seal over the surface of flammable liquids; excluding oxygen and preventing the release of flammable vapour (vapour suppression) which could ignite once the correct fuel loading ratio is achieved.

Class B foams in use as of 2016 with the NZFS are as shown in Table 3:

Table 3 - Class B fire-fighting foam products used by NZFS in New Zealand

Manufacturer	Product
Angus	Alcoseal
Angus	Expandol
Angus	FP70
Angus	Tridol S
Ansul	Ansulite AFFF
Ansul	Thunderstorm
Kerr	Centrifoam A936
Kerr	Filmfoam A836 3-6%
Solberg	RF-3
Solberg	RF3-6
Solberg	RF-ATC
Techno Marine Group	FFF-AR



## 2.1.1 Operational utilisation of Class A and Class B foams – distribution and volumes

Data on the total volume of Class A foam used per region are shown in Table 5; and the total volumes of class B foam concentrate used in NZ is provided by region and by year in **Error! Reference source not found.** The geographical distribution of the incidents where class B foam has been applied is shown in Figure 1.

Region / geographic area*		2011 - 2016	
Region 1	Auckland and Northland	26,611	
Region 2	Central N. Island	10,576	
Region 3	Lower N. Island	30,346	
Region 4	Upper S. Island	13,640	
Region 5	Lower S. Island	13,884	
Total Usage (litres)		95,231	

Table 4 - Volume (litres) of Class A foam used by NZFS regions, 2011 - 2016.<sup>1</sup>

Table 5 - Volume (litres) of Class B foam used	per year by NZFS regions, 2011 - 2016. <sup>1</sup>
--	---

Region / ge	eographic area*	2011	2012	2013	2014	2015	2016	Totals
Region 1	Auckland and Northland	50	375	525	1275	550	50	2825
Region 2	Central N. Island	125	200	375	325	275	250	1550
Region 3	Lower N. Island	100	275	100	200	100	150	925
Region 4	Upper S. Island	0	250	475	275	125	375	1500
Region 5	Lower S. Island	275	175	275	500	300	200	1725
Total Usage (litres)		550	1275	1750	2575	1350	1025	8525

\*Details of the precise geographic boundaries can be found on the NZFS website (<u>New Zealand Fire</u> <u>Service - All Regions</u>)

<sup>&</sup>lt;sup>1</sup> Data courtesy of S.O. M.Wilby, NZFS.



Figure 1 - Geographical distribution of Class B foam usage in New Zealand 2011 – 2016 (courtesy of SO M. Wilby, NZFS)

#### 2.2 ENVIRONMENTAL FATE

The environmental fate of a product or compound describes how it behaves and the reactions it undergoes on entering the environment.

#### 2.2.1 Biodegradability and persistence

The use of fire-fighting foams during the course of operational and training scenarios will cause these products to enter the local receiving environment. Once there they may distribute through all partitions of the environment (soil, water and air) where they will begin, to a greater or lesser extent to undergo degradation through a number of possible routes including biodegradation.

Biodegradation is the process by which microorganisms in the environment break down a compound (product) via aerobic or anaerobic metabolism. The aerobic microbial degradation of a compound uses oxygen that is present in the environment to support the microbial action; the amount of oxygen that is used in this process can be measured and is described as the biological oxygen demand (BOD). OECD guidelines (1992) for assessment of biodegradability utilise the results of the BOD test as a component of the calculation of biodegradability. The guidelines also require determination of theoretical or chemical oxygen demand (ThOD or COD) to calculate the biodegradability. These guidelines have been the benchmark for biodegradability testing since their publication, however OECD do caution that highly recalcitrant substances may not be completely broken down in the COD test and may yield an incorrect result which indicates that a compound is more readily biodegradable than is actually the case.

Persistence is a measure of the resistance to degradation of a compound, whether the degradation be through biological, chemical or physical agents. Persistence is described using environmental half-life ( $T_{\frac{1}{2}}$ ), this is the amount of time that a compound takes to reduce to half it's original concentration. Measurement of persistence provides a guide to the amount of time taken for a compound to be completely removed from the environment or to be reduced to a level that will cause no harmful effects to organisms in the environment. Persistence does not imply that a compound is harmful, and does not provide information regarding intermediate compounds that may be formed as part of the breakdown process.

#### 2.2.2 Environmental relevance

The rate of degradation and the degree to which a compound can be degraded are two key factors in determining the environmental impact and the persistence. Introduction of relatively large<sup>2</sup> volumes/masses of readily biodegradable compound into a receiving environment may cause significant degradation in a short period of time. This degradation will be due to the use of oxygen as microorganisms metabolise the compound that has been introduced. If the increased biological demand for oxygen exceeds the environmental natural ability to replenish, oxygen levels become depleted or exhausted (anoxia). In aqueous environments the visible signs of this are seen as large-scale fish death, and death of other animals such as invertebrates. The death of these organisms adds further oxygen demand

<sup>&</sup>lt;sup>2</sup> Relative to the volume of the receiving environment.



to a system as microbiological decomposition increases resulting in continuation of anoxic conditions.

For a specific compound or mixture of compounds the BOD value will be proportional to concentration; meaning the greater the dilution the lower the BOD. This is an important factor to consider when assessing the impact releases of such compounds may have on a receiving environment. Some indicative BOD values for specific environments and effluents are given in Table 6.

	Indicative BOD (mg O <sub>2</sub> /I)
Natural rivers (uncontaminated)	0.5 – 5 (reference value)
Crude (untreated) Sewage	200 - 800
Treated sewage	3 – 50
Poultry waste	24,000 - 67,000
Silage Liquor	60,000
Dairy waste	300 – 2,000
Milk	140,000
Brewery waste	500 – 1,300
Orange juice	80,000
Paper mill effluent	100 - 400

Table 6 - Indicative BOD values for different products, wastes and effluents (Fire and Rescue Authority,2014)

The Australian and New Zealand Environment and Conservation Council have identified recommended guidelines for both BOD5<sup>3</sup> and COD of water used for aquaculture, as <15 mg  $O_2/L$  and <40 mg  $O_2/L$  respectively (Schlotfeldt and Alderman 1995, ANZECC 2000).

#### 2.3 ENVIRONMENTAL IMPACTS OF FIRE-FIGHTING FOAMS

Class A foams are predominantly mixtures of surfactants and emulsifiers in aqueous suspension. Class A foams may also contain a mixture other functional compounds, such as fire retardants, that suit specific fire-fighting needs, these compounds vary from product to product. Class A foams are inducted into fire-fighting water at a rate of 0.1 - 1 % by volume, this is relatively low when compared to induction rates of 3 - 6 % for many class B foams. The short-term impact of the surfactant, emulsifier and retardant compounds in class A foam has been recognised internationally, but is generally considered to be less than that posed by class B foams, specifically those containing fluorinated compounds.

Class B firefighting foams produced over the last 50 – 60 years have contained perfluoroalkyl and polyfluoroalkyl substances (PFAS) or mixtures of these compounds as these provide excellent thermal and chemical stability. The composition of such

<sup>&</sup>lt;sup>3</sup> The 5 day BOD test



fluorosurfactants in the foam concentrates are rarely clearly identified in material data sheets as it is considered a proprietary secret by manufacturers. Up until the mid-2000's the predominant compounds used for foam manufacturing were perfluorooctane sulphonates (PFOS). These were withdrawn from manufacturing by the 3M Company due to environmental/ecological concerns regarding their persistence, bioaccumulative capacity and toxicity characteristics (collectively known as PBT). PFOS have been replaced with a number of other fluoro-compounds and more recently some fluorine-free foam compounds. It is not the intention of this report to enter into detailed analysis of the impact of PFOS on the receiving environment, biota and human health as it is banned for use in Class B foams in New Zealand and is included under Annex B (restrictions of production and use) of the Stockholm Convention. However, a low concentration continuum of PFOS has been reported in many 'PFOS-free' class B foams, possibly due to either presence in the environment, contamination of production lines or unintentional synthesis due to use of precursors in formulations (Vestergren, Cousins et al. 2008).

A classification diagram for PFAS is shown in **Figure 2**, adapted from an OECD/UNEP PFC Group synthesis paper on per- and polyfluorinated chemicals (2013). Compounds used in fire-fighting are shown in red.

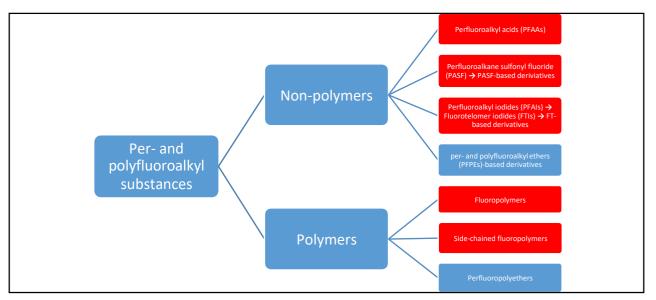


Figure 2 - Classification of per- and polyfluoroalkyl substances (OECD 2013)

The recalcitrant nature of the perfluorinated compounds leads to their long-term persistence in the environment. Many polyfluorinated compounds also exhibit long environmental half-lives. For example, PFOS salts have been reported to undergo no biodegradation or photolysis, and to have a hydrolysis half-life of greater than 41 years (Hekster, de Voogt et al. 2002). They have also been reported as having high persistence in water, soil and air and low mobility<sup>4</sup>.

An overview of three main fluorinated compound groups is given in the following sections.

<sup>&</sup>lt;sup>4</sup> Chemwatch Gold FFS (<u>https://jr.chemwatch.net/chemwatch.web/home</u>), MSDS CAS no 1763-23-1, accessed 11/05/2016.



#### 2.3.1 PFOS

PFOS (including PFOS salts and perfluorooctane sulfonyl fluoride (CAS No. 307-35-7)) is one of the most studied and reported of the PFAS groups of compounds, it is a perfluoroalkane sulfonyl fluoride compound. The high profile withdrawal of PFOS by the 3M Company and the findings of subsequent research mean that the environmental, ecological and health impacts of this group are well described (Moody, Hebert et al. 2003, Yamashita, Taniyasu et al. 2008, Armitage, Schenker et al. 2009, Murakami, Kuroda et al. 2009, Butt, Berger et al. 2010, Guo, Sim et al. 2010, Ahrens 2011, Lee and Mabury 2014, Baduel, Paxman et al. 2015, Anderson, Long et al. 2016, Lindim, van Gils et al. 2016), (Yamashita, Taniyasu et al. 2008, Butt, Berger et al. 2010, Stefani, Rusconi et al. 2014, Xu, Guo et al. 2014) (Jensen and Leffers 2008, Völkel, Genzel-Boroviczény et al. 2008, Fromme, Tittlemier et al. 2009, Olsen, Butenhoff et al. 2009, Haug, Huber et al. 2011, Thompson, Eaglesham et al. 2011, Domingo 2012, Chimeddulam and Wu 2013, Xu, Fiedler et al. 2013, Hoyer, Ramlau-Hansen et al. 2015, Shrestha, Bloom et al. 2015).

In New Zealand a May 2011 - April 2013 nationwide survey of persistent organic pollutants (POPs) performed by Massey University Centre for Public Health Research (CPHR) showed that 100% of returned human serum samples showed presence of PFOS at a concentration between 1.73 – 7.19 ng/mL (weighted mean 3.59 ng/mL, standard deviation (SD) 0.15 ng/mL) ('t Mannetje, Coakley et al. 2013).

#### COMPOSITIO N AND STRUC T URE

PFOS was manufactured using an electrochemical fluoridation technique (ECF). ECF is a process technology used to manufacture fluorinated substances where an organic raw material is dissolved in hydrogen fluoride and electrolyzed, resulting in the replacement of hydrogens with fluorine. The free-radical nature of the process leads to rearrangement resulting in a product mixture of linear and branched isomers of multiple carbon chain lengths.

PFOS and its salts are perfluorinated C8 molecules. Thus, each of the eight carbon atoms in the alkyl chain are fully saturated with fluorine atoms as shown in Figure 3.

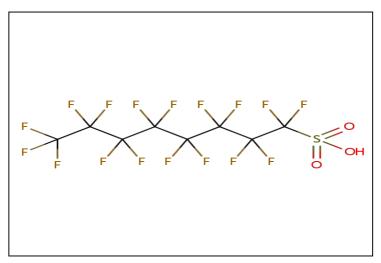


Figure 3 - Chemical structure of PFOS (CAS No. 1763-23-1)



#### Environmental impact

The environmental impact of PFOS has been extensively reported since 2002 (Moody, Hebert et al. 2003, Canada. 2006, Völkel, Genzel-Boroviczény et al. 2008, Yamashita, Taniyasu et al. 2008, Murakami, Kuroda et al. 2009, Guo, Sim et al. 2010, Ahrens 2011, Thompson, Eaglesham et al. 2011, Liu and Mejia Avendano 2013, Zareitalabad, Siemens et al. 2013, Xu, Guo et al. 2014, Chen, Reinhard et al. 2016). The key characteristics of PFOS is the PBT profile as recognised through the inclusion of PFOS under the Stockholm Convention 2009. The New Zealand Fire Fighting Chemicals group standard (ERMA 2006) specifically prohibits use of PFOS.

#### 2.3.2 Perfluorooctanoic Acid (PFOA)

PFOA (CAS No: 335-67-1) is a fully-fluorinated carboxylic acid as shown in Figure 4, it is part of the perfluoroalkyl acid group of chemicals. PFOA and its related salts have been widely used in production of fluorinated fire-fighting foams. A proposal was made to the 11th meeting of the Persistent Organic Pollutants Review Committee for its inclusion as a compound under Annex A, B and/or C of the Stockholm Convention (UNEP 2015). The proposed inclusion of PFOA under the Stockholm convention is due to the PBT characteristics. These are briefly identified within the following section, and can be found in full within the UNEP report<sup>5</sup>. As detailed in section 2.3.3, PFOA can be produced via biotransformation of other fluorinated compounds used in fire-fighting foams, for this reason a brief outline of the justification for the PBT designation of the compound and its related salts has been provided in the following section.

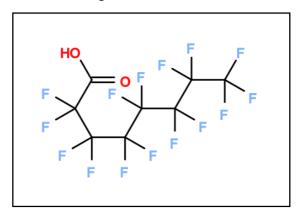


Figure 4 - chemical structure of PFOA

Environmental impact

#### Persistence:

- PFOA does not readily undergo hydrolysis (breakdown by water), an unsighted study from the 3M Corporation estimated a hydrolytic half-life of 97 years, referenced within UNEP/POPS/POPRC.11/5.
- Screening tests carried out using PFOA showed little degradation, indicating that PFOA is not readily biodegradable.

<sup>&</sup>lt;sup>5</sup> POPRC.11 Documents, see document 11/5.



- Efforts to better quantitate the environmental half-lives have been unsuccessful due to the recalcitrant nature of the compound. Under a range of challenging test conditions, no reduction in PFOA concentration was observed.
- Environmental monitoring of PFOA contaminated sites show high levels of PFOA present in soil and underlying groundwater after application or use has stopped. It is also noted that PFOA is environmentally mobile and can enter groundwater via the vadose<sup>6</sup> zone.

The report concluded that PFOA is very persistent and does not undergo degradation via any biological or non-biological pathways.

#### **Bioaccumulation:**

The use of the partition coefficient between octanol and water (Log  $K_{OW}$ ) that is used as an indicator for the likelihood of bioaccumulative capacity for compounds cannot be applied to PFOA as it forms an emulsified layer between the water and octanol phases.

- Ahrens *et al* (2009) reported the preferential binding of PFOA to proteins in the liver and blood of harbour seals.
- The Agency for Toxic Substances and Disease Registry (ATSDR) for perfluoroalkyls published by the US Department for Health and Human Services states that the bioaccumulation potential of perfluoroalkyls is reported to increase with increasing chain length. In living organisms, perfluoroalkyls bind to protein albumin in blood, liver, and eggs and do not accumulate in fat tissue
- High tissue concentrations of PFOA have been reported in terrestrial mammals in remote locations with detectable concentrations in Polar Bear liver, Caribou and Wolf.

#### Toxicity:

- Short-term toxicity data are available for aquatic organisms and indicate low acute toxicity.
- Long-term toxicity test data has been reported for four groups (plants, crustaceans, fish and amphibians).
  - The lowest reported no-observed effect concentration (NOEC) was for fathead minnow (*Pimiphales promelas*) at 0.3 mg/L during a 39 day mesocosm experiment.
  - A low chronic NOEC of 3.125 mg/L in a 7-day experiment was reported for water flea (<u>Moina macrocopa</u>).
- Health Canada cited results of tests on freshwater fish (rare minnow, <u>Gobiocypris</u> <u>rarus</u>) where PFOA concentrations of 3-30 mg/L promoted inhibition of thyroid hormone synthesis genes, and elicited vitellogenin<sup>7</sup> production in males, developed oocytes in male testes and caused ovary degeneration in females.

<sup>&</sup>lt;sup>7</sup> A blood protein associated with production of egg-yolk.



<sup>&</sup>lt;sup>6</sup> The sub-surface region that sits above the saturated zone or water-table.

#### Toxicity to humans:

- In the EU PFOA has been classified under harmonised classification as:
  - $\circ$  Carc.2, H351 suspected of causing cancer
  - o Repr 1B, H360D may damage fertility or the unborn child
  - STOT<sup>8</sup> RE 1 (liver), H372 causes damage to organs through prolonged or repeated exposures.

The report concludes that the currently available experimental and epidemiological evidence shows that PFOA can damage human health and wildlife.

#### New Zealand data

The New Zealand nationwide survey of persistent organic pollutants (POPs) showed that 100% (n = 747) of returned human serum samples showed presence of PFOA at a concentration between 1.53 - 4.20 ng/mL (weighted mean 2.51 ng/mL, standard deviation (SD) 0.09 ng/mL) ('t Mannetje, Coakley et al. 2013). The New Zealand Fire Fighting Chemicals group standard (ERMA 2006) specifically prohibits use of PFOA.

#### 2.3.3 Fluorotelomer compounds

Telomerisation is a process technology used to manufacture fluorinated substances where a perfluoroalkyl iodide (e.g., pentafluoroethyl iodide,  $C_2F_5I$ , telogen) is reacted with tetrafluoroethylene (TFE,  $CF_2=CF_2$ , taxogen) to yield even carbon numbered perfluoroalkyl iodides. These compounds are fluorotelomer iodide based derivatives. Unlike ECF, telomerisation does not produce incidental PFOS compounds as process contaminants.

Fluorotelomers do not degrade to PFOS and contain 30 – 60% less fluorine than PFOS based products. Telomer based foams are not manufactured from PFOA, but may contain trace levels as a by-product of the manufacturing process (Seow 2013).

#### Composition and structure

The manufacturing process produces compounds which have homologous fluoroalkyl chains, meaning that the number of carbon atoms attached to fluorine will be an even number (n = 2, 4, 6 etc.); two non-fluorinated methylene groups are also present between the fluoroalkyl chain and the terminal functional (R-) group. Fluorotelomer compounds are referred to by the number of fluorocarbons groups and methylene groups that are present in the molecule; hence 6:2 fluorotelomer (6:2 FT) contains a 6 fluorocarbon chain with 2 methylene at one end connecting to the R- group as shown in , where the alcohol (-OH) group is the R group.

<sup>&</sup>lt;sup>8</sup> STOT = specific target organ toxicity



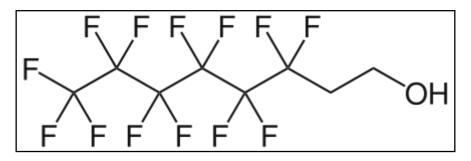


Figure 5 - chemical structure of 6:2 fluorotelomer alcohol <sup>9</sup>

#### Environmental impact

On entry into the environment the degradation of the 6:2 FT compounds results in a variety of pathways and end-products. Butt *et al* (2014) produced an extensive critical review of literature reporting the biotransformation pathways and products of fluorotelomer based PFA substances. The review identifies that there has been universal agreement that the initial degradation steps of 8:2 FTOH are the formation of 8:2 FT-aldehydes followed by 8:2 FT-carboxylates, followed by 8:2 FT-unsaturated carboxylates (FTUCA); and that there is an analogous pathway demonstrated for degradation of 6:2 FTOH. Furthermore, the research concludes, with the exception of one author, that the current body of evidence indicates that 8:2 and 6:2 FTUCA yield PFOA or to a lesser extent perfluorohexanoic acid (PFHxA). Similar breakdown and synthesis processes have been reported in humans occupationally exposed to fluorotelomer compounds, with PFOA being the terminal product in the chain (Nilsson, Karrman et al. 2013).

The Australian Government Department of Health National Industrial Chemicals Notification and Assessment Scheme (NICNAS) has carried out a tier 2 environmental assessment of a range of fluorotelomer compounds as they are indirect precursors to the production of shortchain perfluorocarboxylic acids (NICNAS 2016). The fluorotelomer (FT) compounds identified are 6:2 FT-alcohol (6:2 FTOH, CAS reg. no. 647-42-7); 6:2 FT-methacrylate (6:2 FTMAC, CAS reg. no. 2144-53-8); and 4:2 FT-methacrylate (4:2 FTMAC, CAS reg. no. 1799-84-4).

#### 2.4 CLASS B FOAM PRODUCT TYPES

#### 2.4.1 Fluoroprotein Foam

Fluoroprotein foams are composed of hydrolysed protein, fluorosurfactants or telomers, solvent, sodium chloride, iron, magnesium, zinc and preservatives in a neutral aqueous solution (Johnson 1991). An extension to the fluoroprotein product is the film forming fluoroprotein (FFFP) this product is achieved by addition of a film forming fluorosurfactant in the place of the 'simple' fluorosurfactant. The presence of protein in a product means that biodegradability is enhanced, although the fluorinated residue is likely to have greater environmental persistence. The effect in a receiving environment is that there may be an

<sup>&</sup>lt;sup>9</sup> from https://commons.wikimedia.org/wiki/File:6-2\_FTOH.svg last accessed 10/08/16.



initial increase in biological or chemical oxygen demand leading to an acute oxygen deficiency in the local environment; followed by potential for PBT depending on the fluorosurfactant present.

The composition of fluoroprotein foams varies by manufacturer. The chemical structure of the components do not necessarily fall into a specific class that adheres to a defined structural form such as that of fluorotelomers

#### **Environmental Impact**

The impact of fluoroprotein foams on the environment is driven via two routes, acute and chronic effects (PBT potential). Acute effects include increased BOD, this is in common with other products containing biodegradable compounds leading to production of an anoxic environment. As biological breakdown of these products occurs further issues may arise with the nitrification of the system through the breakdown of proteins. The impact of the nitrification will be dependent on the rate at which proteins are broken down and processed through the aquatic nitrogen cycle. Initial microbial breakdown products of proteins will include ammonia. Ammonia is toxic to fish and other aquatic invertebrates, with different species being able to tolerate different concentrations before exhibiting intoxication culminating in death if not removed or the water remediated.

The potential chronic effects of the fluorinated component of the product will vary depending on the compound that is utilised.

#### 2.4.2 Aqueous Film Forming Foam (AFFF)

AFFF products have been used extensively across all areas of operational fire-fighting to control and extinguish fires fuelled by polar and non-polar combustible liquids (Pabon and Corpart 2002, Hagenaars, Mever et al. 2011, Houtz, Higgins et al. 2013), AFFF products are composed of fluorocarbon surfactants, solvents, hydrocarbon surfactants and a low proportion of halide ions (fluorine, chlorine, bromine and iodine) in slightly alkaline solution. Alcohol resistant (AR) AFFF are produced with the use of water soluble polymers to prevent mixing of alcohol and water that would reduce the efficiency of film-formation. The types of fluorocarbon surfactants present in products has changed since their introduction into service in the 1960s. 3M AFFF products reportedly used perfluorinated carboxylates from 1960s to early 1970s, PFOS from 1970s to 2001. 3M also used a range of other polyfluorinated surfactants between 1984 and 2001, these were C4-C6 perfluorinated chains with a sulphonamide link to an alkyl group; there were no C8 perfluorinated chains in these compounds (Houtz, Higgins et al. 2013). Six other formulators were producing fluorotelomer products from 1984 – 2010, these contained polyfluorinated surfactants with C4 – C10 perfluorinated chains linked by 2 or 3 non-fluorinated carbon atoms to a charged alkyl group (Houtz, Higgins et al. 2013). More recent AFF products contain 6:2 pure fluorotelomer products.

The environmental and human impact of PFOS and the biotransformation products of fluorotelomer products have been discussed in section 2.3.

#### 2.4.3 Fluorine free foams (F3)

A new generation of F3 products have begun to be manufactured in response to concerns regarding the PBT characteristics of fluorine-based foam technologies, be that due directly to



the compounds present or indirectly from the breakdown products acting as precursors for perfluorocarboxylic acid generation (PFOA in particular). The F3 products developed since 2000 contain water-soluble non-fluorinated polymer additives and increased levels of hydrocarbon surfactants (Seow 2013).

#### **Environmental impact**

The environmental impact of fluorine free foams is not well described in peer reviewed literature, perhaps literature, perhaps because the products are 'relatively' new to market. A review of the ecological data, ecological data, sourced from Chemwatch gold MSDS software<sup>10</sup> using CAS registry numbers provided numbers provided by the manufacturer and relating to individual compounds in the F3 follows in

<sup>&</sup>lt;sup>10</sup> Chemwatch Gold FFX accessed 30/05/2016.



Table 7.



Ingredient	Endpoint	Test	Species	Value	Source
		duration (hr)			
2-(2 butoxyethoxy)	EC50	48	Crustacea	>100 mg/L	1
ethanol	LC50	96	Fish	488 mg/L	3
CAS reg. no.	EC50	96	Algae*	>100 mg/L	2
112-34-5	NOEC	96	Algae*	>=100 mg/L	2
	bioaccumulation			Low, BCF = 0.46	
	Persistence (water)			Low	
2-methyl-4-	EC50	96	Algae*	0.538 mg/L	3
isothiazolin -3-one	EC50	48	Crustacea	0.18 mg/L	4
CAS reg. no.	EC50	72	Algae*	0.05 mg/L	4
2682-20-4	LC50	96	Fish	0.07 mg/L	4
	bioaccumulation			Low (Log	
				$K_{ow} = -$	
				0.8767)	
	Persistence (water)			High	
Cocamido-	EC50	48	Crustacea	6.5 mg/L	1
propylbetaine	NOEC	504	Crustacea	0.9 mg/L	1
CAS reg. no.	EC50	96	Algae*	0.09 mg/L	1
61789-40-0	EC0 (zero)	96	Algae*	0.55 mg/L	1
	EC50	96	Fish	1 mg/L	1
	bioaccumulation			No data	
	Persistence (water)			No data	
Decyl glucoside	EC50	384	Crustacea	15 mg/L	3
CAS reg. no.	EC50	96	Algae*	187 mg/L	3
58846-77-8	LC50	96	Fish	62 mg/L	3
	bioaccumulation			Low (Log	
				$K_{ow} = 1.916$	
	Persistence (water)			Low	
Legend         Extracted from: 1, IUCLID toxicity database; 2, Europe ECHA Registered Substances –           Ecotoxicological Information – Aquatic Toxicity; 3, EPIWIN Suite V3.12 – Aquatic Toxicity           Data (estimated); 4, US EPA, Ecotox Database – Aquatic Toxicity Data.					

 Table 7 - Ecotoxicity endpoint data for compounds making up a representative fluorine-free foam

\* or other aquatic plant



# 3. FIRE-FIGHTING FOAM ANALYSIS AND DATA INTERPRETATION

This project has undertaken to establish the presence and concentration of a range of perfluoroalkylsulfonic acids, perfluoroalkylcarboxylic acids and other perfluorinated compounds in products used by the NZFS. Additionally, the chemical oxygen demand (COD) and biological oxygen demand (BOD) of the products have been determined. Results of chemical analysis of foam mixtures as used are applied to prepare scenario-based environmental risk assessments.

The original suite of products for analysis included all class A and B foams used by the NZFS, and was going to be carried out by determination of the product composition through reference to material safety data sheets (MSDS). The approach was subsequently modified after discussion with the NZFS foam procurement team and hazardous substances technical liaison. The modification was due to two main factors; first, the MSDS contain limited data with respected to fluorinated compounds for use in ecotoxicological or toxicological modelling as they are reported as proprietary information and their formulation concentrations not disclosed. Second, although there were five class A foams and 12 class B foams, only a handful were held in quantities considered significant by NZFS. The shortlist of products produced by the NZFS foam procurement team and submitted for analysis is shown in Table 8. Samples of each foam product identified were collected from a number of regions and a composite sample was produced for each product. Samples were submitted for analysis of a range of per- and polyfluoroalkyl substances (see Appendix A.1 for full list of determinands), BOD, COD, pH and conductivity (Appendix A.2).

Manufacturer & 'Product name'	Foam type
Solberg 'Fire Brake'	Class A
	Class B, Alcohol-resistant film forming
Angus 'Alcoseal 3x6'	fluoroprotein
Angus 'FP-70'	Class B, Fluoroprotein
	Class B, Aqueous Film Forming Foam/ Alcohol
Kerr 'A836/AR' <sup>11</sup>	resistant
Solberg 'RF3x6	
ATC'	Class B, fluorine free foam (3F)
Angus Tridol S6	Class B

Table 8 - Fire-fight	ing foam product	s submitted for analysis
Table & The light	ing roam produce	o ousilillou loi ulluiyolo

<sup>&</sup>lt;sup>11</sup> Production of Kerr A836/AR has been discontinued by the manufacturer. An archive copy of the MSDS was provided by the manufacturer on request (private communication Huntley-Ashworth, 25/05/16).



#### 3.1 PRODUCT COMPOSITION

The MSDS of four of the five foam products identified for further analysis were obtained in order to establish the composition of bulk ingredients and excipients that the manufacturers describe. At the time of writing the author had not been able to obtain a copy of the Kerr A836/AR MSDS. The composition data have been extracted from the respective MSDS and are presented in Table 9, the full MSDS for each product is provided in APPENDIX B:

Hazardous	CAS	Concentration	Hazards	Hazard		
ingredients	Number <sup>12</sup>	in product (%)		statement <sup>13</sup>		
Solberg Fire-Brake						
2- (2-butoxyethoxyl)	112-34-5	< 10	Eye Irrit. 2	H319		
ethanol						
Alcohol sulphate C12-	90583-18-9	< 5	Acute Tox. 4	H302		
14, triethanolamine salt			Skin Irrit. 2	H315		
			Eye damage	H318		
			1	H412		
			Aquatic			
			Chronic 3			
1-propanaminium, 3-	61789-40-0	< 2	Skin Irrit. 2	H315		
amino-N-			Eye Irrit. 2	H319		
(carboxymethyl)-N,N-			Aquatic	H410		
dimethyl-,N-coco acyl			Acute 1			
derivatives.						
Hydroxides, inner salts						
Anionic surfactants	Proprietary	< 5	Skin Irrit. 2	H315		
	(not disclosed)		Eye Irrit. 2	H319		
	Angus	Alcoseal 3x6	·	<u>.</u>		
2-Methylpentane-2,4-	107-41-5	1 - 5	Skin Irrit. 2	H315		
diol	203-489-0		Eye Irrit. 2	H319		
Sodium chloride	7647-14-5	1 - < 3	None	None		
	231-208-0					
1,3,5-tris(2-	4719-04-4	0.1 – 0.5	Acute Tox. 4	H302		
hydroxyethyl)hexahydr	225-208-0		Skin Sens. 1	H317		
o-1,3,5 triazine						
Angus FP70						
	7647-14-5	5 - < 10	None	None		
Sodium Chloride	231-208-0					
2-Methylpentane-2,4-	107-41-5	1 - < 3	Skin Irrit. 2	H315		
diol	203-489-0		Eye Irrit. 2	H319		
Ferrous sulphate	7720-78-7	< 1	Acute Tox. 4	H302		

<sup>&</sup>lt;sup>13</sup> Hazard statements are using the Globally Harmonised System of Classification and Labelling of Chemicals - <u>GHS reference document</u>



<sup>&</sup>lt;sup>12</sup> Chemical Abstracts Service reference number - <u>Chemical Substances - CAS REGISTRY</u>

	240-619-9		Skin Irrit. 2	H315
	240-019-9		Eye Irrit. 2	H319
Zinc oxide	1314-13-2	< 1		H410
Zinc oxide		< 1	Aquatic	H410
	215-222-5	0.4.05	chronic 1	11000
1,3,5-tris(2-	4719-04-04	0.1 – 0.5	Acute Tox. 4	H302
hydroxyethyl)hexahydr	225-208-0		Skin Sens. 1	H317
o-1,3,5 triazine				
Water	7732-18-5	Balance of	None	None
	231-791-2	volume		
	Kerr AR-	AFFF A836 3x6		
2- (2-butoxyethoxyl)	112-34-5	10 - 20	Eye Irrit. 2	H319
ethanol	203-961-6			
Hydrocarbon	Proprietary	1 - < 10	Skin Irrit. 2	H315
surfactants	(not disclosed)		Eye Irrit. 2	H319
Water	7732-18-5	Balance of	None	None
	231-791-2	volume		
		g RF 3x6 ATC		
2- (2-butoxyethoxyl)	112-34-5	< 10	Eye Irrit. 2	H319
ethanol	112-34-3		Lye IIII. Z	11313
Anionic surfactants	Proprietary	< 3	Skin Irrit. 2	H315
	(not disclosed)		Eye Irrit. 2	H319
Amphoteric surfactants	Proprietary	< 1	Skin Irrit. 2	H315
	(not disclosed)		Eye Irrit. 2	H319
Decyl glucoside	58846-77-8	< 2	Skin Irrit. 2	H315
Decyl glucoside	50040-77-0	< 2		H318
			Eye dam. 1	пэто
1-propanaminium, 3-	61789-40-0	< 1	Skin Irrit. 2	H315
amino-N-			Eye Irrit. 2	H319
(carboxymethyl)-N,N-			Aquatic	H410
dimethyl-,N-coco acyl			Acute 1	
derivatives.				
Hydroxides, inner salts				
Thiazolones	2634-33-	0.05	Skin Sens. 1	H317
	5/2682-20-4			
2 (2 butowysthowy)	•	s Tridol S 6	Evo Irrit 0	
2- (2-butoxyethoxyl) ethanol	112-34-5	1470	Eye Irrit. 2	H319
Hydrocarbon	Proprietary	< 5%		
surfactants, unspecified	(not disclosed)			
Magnesium sulphate	14168-73-1	< 5%		
monohydrate	14100-73-1			
Fluorosurfactants	Proprietary	< 5%		
Thuurusunaulants	(not disclosed)			



#### 3.2 STANDARDISING THE APPROACH

Samples of the five foam products nominated by the NZFS were collected from around the fire regions of New Zealand. Samples were requested to be provided from previously unopened containers and from different batch numbers. On receipt of samples from the regions, composite samples of each product were made, ensuring equal volumes of each sample were added to the composite. Composite samples were then submitted to the laboratory (AsureQuality, New Zealand) for determination of a suite of per- and polyfluorinated compounds, fluorotelomer compounds, COD and BOD (5-day) as described in Appendix A.1 and A.2<sup>14</sup>. Additional analyses were carried out by ESR to determine pH and conductivity of samples as used at 3 % solution and at a 100-fold dilution factor.

The aim of these analyses was to provide a data set which would allow direct comparison of products with regard to their potential environmental impact in both the short and long-term. This is achieved through obtaining quantitative or qualitative data for the products and can be characterised through the following steps:

- Focussing on ready biodegradability parameters allows a quick assessment of the immediate effect on the dissolved oxygen levels in a receiving environment -Quantitative
- 2. Identifying and weighting the short term impact of toxic substances in the product using data from the MSDS Qualitative
- 3. Identifying and weighting the long-term impact of toxic substances in the product using data from the MSDS Qualitative
- 4. Identifying and weighting the long-term impact of per- and polyfluorinated compounds in the products as identified from the analyses undertaken in this project Quantitative

#### 3.2.1 Comparing potential environmental impact of fire-fighting foam products

To provide a meaningful comparison of the potential environmental impacts of the foam products a grading framework can be used. Such a framework will use information from analysis and review of MSDS and apply numerical values to these; from here a notional value can be calculated; this value will be used to rank a product in order of potential significance environmental impact. The following equation describes how an impact score is derived for each product. Both short-term and long-term hazard values include adjustment related to the stated maximum percentage contained in a product. Short-term and long-term hazard values are assigned on the basis of the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) codes assigned for environmental hazards. These codes are found in the product MSDS, and reported as required by the Firefighting Chemicals Group Standard (2006).

 $Impact\ score = Biodegradability \times \sum ST\ hazard \times \sum LT\ hazard \times \sum PFAS\ hazard$ 

Where:

Biodegradability = score from BOD/COD ratio (Table 10)

<sup>&</sup>lt;sup>14</sup> Sample analysis results forms are presented in Appendix A.2



 $\Sigma$ ST Hazard = sum of short term hazard scores derived from MSDS (Table 11)

ST hazard = Framework score  $\times (\frac{Max \%}{100})$ 

ΣLT Hazard = sum of long-term hazard score derived from MSDS (Table 12)

LT hazard = Framework score 
$$\times (\frac{Max \%}{100})$$

 $\Sigma$ PFAS hazard = sum of additional hazard from PFAS identified by analysis and checked against MSDS (Table 11 and Table 12).

Biodegradability

Analysis of biodegradability undertaken in this project is represented by the BOD:COD ratio. Although it is recognised that this ratio is not optimal, due to incomplete oxidation of per- and polyfluorinated compounds, it does provide a guide to the readiness of biodegradability of the non-fluorinated compounds in a product.

BOD5 value (g/m <sup>3</sup> )	Descriptor	Framework score
>0.6	Readily biodegradable	1
0.5 – 0.6	Biodegradable	1.5
0.4 – 0.5	Somewhat biodegradable	2
0.2 – 0.4	Poorly biodegradable	3
<0.2	Not biodegradable	4

Table 10 - Framework scoring criteria for biodegradability

Short-term environmental hazard

The derivation of a framework score for short-term environmental hazard is achieved by assigning a numerical value to the GHS codes for environmental effects (see Table 11). Where a product contains only one compound that is awarded a GHS code 400 - 402, a single multiplier should be entered into the calculation. If a product has more than one compound which has a GHS code 400 - 402, the scoring for each individual occurrence of a code are summed to produce the multiplier for the calculation. For example if a product contains three compounds each with a GHS 401 code ascribed to them and maximum percentage compositions of 1, 3 and 10% respectively, the short-term hazard score would be:

$$(400 \times \frac{1}{100}) + (400 \times \frac{3}{100}) + (400 \times \frac{10}{100}) = 55$$

Where a product has no compounds that are ascribed a GHS 400 - 402 code, then no value should be entered.

GHS code	Descriptor	Framework score
H402	Harmful to aquatic life	200
H401	Toxic to aquatic life	400
H400	Very toxic to aquatic life	600



#### Long-term environmental hazard

The derivation of a framework score for long-term environmental hazard is achieved by assigning a numerical value to the GHS codes for environmental effects (see Table 12). Where a product contains only one compound that is awarded a GHS code 410 - 413, a single multiplier should be entered into the calculation. If a product has more than one compound which has a GHS code 410 - 413, the scoring for each individual occurrence of a code are summed to produce the multiplier for the calculation. For example if a product contains two compounds one with a GHS 410 code the other a GHS 412 code ascribed, both at 5% maximum composition, the short-term hazard score would be:

$$(800 \times \frac{5}{100}) + (400 \times \frac{5}{100}) = 60$$

Where a product has no compounds that are ascribed a GHS 400 – 402 code, then no value should be entered.

GHS code	Descriptor	Framework
		score
H413	May cause long lasting harmful effects to aquatic life	200
H412	Harmful to aquatic life with long lasting effects	400
H411	Toxic to aquatic life with long lasting effects	600
H410	Very toxic to aquatic life with long lasting effects	800

Table 12 - Framework scoring criteria for	r long-term hazard identified by GHS code
---	---

#### PFAS hazard

Where a PFAS compound has been detected by analysis it shall receive a framework score that is consistent with what is reported in the Chemwatch Gold system MSDS. In the event of a detected compound being widely shown to degrade to a more persistent product; as is the case with 6:2 fluorotelomer sulphonate undergoing biotransformation to PFOA, it shall take on the framework score of highest value from either compound. Where a product has had the % concentration of a PFAS determined analytically or stated in the manufacturers MSDS an adjustment for percent composition should be made as previously demonstrated. Where no data is provided in the MSDS regarding the percentage composition of a PFAS compound, the full framework score weighting will be applied in the calculation. For 6:2 fluorotelomer, the PFOA (H412) GHS code will be used.

#### 3.3 RESULTS OF ANALYSIS OF EXISTING NZFS CLASS B FOAM STOCK

#### 3.3.1 Fluorinated compounds

Sample analysis undertaken by AsureQuality (Wellington, New Zealand) reported that three samples showed traces of 6:2 fluorotelomer sulphonate. At the dilution levels used for analysis by the lab these were not greater than the limit of reporting of 50  $\mu$ g/L. The products containing 6:2 fluorotelomer sulphonate were Kerr A386, Angus Alcoseal and Angus Tridol S 6.



#### 3.3.2 BOD and COD

All samples were submitted for BOD5 and COD analysis, the results are shown for products at the 33-fold dilution level and the 3300-fold dilution level.

· · · ·		• •		-
Product	BOD5 (mg O <sub>2</sub> /L)	COD (mg O <sub>2</sub> /L)	BOD/COD	Framework score
Solberg Firebrake <sup>15</sup>	541	994	0.54	1.5
Angus FP70	4060	17900	0.23	3
Kerr A836	6590	11600	0.57	1.5
Alcoseal	2950	13700	0.22	3
Solberg RF 3x6 ATC	6110	10400	0.59	1.5
Angus Tridol S 6	4690	6880	0.68	1
Reagent blank	<1	<15		

Table 13 - BOD and COD for products at 33-fold dilution (equivalent of 3% induction rate)

Table 14 – BOD and COD for products at 3300-fold dilution (equivalent of 3% induction rate x 100
dilution)

Product	BOD5 (mg O₂/L)	COD (mg O <sub>2</sub> /L)	BOD/COD	Framework score
Solberg, Firebrake <sup>15</sup>	6	11	0.54	1.5
Angus FP70	40	186	0.22	3
Kerr A836	64	127	0.50	1.5
Alcoseal	27	139	0.19	4
Solberg RF 3x6 ATC	34	110	0.31	3
Angus Tridol S 6	36	32	1.13	1
Reagent blank	<1	<15		

#### 3.3.3 pH and conductivity

Table 15 - Conductivity and pH values for 33-fold and 3300-fold dilution

	33-fold dilution		3300-fold dilution	
Product	рН	conductivity (µs)	рН	conductivity (µs)
Solberg Firebrake	6.4	529	5.6	9.7
Angus FP70	7.1	5650	6.6	65.2
Kerr A836	5.8	197	5.8	5.1
Alcoseal	7.5	1825	5.8	34.8

<sup>&</sup>lt;sup>15</sup> BOD and COD values for Solberg Firebrake have been divided using a 10-fold correction factor to account for the lower induction rate of Class A foam (0.3%) over Class B foam (3%).



Solberg RF 3x6 ATC	7.7	340	5.8	14.8
Reagent blank	5.5	11.6	5.5	11.6

### 3.4 CALCULATION OF ENVIRONMENTAL IMPACT OF INDIVIDUAL PRODUCTS IN USE BY NZFS

The separate components of each of the hazard types identified in the framework are brought together in brought together in the following tables (Table 16, Table 17, Table 18, Table 19,



Table 20 and Table 21) and the scores are collated and reported by product in Table 22. The total value displayed in each table is the overall environmental hazard framework score attributed to the product. The relative environmental impact increases with increasing total score. The score is relative, and is only valid when used to compare across products which have undergone the same assessment. The single Class A foam analysed in this report, Solberg Fire Brake, was tested at the same concentrations as the Class B foams, equivalent to a 3% induction rate at the branch. This concentration is not representative of operational use of Class A foams, where induction rates of between 0.1 - 0.3% are typical. To allow this to be represented in the model a conservative correction factor has been applied, and the framework score is divided 10-fold (3 % scaled down to 0.3%).

Solberg Firebrake		
CAS registry number	GHS code (max %)	Framework score
Σ Short-term hazard		
nil		0
Σ Long-term hazard		
90583-18-9	H412 (5)	20
61789-40-0	H410 (2)	16
Σ PFAS hazard		
nil		0
BOD/COD	0.54	1.5
Class A correction factor		0.1
Framework score total		5.4

Table 16 – Environmental hazard ranking framework results for Solberg Firebrake

 Table 17 - Environmental hazard ranking framework results for Angus Alcoseal 3x6

Angus Alcoseal 3 x 6		
CAS registry number	GHS code (max %)	Framework score
Σ Short-term hazard		
nil		0
Σ Long-term hazard		
nil		0
Σ PFAS hazard		
6:2 fluorotelomer (as per PFOA)	H412 (5)	20
BOD/COD	0.22	3



#### Table 18 - Environmental hazard ranking framework results for Angus FP70

Angus FP70		
CAS registry number	GHS code (max %)	Framework score
Σ Short-term hazard		
nil		0
Σ Long-term hazard		
1314-13-2	H410 (1)	8
Σ PFAS hazard		
nil		0
BOD/COD	0.23	3
Framework score total		24

Table 19 - Environmental hazard ranking framework results for Kerr 836 AFFF

Kerr 836		
CAS registry number	GHS code (max %)	Framework score
Σ Short-term hazard		
Nil		0
Σ Long-term hazard		
Nil		0
Σ PFAS hazard		
6:2 fluorotelomer (as per PFOA)	H412 (5)	20
BOD/COD	0.57	1.5
Framework score total		30



Table 20 - Environmental hazard	l ranking framework	results for Solberg RF 3x6 ATC

Solberg RF 3x6 ATC		
CAS registry number	GHS code (max %)	Framework score
Σ Short-term hazard		
nil		0
Σ Long-term hazard		
61789-40-0	H410 (1)	8
Σ PFAS hazard		
nil		0
BOD/COD	0.54	1.5
Framework score total		12

#### Table 21 - Environmental hazard ranking framework results for Angus Tridol S 6

Angus Tridol S 6		
CAS registry number	GHS code (max %)	Framework score
Σ Short-term hazard		
nil		0
Σ Long-term hazard		
nil		0
Σ PFAS hazard		
6:2 fluorotelomer (as per PFOA)	H412 (5)	20
BOD/COD	1.13	1
Framework score total		20

#### Table 22 – Collated framework scores for fire-fighting foams selected by NZFS

Product	Framework score
Solberg Firebrake	5.4
Solberg RF 3x6 ATC	12
Angus Tridol S 6	20
Angus FP70	24
Kerr A836	30
Alcoseal	60



As detailed previously, the overall framework scores shown in Table 22 provide the opportunity to rank products in order of potential for negative environmental impact. A higher score represents increasing environmental impact.



# 4. CONCLUSIONS

The growing recognition of the opportunity to reduce and minimise the impact of fire-fighting on receiving environments and the regulatory requirement to minimise harm means that the impact of additives has come under scrutiny in the last decade. The recognition was initially prompted by the high visibility withdrawal of PFOS from the US market in 2001 and it's inclusion under the Stockholm convention in 2009. The scrutiny has become greater as the suite of compounds used in fire-fighting additives has been more widely investigated and the potential for negative environmental outcomes identified.

This report has given a brief overview of the some of the reasoning behind the environmental concerns and has addressed the question of how fire-fighting foam products can be assessed with regard to their potential for negative environmental impact in both the short- and long-term.

The principal requirement of the report was to provide an assessment of the environmental impact of existing NZFS fire-fighting foam stocks. The products were those nominated by the NZFS foam procurement team on the basis of size of stockpiles retained in the Fire Regions; five products were initially identified for analysis. A framework for determining the potential environmental impact was developed utilising data from chemical analysis and data from literature, mainly the product material safety data sheets or the Chemwatch Gold FFS online resource. The framework takes into account four key factors, and provides weighting of these to deliver an overall value for individual products. The framework should be used as a comparison tool, to allow products to be compared against the same set of parameters thereby providing equitable assessment for existing and future products. The framework is currently weighted in such a way that PFAS compound framework values use the full (non-adjusted) GHS code score. This may be considered as a punitive parameter, but is solely intended to represent a precautionary approach to environmental release of PFAS compounds. If manufacturers declare the percentage composition of PFAS compounds within their products, a pro-rated framework value could be calculated.

The framework has created a systematic approach to ranking the potential long-term environmental impact of a product thereby allowing end-users to factor this aspect of foam performance into their considerations. The products assessed in the report are ranked as follows with the lowest score representing the lower potential impact to the environment:

- 1. Solberg Fire Brake (5.4)
- 2. Solberg RF 3x6 ATC (12)
- 3. Angus Tridol S 6 (20)
- 4. Angus FP70 (24)
- 5. Kerr A836 (30)
- 6. Alcoseal (60)

The report recognises the importance of awareness of environmental impact over the shortterm and the long-term. The identification of the BOD5:COD ratio as an appropriate and



readily practicable system for comparison of the relative biodegradability of compounds is valuable as it allows recognition of acute environmental effects from products. Hence this process may become a step in recognising the receiving environment in the context of operational decision making.





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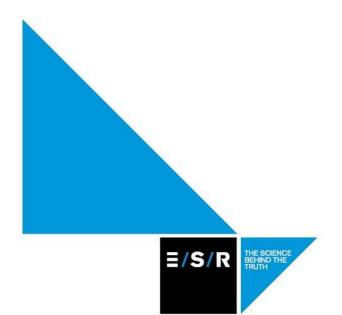
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