

FINAL VERSION

Fire Fighting Foams with Perfluorochemicals - Environmental Review



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7 June 2013

Contents

Executive Summary	2
Acknowledgment	5
Introduction	7
Background	10
PFOS	10
PFOA	11
Fluorine-free Foams	11
Fluorotelomer-based Foams	12
Environmental and Human Impact	14
PFOS and PFOA	14
Fluorotelomers	19
Environmental Considerations When Using Fire Fighting Foam	22
Environmental Acceptance Criteria	22
Remediation and Groundwater Contamination	28
Current Legislation and Policy	30
Australia	30
NICNAS	30
Department of Defence	31
Airservices Australia	32
Metropolitan Fire Board, Melbourne, Victoria (MFB)	32
Australian State Environmental Departments	32
US	32
Canada	34
UK (United Kingdom)	35
Germany	38
Norway	39
EFSA – EU Food and Safety Authority	40
European Union (EU)	41
OECD	43
Stockholm Convention on Persistent Organic Pollutants (POPs)	44
United Nations Environment Programme (UNEP)	46
United Nation's Economic Commission for Europe (ECE)	47
Conclusions	49
Recommendations	51
Glossary	55
References	58

Fire Fighting Foam with Perfluorochemicals – Review

Executive Summary

Fluorochemicals containing fully fluorinated carbon chains do not occur naturally in the environment and are man-made chemicals. They are widely used in a whole range of industrial applications from textiles, preservatives, fluoropolymer and fluoroelastomer production, surface treatment, food packaging, hydraulic oil for aeroplanes, cosmetics, floor wax, polish, paint and lacquer to fire-fighting foams.

There are various types of fire fighting foams available for containing and controlling Class B fires; and those that are capable of aqueous film-formation – AFFF-type foams – all contain fluorosurfactants, which may be either perfluorinated or polyfluorinated materials. Until the announcement by the 3M Company in May 2000 that production of PFOS (perfluorooctanesulphonate)-based fluorosurfactants using the electrochemical fluorination (ECF) process was being phased out, the most common perfluorochemicals used in fire fighting foams were PFOS and its derivatives, with PFOA (perfluorooctanoic acid) now present only as a contaminant although it was used in early AFFF formulations. Over the last few years the fire fighting foam industry has moved away from PFOS and its derivatives as a result of legislative pressure with the manufacture of predominantly fluorotelomer-based fluorosurfactants as the main source of film-forming fire fighting foams (except in countries like India and China), or has explored alternatives to using fluorochemicals by developing and putting on the market commercially available fire fighting foams which do not use fluorochemicals, i.e., that are fluorine-free. Manufacturers of fluorine-free fire fighting foams maintain that the fluorine-free foams are environmentally more benign whilst at the same time meeting international approvals for fire fighting requirements and end-user expectations; whilst fluorotelomer manufacturers for their part maintain based on extensive studies that fluorotelomers (based on 6:2 FTS as the predominant chain-length fluorotelomer sulphonate) are less bioaccumulative and toxic than PFOS and PFOA although environmental persistence is still a concern. Fluorotelomers cannot degrade to PFOS nor are they made with PFOA, although 8:2 FTS, which is often present together with homologous 4:2 FTS, 6:2 FTS, 10:2 FTS and 12:2 FTS, can degrade to PFOA under appropriate conditions. Very recent C6-compliant AFFFs, produced using substantially pure C6 fluorotelomer, eliminate the problem of potential breakdown to PFOA.

It is now well recognised that many fluorochemicals have a potential impact upon the environment and human health due to pronounced persistence of their degradation products, and variable degrees of bioaccumulation potential and toxicity dependent on chemical structure (their PBT profile). The impact of perfluorochemicals on the environment and human health is now well documented, established and recognised worldwide, in particular in the United States of America (USA), Canada, United Kingdom (UK), Sweden, Norway, Germany and Australia. As a result many countries have now either banned or restricted the use of fire fighting foams with perfluorochemicals in particular those foams containing PFOS and their salts and precursors, which are recognised as POPs under the Stockholm Convention. Fluorotelomer-based fire fighting foams are currently still allowed to be used.

The environmental impacts of fire fighting foams containing perfluorochemicals are not only due to bioaccumulation, persistence or toxicity but can also be caused by BOD (biological oxygen demand) and COD (chemical oxygen demand), as is the case for all fire fighting foams to a greater or lesser degree whether or not they contain fluorine or are fluorine-free, due to their effect upon water quality (caused by a decrease in water oxygen content) and aquatic ecology. Therefore, the environmental impact of perfluorochemicals and their use in fire fighting foams needs to be considered as a part of 'bigger picture' using an holistic approach and not only based upon acute toxicity, i.e., a foam may have low and acceptable toxicity, however, it may still impact upon the receiving environment if it has unacceptable levels of BOD or COD, or is persistent. At the same time due consideration should also be given to fire fighting safety and net environmental gain/comparative risks when using fire fighting foams containing fluorochemicals. A similar holistic approach should be also taken with fire fighting foam if it is free of fluorochemicals.

Many countries have now taken steps to ban, curtail or restrict the use of certain perfluorochemicals in fire fighting foams. For example, the production or importation of PFOS-based fire fighting foams has been banned in most developed countries including the US, Canada, the European Union, Australia and Japan. Currently restrictions on the use of existing stocks of PFOS-based foams only apply in Canada and the European Union, which has in addition banned even holding PFOS-based foam stocks as from 27 June 2011 requiring these to be disposed of as hazardous waste. The voluntary US EPA PFOA Stewardship Program is aimed at drastically reducing levels of PFOA and higher homologous chemicals from manufacturing plant emissions and products by 2015; eight manufacturers from the US, Europe and Japan have agreed to participate. Norway and Germany intend to legislate to restrict PFOA use by 2012. In May 2009, the Stockholm Convention was rectified to ban PFOS production and use of PFOS and its salts; together with perfluorooctane sulphonyl fluoride (PFOSF) these materials were restricted under Annex B as persistent organic pollutants (POPs). Australia has yet to formally ratify the PFOS POPs amendment to the Stockholm Convention. A recent study has shown that there are about 10,000 tons of PFOS-based fire fighting foam still in stock or service in the United States in 2011. Estimates for the Asia-Pacific region are that somewhere in the region of 30-40% of all foam stocks are still PFOS-based.

Some agencies in Australia and overseas have already recommended against the use of fire fighting foams with perfluorochemicals and have taken measures to reduce their use, e.g., by advocating the use of fire fighting foams containing no perfluorochemicals, i.e., that are fluorine-free, and advising against their use in fire fighting training. The Queensland Department of Environment and Heritage Protection (EHP) in its draft Procedural Guide for Managing Contaminated Fire Water run-off does not allow fluorinated foams contain bio-accumulating, persistent organic pollutants (POPs) as defined under the *Stockholm Convention* to be released to the environment and requires that this fire water run-off must be contained and disposed of properly. Moreover, the Queensland EHP Procedural Guide on Managing Contaminated Firewater has introduced the very low "major incident" environmental reporting trigger level for AFFF discharge of >10 litres, whether PFOS or fluorotelomer based, or >1000 litres for non-fluorinated foams based on the precautionary principle.

There are still large quantities of legacy (or left over) fire fighting foam containing perfluorochemicals which need to be rendered safe for discharge to the environment. Currently the preferred method to dispose and degrade perfluorochemicals in order to make

them safe for the environment is high temperature thermal incineration (at greater than 1100 degrees C due to the stability of the C-F bond).

Remediation of soil and groundwater contaminated by perfluorochemicals in fire fighting foams is another environmental issue and of concern due to the widespread use of fire fighting foams with perfluorochemicals. Contamination of groundwater is now well documented particularly in the state of Minnesota USA where perfluorochemicals were manufactured by 3M. These fire fighting foams were also widely used for training over a number of years resulting in substantial groundwater contamination, including at former US military fire fighting foam training sites where both PFOS-based and fluorotelomer-based foams were used and at ICAO categorised airports worldwide both for firefighter training and equipment maintenance. Other potential sources of groundwater contamination include landfill sites and waste water treatment plant (WWTP). Currently in Australia there are no landfill acceptance criteria, or soil, surface and groundwater contamination assessment trigger values for perfluorochemicals (such as PFOS, PFOA and fluorotelomer 6:2 FTS). Direct contamination of groundwater and whole water catchment areas can also occur as a result of the practice of using bio-sludge from waste water treatment plant (sewage works or WWTP), sediments in which fluorinated degradation products have been shown to concentrate, as fertiliser for agricultural top-dressing. Additionally both landfill and WWTP have been shown to produce volatile fluorinated degradation products that can diffuse into the upper atmosphere. In Australia, environmental agencies, consultants and practitioners commonly use the USEPA and the Minnesota Department of Health guidelines for water quality and contamination screening for groundwater and soil as references to determine remediation completion acceptance.

Acknowledgment

The author would like to acknowledge the following people listed below for their assistance, encouragement and support in particular Dr Annegret Biegel-Engler, Tom Cortina, Dr Roger Klein, Dr Stephen Korzeniowski, Dr Rick Krassoi, Bruce McGlashan, Ingunn Correll Myhre, Dr Sneha Satya, Ted Schaefer, Jan Solberg, Toni Krasnic, Mike Willson and Virginia Yingling (in alphabetical order).

Dr Craig Barnes, Senior Environmental Specialist, Airservices Australia.

Dr Annegret Biegel-Engler, Federal Environment Agency (Umweltbundesamt), Germany.

Dr Sara Broomhall, Director Chemical Policy Section, Australian Government Department of Sustainability, Environment, Water, Population and Communities, Australia.

Ian Collins, Solberg Asia Pacific Pty Ltd, Australia.

Tom Cortina, Fire Fighting Foam Coalition, USA.

Henrik H. Eriksen, Deputy Director, Section for Chemicals and Waste, Ministry of the Environment, Norway

Nile Fellows, Minnesota Pollution Control Agency, USA.

John Gaglia, Kidde Australia.

Roger Harman, University of Bangor, UK.

Dr Marion Healy, Director, National Industrial Chemicals Notification and Assessment Scheme (NICNAS), Australian Government Department of Health and Ageing (DoHA), Australia.

Dr Roger Klein, Cambridge, UK.

Dr Stephen Korzeniowski, Global Technology Manager, DuPont USA.

Toni Krasnic, USEPA, Washington, DC, USA.

Dr Rick Krassoi, Director, Ecotox Services Australasia.

Dr Mike Logan, QFRS Scientific Branch.

Bruce McGlashan, Technical Advisor - Operational Partnerships, Environment Management Technical Services, UK Environmental Agency, UK.

Dr. Rita Messing, Site Assessment and Consultation, Minnesota Dept. of Health, USA.

Ingunn Correll Myhre, Senior Adviser, Climate and Pollution Agency, KLIF, Norway.

Ralph Pribble, Minnesota Department of Health, USA.

Ian Raymond, Fire Safety Technology Manager, Directorate of Total Ship Survivability (DTSS), Royal Australian Navy, Australia.

Dr Sneha Satya, Program Head, Science Strategy & International Program, National Industrial Chemicals Notification & Assessment Scheme (NICNAS), Australian Government Department of Health & Ageing. Australia.

Ted Schaefer, Solberg Asia Pacific Pty Ltd, Australia.

Jan Solberg, Solberg Scandinavian AS, Norway.

Brett Staines, Technical Development Manager, Fellow, UTC Fire & Security, Australia.

Sanjay Vancheeswaran, Senior Project Manager, CH2M HILL, Inc., USA.

Virginia Yingling, Minnesota Department of Health, USA.

Chris Watt, Executive Manager, Dangerous Goods Department, Metropolitan Fire Board, Victoria, Australia.

Mike Willson, Willson Consulting, Tasmania, Australia.

Introduction

There is now much greater awareness that fire fighting foams with perfluorochemicals and their degradation products can be detrimental to the environment and also potentially to human health. Over the years the Department of Environment and Conservation Pollution Response Unit (PRU) has been asked to provide advice on the use of fire fighting foams to fire fighting agencies such as the Department of Fire and Emergency Services (DFES), port authorities, agencies and companies, regarding the types of fire fighting foam which will be deemed environmentally suitable or 'approved', as well as its policy on containment, confinement, clean up and disposal when these are used at a fire. The PRU also makes decisions and provides advice when responding to pollution, chemical and HAZMAT (hazardous material) incidents and emergencies, for environmental protection and public health and safety, enforcement, as well as directing clean up and disposal of waste and polluted materials resulting from the incident or fire. Currently neither the PRU nor the DEC have a formal or written policy or position on the use of fire fighting foams with perfluorochemicals and advice provided by the PRU or the DEC is based mainly upon the officer's personal technical knowledge, expertise and experience concerning fire fighting foams. There is, therefore, there is a degree of subjectivity and this is not the preferred or desired method. It seems this is also the case with other environmental agencies in Australia. It is for this reason the author is writing this review and position paper for DEC Corporate Executive to consider so that the DEC can adopt a formal position on the use of fire fighting foams with perfluorochemicals.

This review and position paper discusses the current issues regarding the use of fire fighting foams containing perfluorochemicals and of fluorine-free foams now commercially available on the market. Information presented in this paper has been obtained through a review of the available literature, published reports and documents, and information publicly available on the internet, as well as through information provided and shared by various agencies in Australia and overseas. Additionally, by dialogue with the author by those agencies and industry practitioners who are well versed and knowledgeable on the subject matter.

The scope and purpose and of this position paper is to highlight and discuss the following:

- environmental and potential human health¹ issues associated with the use of and exposure to perfluorochemicals in fire fighting foams;
- current legislation and policy in Australia and overseas (namely the US, UK, Norway, Germany and the EU) pertaining to the use of perfluorochemicals in fire fighting foams;
- environmental acceptance criteria for the use of fire fighting foams;
- recommendations for the use of fire fighting foams containing fluorochemicals and fluorine-free foams in Western Australia for the Department of Environment and Conservation to consider or adopt as its policy.

The paper purposely does not cover fluorochemicals that are used in other industrial applications, for example, for stain resistance in carpets, wall papers, non-stick frying pan,

¹ US fire fighters show elevated cancer rates and higher blood levels compared to the average US population for a number of fluorochemicals (LeMasters et al J. Occup. Env. Med. 2006 48(11), 1189-1202; Tao et al Env. Sci. Technol. 2008 42(9), 3472-3478; Shaw et al Chemosphere 2013 91(10), 1386-1394). The need for further monitoring and concerns over exposure to PFCs is recognised by the establishment of the Fire Fighter Biomonitoring Project < <http://ffresults.org/exposure.pfcs.php> >.

paints and varnishes, photographic and semi-conductors industries and others; its principal focus is on fire fighting foams of the AFFF-type using fluorosurfactants, i.e., perfluorochemicals, or those that are fluorine-free.

Intentionally, moreover, this paper does NOT discuss the following:

- Class A fire fighting foams or additives with an impact upon the environment or human health as these do not contain fluorochemicals,
- The operational suitability, performance and efficiency of various types of fire fighting foams containing perfluorochemicals and fluorine-free foams,
- The costs and benefits when alternative foams or additives are used and implemented (requiring, for example, changes involving management and operation methodology) to meet requirements for environmental and human health protection and safeguards,
- Comparison of the various commercially available fire fighting foams on the market as this paper neither seeks to endorse nor to advocate any particular type of fire fighting foam or technique but rather focuses on environmental issues of fire fighting foam, and
- Advocacy of a particular type of technology that could be used for treating or disposing of fire fighting foams with fluorochemicals such as PFOS or PFOA, or for the remediation of soil or groundwater contaminated with fluorochemicals, will not be included or discussed.

This paper does not represent Australian Commonwealth government's position in regard to its party to the Convention on Persistent Organic Pollutants (i.e., the Stockholm Convention) which also covers perfluorochemicals. The Australia Commonwealth government's position is represented by the Commonwealth Department of Sustainability, Environment, Water, Population and Communities in collaboration with NICNAS (National Industrial Chemicals Notification and Assessment Scheme) and other Commonwealth and state agencies.

The author is also aware of the various semantic opinions and arguments put forth distinguishing between perfluoroalkyl and polyfluoroalkyl compounds (which have recently been discussed at length by Buck *et. al.* 2011); however, perfluorochemicals, mentioned in the glossary, are defined in this paper as any fluorinated organic substance that contains a perfluorinated moiety anywhere within its structure. This definition, which includes both PFOS-based fluorosurfactants as well as those based on fluorotelomer chemistry, is important from an environmental regulator's point of view since it highlights the potential for an unfavourable PBT (persistence, bioaccumulation and toxicity) profile, especially extreme environmental persistence, of either the parent compound or its degradation products. This definition also relates closely to the legislative controls and restrictions on the discharge of organohalogen to groundwater in the European Union.

It is also to be noted that as this paper is being drafted, legislative and policy changes on perfluorochemicals are ongoing in Australia and a number of countries, and by the time this paper is endorsed by DEC Corporate Executive, the information presented in this paper related to legislation and policy may have changed. Although organisations in Australia and overseas have various positions and policies on the use of fire fighting foams with fluorochemicals, it is believed no one has collated this information into a single review document previously and proposed a definitive formal position on the use of fire fighting foams with perfluorochemicals or without perfluorochemicals (i.e. fluorine-free foams).

Hence this paper endeavours to present current positions, policies, legislation and thinking on the use of fire fighting foams with or without perfluorochemicals so that the DEC can have a formal position on the matter which will hopefully be of use to other agencies or organisations who are considering their position on the same subject matter. This paper may also provide a starting point or framework for further dialogue and debate on the use of fire fighting foams. The author requests that the reader view this paper in the light of these purposes and intentions.

Background

There are a number of fire fighting foams used for fire fighting depending on the type and nature of the fire, e.g., Class B fire foam products - 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 and also Class A Foam. Fluorine-free foams and foams formulated with fluorotelomers are now used for Class B fire fighting Australia and many countries.

PFOS

PFOS is a member of a large family of perfluoroalkyl sulphonate (PFAS) based chemicals. PFAS refers to the general category of perfluorinated sulphonates and is generally considered to include compounds of carbon chain lengths of four or greater. PFOS refers to a specific PFAS compound that has an eight-carbon chain length and contains carbons that are completely substituted with fluorine. It is the strength of the C–F bonds that contributes to the extreme stability and physical-chemical properties of these perfluorochemicals.

PFOS-related substances may be salts of PFOS, e.g., potassium, lithium, ammonium or diethanolamine, or polymers that contain the PFOS as a portion of the entire structure. A PFOS-related substance is any substance which contains the PFOS moiety and may break down in the environment to give PFOS.

There are no known natural sources of PFOS (Key *et. al.* 1997), and its presence in the environment is due solely to man-made activity.

PFOS and PFAS chemicals have unique surfactant properties and many specialty applications including heat, chemical and abrasion resistance, and as dispersion, wetting and surface treatment agents (hence their use in fire fighting foams).

Once PFOS is present in the environment it does not undergo any further chemical, microbial or photolytic degradation or breakdown. PFOS is also, of course, the final degradation product from POSF-derived fluorochemicals (Dimitrov *et. al.* 2004). It is, therefore, expected that once these substances undergo biotic or abiotic degradation, the perfluorinated moiety that remains will be PFOS. The rate of degradation to PFOS is not considered significant and over time these substances are all expected to degrade in the environment to environmentally persistent PFOS.

PFOS releases to the environment involving water and soil come from a number of sources, e.g., grease repellents for packaging (Environment Canada 2001), surface treatments for rugs and carpets (USEPA OPPT AR226-0550), households (from vacuuming and cleaning of carpet waste to landfills) (USEPA OPPT AR226-0550), fire-fighting foams (final disposal primarily to sewers and wastewater treatment plants), and from incomplete combustion during incineration of PFOS-containing products (USEPA 2002) amongst other sources due to its wide use. Short chain PFASs such as perfluorobutyl sulphonate (PFBS) have been introduced by the 3M Company as substitutes for PFOS applications but only for non-dispersive use.

PFOA

Perfluorooctanoic acid (PFOA) is an anthropogenic or synthetic compound with a chain length of eight carbons, seven of which are perfluorinated. It belongs to the broad class of chemicals known as perfluorocarboxylic acids (PFCAs), which, in turn, belong to the broader class of chemicals known as perfluoroalkyls (PFAs). The term "PFOA" may refer to the acid, its conjugate base or its principal salt forms. The most common commercially used salt form of PFOA is its ammonium salt, referred to as APFO. The term PFOA is not interchangeable with commercial mixtures containing PFOA, as these mixtures are often not well characterised and could include any product that contains even a small amount of PFOA or may act as a precursor for PFOA.

PFOA is often called "C8." Companies use PFOA in the form of its salts in the production of fluoropolymers which have special properties in manufacturing and industrial applications, e.g., fire resistance, and oil, stain, grease and water repellence. They are used to provide non-stick surfaces on cookware, waterproof and breathable membranes for clothing, and are used in many industries such as aerospace, automotive, building/construction, chemical processing, electronics, semiconductors, and textile industries. PFOA continues to be used as a reactive intermediate in the production of fluoropolymers and fluoroelastomers.

PFOA can also be produced by the breakdown of some fluorinated telomers that are used in surface treatment products to impart soiling, stain, grease, and water resistance. Some fluorotelomers are also used as high performance surfactants in products that must flow evenly, such as paints, coatings, and cleaning products, fire-fighting foams for use on liquid fuel fires, or for the engineering coatings used in semiconductor manufacture. However, consumer products made with fluoropolymers and fluorinated telomers, including Teflon® and other trademark products, are not PFOA. Rather, some of them may contain trace amounts of PFOA and other related perfluorinated chemicals as impurities.

The USEPA began investigating PFOA in 1990s and found that it, too, like PFOS, is very persistent in the environment, is found at very low levels both in the environment and in the blood of the general US population, and causes developmental and other adverse effects in laboratory animals (USEPA 2006, 2009, 2010). It has been classified as a potential carcinogen by the USEPA (USEPA 2006).

Fluorine-free Foams

Fluorine-free fire fighting foams are formulated without using fluorochemicals. To be genuinely fluorine-free the foam concentrate must not contain either fluorosurfactants or fluoropolymers. After 2000, significant developments were made to produce a new generation of fire fighting foams that were fluorine-free, i.e., not containing fluorochemicals. They contain instead water-soluble non-fluorinated polymer additives and increased levels of hydrocarbon detergents. Fluorine-free foams are now at least second generation and some third generation. Several types of fluorine-free foams are now available commercially on the market and are being used by fire fighting agencies, oil and gas companies, airports and government organisations in Australia (such as Airservices Australia, Metropolitan Fire Brigade Victoria and Queensland Fire and Rescue Service) as well as overseas. Apparently there are foams labelled as fluorine-free which do still contain small amounts of

fluorochemicals and are thus not truly fluorine-free; however, the technology of producing 'pure' fluorine-free foams is still evolving.

Fluorotelomer-based Foams

Fluorosurfactants contained in fire fighting foams have historically been produced from fluorochemicals manufactured by two methods: electrochemical fluorination (ECF) and telomerisation. Foams containing ECF-based fluorosurfactants have not been manufactured in the USA and Europe since 2002 because they contain PFOS (perfluorooctanesulphonate). All modern foams (except some produced in China and India) contain fluorosurfactants produced by telomerisation, usually referred to as fluorotelomers or just telomers.

The fluorotelomerisation process yields products characterised by homologous (n, n+2, n+4...) fluoroalkyl chains that are linear and usually contain only even numbers of fluorinated carbons whereas the electrochemical fluorination process produces mixtures of linear and branched chains with odd and even numbers of fluorinated carbons. In addition the fluorotelomerisation process inserts two methylene groups (-CH₂-CH₂-) between the perfluoroalkyl chain and the end-group that determines the compound's functionality. The dimethylene moiety distinguishes fluorotelomer based chemicals from those produced by the electrochemical fluorination process. In referring to fluorotelomer sulphonates, the number of fluorocarbons (X) and hydrocarbons (Y) are designated by the abbreviation X:Y, e.g., 6:2 fluorotelomer sulphonate (6:2 FTS) has six fluorinated carbons and two methylene carbons in the fluoroalkyl chain.

Telomer-based foams do not contain or degrade into PFOS and have about 30 - 60% less fluorine than PFOS-based foams. Telomer-based foams are not made from PFOA (perfluorooctanoic acid) but may still contain trace levels as an unintended byproduct of the manufacturing process.

Over the next two to four years feedstock manufacturers will be introducing fluorotelomer surfactants that are substantially purer as regards the 6:2 component (so-called pure C6 fluorotelomers although these in fact contain eight carbon atoms of which six are perfluorinated); this is in-line with the EPA 2010/2015 PFOA Global Stewardship Program aimed at reducing PFOA and potential precursors of PFOA, i.e., the 8:2 FTS moiety, as well as higher homologues with longer chain lengths, with targets of 95% reduction by 2010 for plant emissions and product content and working towards complete elimination by 2015. PFOA has been identified as a potential carcinogen by the USEPA. There have, however, been substantial challenges for the industry in re-formulating foam concentrates using the new pure C6 technology, in particular for fluoroprotein foam, that reach operational requirements of fire suppression efficiency, especially as regards burn-back resistance. These difficulties have resulted in very few manufacturers attaining pure C6 and EPA 2015 compliance. Many others have made a conscious decision to remain with the current C6/C8 technology for the meantime; it should be noted that the acrylamide-based fluorosurfactant CAS #70969-47-0, which contains chain length distributions from C8-C20 with potential to act as a PFOA and higher perfluorocarboxylic precursor, remains in use for fire fighting foams from major manufacturers (note: the given chain length distribution C8-C20 for CAS #70969-47-0 actually means that there is a range of n=C6-C18 n:2 fluorotelomer perfluorinated chains present; the confusion arises because industry insists incorrectly on

only using the number of perfluorinated carbons atoms when referring to the structure, e.g., C6 for the 6:2 fluorotelomer derivative, rather than the accepted chemical nomenclature which includes all the carbon atoms in the chain, e.g. C8, as required under CAS and IUPAC rules, thus obscuring any potential comparisons with homologous chain length compounds such as PFOS or PFOA). This makes it highly likely that re-testing and re-approval of most current AFFF, fluoroprotein (FP), and film-forming fluoroprotein (FFFP) foams reformulated between 2010 and 2015 using the newer C6 technology will be required even if fire suppression efficiency can be achieved.

The predominant breakdown product from six-perfluorinated carbon (C6) based fluorotelomer surfactants is 6:2 fluorotelomer sulphonate (6:2 FTS) which has the potential to eventually degrade to PFHxA (perfluorohexanoic acid), PFPeA (perfluoropentanoic acid) and the 5:3 fluorotelomer acid, $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{COOH}$, depending on environmental conditions (Wang et al., 2011; Korzeniowski, 2013 – 5th Reebok Conference). Recent studies on 6:2 FTS and AFFF-type surfactants which are likely to break down to 6:2 FTS, showed 6:2 FTS to have low acute, sub-chronic and aquatic toxicity, negative genetic and developmental toxicity, not to be bioaccumulative according to regulatory criteria, and to be significantly lower than PFOS in biopersistence. Extensive data on PFHxA show it to have low toxicity, low biopersistence, and not to be bioaccumulative (Martin *et. al.*, 2003b). Biopersistence must, however, be distinguished from the environmental persistence of these fluorinated materials and any perfluorinated ultimate degradation products. All of these fluorinated materials are highly persistent in the environment. Measurements made of groundwater concentrations at former US military fire fighting foam training sites indicate that PFOS, PFOA and 6:2 FTS all have environmental half-lives of at least a decade, with some samples still foaming 10-15 years after the sites were last used.

Environmental and Human Impact

PFOS and PFOA

The impact of fire fighting foams containing PFOS and PFOA are due mainly to legacy use as these substances are no longer used in the manufacture of fire fighting foams in most countries. However, existing stocks of PFOS-based foams continue to be used in many countries and, additionally, may be present in fixed systems. The presence of PFOS and PFOA, and similar substances in the environment, originates from the industrial use and environmental release of these substances, from use and disposal of consumer products that may contain them as an impurity, and from the abiotic or biotic degradation of larger functional derivatives and polymers that contain a perfluoroalkyl moiety and degrade in the environment to form PFOS, PFOA and similar substances. These precursor substances are more commonly used commercially and may be released to the environment from industrial raw materials and products and from consumer products and articles (Prevedouros *et. al.* (2006, Paul *et. al.* 2009).

PFOS and PFOA are now known to be persistent in the environment, bioaccumulative in fauna and toxic, with very long half lives in humans (Olsen *et.al.*, 2007).

PFOS levels found in the environment come from a number of sources as described above, including discharge to wastewater and air (Armitage *et. al.* 2006, Weinberg *et. al.* 2011) during applications and losses from consumer products containing PFOS. It may also be released by incomplete combustion during incineration of PFOS-containing products (USEPA 2002).

PFOA may also be released to the environment during manufacturing and processing operations, or from indirect releases due to the degradation or transformation of PFOA precursors as reported by Ellis *et. al.* (2001, 2003b),. Hatfield *et. al.* (2002), Wang *et. al.* (2005), Wallington *et. al.* (2006), D'Eon and Mabury (2007).

The final disposal of fire-fighting foams is primarily to sewers (wastewater treatment) and storm water drains although uncontrolled releases to surface waters or open land do occur especially during fire fighting, as containment and confinement depends on the manner in which the foam is used and the fire location.

PFOA has been widely detected in a number of locations, e.g., in ambient air (Stock *et. al.* 2004), indoor air (Dreyer and Ebinghaus, 2009) and dust (Kubwabo *et. al.* 2005, Shoeib *et. al.* 2005, Environment Canada Report 2010), in non-stick cooking utensil head-space gases (Sinclair *et. al.* 2007), food samples (Tittlemier *et. al.* 2007, Del Gobbo *et. al.* 2008, Ostertag *et. al.* 2009), drinking water (Hoelzer *et. al.* 2008), tap water (Lien *et. al.* 2006), surface water (Boulanger *et. al.* 2004), lakes (Sinclair *et. al.* 2006, Bononi and Tateo 2007), and groundwater (Field, 2003), as well as in the aquatic environment (Moody *et. al.* 2002; 2008) and in terrestrial biota and humans (Tittlemier *et. al.* 2004; Tao *et. al.* 2008, Monroy *et. al.* 2008; 2009) for many countries as far north as the Arctic (Stock *et. al.* 2007). The presence of PFOS and PFOA in surface water, groundwater, sediments, sewage treatment effluents and sludge, landfill leachate and drinking water in various parts of the world is well documented, e.g., studies done by Moody and Field (1999), Moody and Field (2000), Giesy and Newsted (2001), Hansen *et. al.* (2002), Moody *et. al.* 2002, Muir and Scott (2003), Scott *et. al.* (2003),

Kallenborn *et al.* (2004), Boulanger *et al.* (2004, 2005), Caliebe *et al.* (2004), Crozier *et al.* (2005), Yamashita *et al.* (2005), Ikonomou (2006), Stock *et al.* (2007), Dreyer and Ebinghaus (2009), Aherns *et al.* (2010), Oakes *et al.* (2010),

PFOS is resistant to hydrolysis, photolysis, aerobic and anaerobic microbial biodegradation and metabolism by vertebrates. Its persistence has been documented in several studies and reports, e.g., Key *et al.* (1997), Giesy and Kannan (2002), Hekster *et al.* (2002), OECD (2002a), Boudreau *et al.* (2003b), Moody *et al.* (2003), Schlummer *et al.* (2008), Awad *et al.* (2011), USEPA OPPT AR 226-0547, USEPA OPPT AR226-1107. Once PFOS is in the environment, it may enter the food chain or be further distributed at a distance from its source. PFOS has been detected in wildlife at remote sites far from known sources or manufacturing facilities (Martin *et al.* 2004a). If PFOS does bind to particulate matter in the water column, it may then settle and reside in sediment. However, desorption into the water body may also occur. A review carried out by OECD suggested that any PFOS released to a body of water would tend to remain in that medium, unless otherwise adsorbed onto particulate matter or taken up by organisms (OECD 2002a). Certain tests with PFOS, perfluorooctanoic acid (PFOA) and POSF show no photodegradation at all (Hekster *et al.* 2002; USEPA OPPT AR226-0184, AR226-1030a041).

Field (2003) showed the presence of PFOS, PFOA and telomer sulfonate (from AFFFs used for training) in ground water at three military sites in the USA (Naval Air Station Fallon Nevada, Tyndall Air Force Base Florida and Wurtsmith Air Force Base Michigan). At one of the sites where a KC-135 aircraft had crashed and AFFF had been used, PFOS, PFOA and telomer sulfonate were still detected in the groundwater even after 10 years; as only a one-time application of AFFF had taken place this finding indicates the extreme persistence of these chemicals in groundwater. Moody *et al.* (2003) showed the occurrence and persistence of PFOS (as well as PFOA and 6:2 FTS) in groundwater at the Wurtsmith Air Force Base in north eastern Michigan, US, as a result of fire-training exercises conducted there from the 1950s until the air force base was decommissioned in 1993. Furthermore Schultz *et al.* (2004) reported measurements from a series of former US military foam training areas with particularly high concentrations of 6:2 FTS, PFOS and PFOA in groundwater at Tyndall Air Force Base (TAFB), considerably higher than those found at Wurtsmith Air Force Base (WAFB); 6:2 FTS concentrations were as high as 14,600 micrograms/litre at TAFB.

In Norway, the Norwegian Pollution Control Authority (SFT) survey for the presence of PFOS in soil at four selected fire training or manufacturing facilities reported that the soils were severely contaminated by perfluorinated organic compounds (PFCs) coming from AFFFs, and that soil may be an important source for long term environmental pollution by PFCs (Norway SFT 2008a). The concentration of PFOS in the soils exceeded the Norwegian guideline value for PFOS in soil of 100 ng/g, and rough estimates of the total amounts of PFCs in the soils around two of the investigated facilities showed that 10%–40 % of PFOS used in the AFFFs may still be present in the soil.

Schlummer *et al.* (2008) found PFOS in fish ponds and receiving bodies of water in St. Wendel Germany at concentrations ranging from 8 to 610,000ng/l after 30 tons of fire fighting foam containing PFOS had been used to contain a fire. However, four months later the level of PFOS had decreased by three orders of magnitude in the most highly contaminated area but the amount and decline in PFOS concentration was much lower further downstream. Their study also showed that PFOS bioaccumulated in fish. Awad *et al.* (2011) showed that even a decade after an accidental release of fire fighting foam containing PFOS at Toronto International Airport, Canada, the presence of PFOS in water, sediments

and fish in the nearby creeks was still detectable and at some sampling locations remained at elevated levels. Once in the environment, PFOA is persistent and not known to undergo any further abiotic or biotic degradation under relevant environmental conditions. Available data indicate that PFOA does not significantly photodegrade under relevant environmental conditions (Todd 1979; Nubbe *et al.* 1995; Scrano *et al.* 1999; Hatfield 2001; Hori *et al.* 2004, 2005, 2008), hydrolyse (Ellis *et al.* 2004b) or undergo abiotic or biotic degradation (Reiner 1978; 3M Company 1979, 1980b, 1985b; Pace Analytical 1997; Oakes *et al.* 2004; Moriwaki *et al.* 2005; Cheng *et al.* 2008). The global regulatory community is very much interested in 'long-chain' perfluoroalkyl sulfonic acids (PFSAs $n \geq 6$) and perfluoroalkyl carboxylic acids (PFCAs $n \geq 7$) and their corresponding anions (USEPA 2009, OECD 2011a), which have been shown to be more bioaccumulative than their short-chain analogues (Martin *et al.* 2003a, 2003b; Conder *et al.* 2008; Olsen *et al.* 2009).

In the case of PFOS, the site of toxic action is often considered to be the liver. It has been shown in numerous studies and reports that PFOS bioaccumulates and bioconcentrates in birds (e.g., bald eagles, common loons, eider duck, gull, long-tailed duck, razorbill, red-throated loon), fish (e.g., cod, bluegill sunfish, juvenile and adult rainbow trout, round goby, redfish, smallmouth bass), cetaceans (e.g., beluga, dolphins, narwhal), mammals (e.g., arctic fox, mink monkeys, polar bears, rats, ringed seals, walrus), marine biota (e.g., clam, zebra mussel, water-algae, zooplankton), as shown in a number of studies carried out by Giesy *et al.* (2002), Moody *et al.* (2002), OECD (2002a), Martin *et al.* 2003a, Martin *et al.* 2003b, Taniyasu *et al.* (2003), Tomy *et al.* (2004), Gulkowska *et al.* (2005), Kannan *et al.* (2005a), Newsted *et al.* (2005), Smithwick *et al.* 2005a, USEPA OPPT AR226-1030a042. There is clear evidence for significant trophic magnification for PFOS up the marine predator food-chain (clams through to gulls) as shown by data in the Arctic Council report (2009). Species differences for the elimination half-life of PFOS in biota have been determined to vary significantly, e.g., 15 days (fish); 100 days (rats), 200 days (monkeys) and years (humans) (OECD 2002a; Martin *et al.* 2003b). Clearance rates have also been found to depend on hormonal status, i.e., male or female, as well as oestrogen/testosterone balance.

Like PFOS, PFOA is also bioaccumulated in aquatic biota (Arctic cod, Arctic copepods, bass, carp, bivalves, fathead minnow, flounder, juvenile rainbow trout, lake trout, Pacific herring, pelagic amphipods), mammals (bottlenose dolphin, polar bear, beluga whale, ringed seal, rat, walrus) and humans as shown in a number of studies carried by Ylinen and Auriola (1990), the Kurume Laboratory (2001), Kudo and Kawashima (2003), Martin *et al.* (2003a), Martin *et al.* (2004b), Houde *et al.* (2005), Kannan *et al.* (2005a), Morikawa *et al.* (2006), Olsen *et al.* (2007), Kelly *et al.* (2009), Tomy *et al.* (2009), van den Heuvel-Greve *et al.* (2009). Although, the bioaccumulation potential of PFOA in fish may be low, the presence of detectable concentrations in higher trophic levels (e.g., polar bear, caribou, walrus) has generated concerns regarding the biomagnification potential of PFCAs, including PFOA, in food webs (Conder *et al.* 2008). Martin *et al.* (2004a) found that polar bears, which occupy the highest trophic level in the Canadian Arctic, have higher levels of PFOA than all other Arctic organisms examined, findings reflected in the work by Butt *et al.* (2008). In the case of PFOA, the site of toxic action is often considered to be the liver. However, when the potential for toxicity in consumer organisms is being determined, it is the concentration in the whole body of the prey that is of interest, since the prey is often completely consumed by the predator (including individual tissues and organs, such as the liver and blood).

Microbes can degrade and biotransform fluorinated compounds and this topic have been reviewed recently by Parsons *et al.* (2008). Many studies have now been made showing the biodegradation and biotransformation capabilities of microbes for fluorochemicals, e.g.,

studies done by Saez *et. al.* (2008), Iwai *et. al.* (2009), Murphy (2010), Wang *et. al.* (2011), all building on earlier observations by Key *et.al.* (1998) who demonstrated that under sulphur limiting conditions microorganisms in sludge could partially degrade fluorotelomer type materials. In a study where a mixture of fluorinated substances was incubated in the presence of municipal sewage sludge, no biotransformation was observed (Saez *et. al.* 2008). One must distinguish between completely perfluorinated compounds (usually no biotransformation) and fluorinated compounds like fluorotelomers where there are CH₂ groups next to CF₂ groups (limited biotransformation yielding a perfluorinated end-product as demonstrated by Key *et. al.* (1998)).

PFOA and PFOS has been detected in humans via various exposure pathways e.g., food, food-contact materials, drinking water, breast milk, airborne dust, air and so forth; findings recently reviewed by D'Hollander *et. al.* (2010). PFOS has been detected in the blood plasma of humans not directly linked to the use of fluorinated chemicals (Hansen *et. al.* 2001), and in various animal tissues from less densely populated regions of the world where there are no local commercial, municipal or industrial sources of fluorinated alkyl substances (Giesy and Kannan, 2001), due possibly to the long range atmospheric transport of PFOS to these locations as reported by Martin *et. al.* (2002, Giesy and Kannan, (2002), Hekster *et. al.* (2002), USEPA OPPT AR226-0620, Dreyer and Ebinghaus (2009). PFOA and perfluorohexane sulphonate (PFHxS) have very long half lives in humans (Burris *et. al.* 2002, Olsen *et. al.* 2007) and are now recognised to be biopersistent. However, in contrast to PFOS, PFHxS and PFOA, the shorter chain compounds PFBS and PFBA have shorter half-lives in humans and monkeys (Lieder *et. al.* 2006, Chang *et. al.* 2008, Olsen *et. al.* 2009). PFCAs and PFASs with five or fewer fluorinated carbons such as PFBA (perfluorobutanoate) and PFBS (perfluorobutane sulphonate) have also been detected in the environment (Falandysz *et. al.* 2006 in Loveless *et. al.* 2009, Lange *et. al.* 2007, Hoelzer *et. al.* 2008). Norwegian professional ski waxers using fluorotelomer alcohols for hot-treating racing skis have been reported to have blood levels of PFOA 800 times normal values (Nilsson *et. al.* (2010).

The toxicity of PFOS has been studied in a variety of aquatic and terrestrial species, including aquatic plants (duckweed, green algae), invertebrates (aquatic midge, fresh water mussel, saltwater mysid, water flea, zooplankton) and aquatic vertebrates (bluegill sunfish, fathead minnow, rainbow trout) and terrestrial invertebrates (earthworm, honey bees), birds (bobwhite, quail, Japanese quail, northern bobwhite, mallard) and mammals (rabbits, rats, monkeys). Lithium PFOS is classified by the USEPA as an insecticide for use against fire ants, hornets and wasps. Toxic effects in mammals include: histopathological effects, increased tumour incidence, hepatocellular adenomas, hepatocellular hypertrophy, increased liver, kidney, brain and testes weight, reduced body weight, change in oestrous cycling, changes in levels of neurotransmitters, decreased serum cholesterol, decreased bilirubin, and decreased triiodothyronine, e.g., studies done by Haughom and Spydevold 1992, Campbell *et. al.* 1993a, 1993b; Covance Laboratories, Inc. 2002, Covance Labs 2002a, Berthiaume and Wallace (2002), Hu *et. al.* (2002), Luebker *et. al.* (2002), OECD (2002a), Sanderson *et. al.* (2002), Boudreau *et. al.* (2003a,b), Health Canada (2004). McNabb *et. al.* (2005), USEPA OPPT AR226-0091, USEPA OPPT AR226-0097, USEPA OPPT AR226-0101, USEPA OPPT AR 226-0103, USEPA OPPT AR226 AR226-0144, USEPA OPPT AR226-0167, USEPA OPPT AR226-0169, USEPA OPPT AR226-0240, USEPA OPPT AR226-0569, USEPA OPPT AR226-0949, USEPA OPPT AR226-0953, USEPA OPPT AR226-0956, USEPA OPPT AR226-0957, USEPA OPPT AR226-0958, USEPA OPPT AR226-0967, USEPA OPPT AR226-1030a042, USEPA OPPT AR226-1030a047, USEPA OPPT AR 226-1738, USEPA OPPT AR226-1831.

Like PFOS, the toxicity of PFOA towards animals and humans has also been well studied and documented, e.g., in humans (Olsen *et al.* 2004a, 2004b, Tittlemier *et al.* 2004, Apelberg *et al.* 2007a, 2007b, Calafat *et al.* 2007, Monroy *et al.* 2008, Tao *et al.* 2008, EFSA 2008, Kato *et al.* 2009, OECD 2009, Jin *et al.* 2011.). Tao *et al.* (2008) detected PFOA in 44 out of 45 samples of human breast milk taken in Massachusetts, US, with concentrations ranging from < 0.0301 to 0.161 µg/mL), and Tittlemier *et al.* (2004) and Monroy *et al.* (2008) in their studies found PFOA in cord blood of newborn babies in Canada. Over the years more and more studies have been made to investigate the impact of perfluorochemicals used in fire fighting foams on humans, in particular amongst fire fighters. Once in the body, PFOA can bind to certain proteins (Han *et al.* 2003, 2005) but there is no evidence that it is modified by metabolism, conjugation or defluorination (Van den Heuvel *et al.* 1991). PFOA has a relatively long half-life in humans, in the range of 2–13 years (Burris *et al.* 2002; Olsen *et al.* 2007), mice (Lau 2006), monkey (Thomford 2001a, 2001b; Butenhoff *et al.* 2002, 2004a, 2004b), rat (Sibinski 1987, Biegel *et al.* 1995, 2001, Kennedy *et al.* 1986, Palazzolo 1993; Perkins *et al.* 2004). Kennedy *et al.* (1986) in a study on rats found pathological effects and histopathological changes such as liver necrosis. Jin *et al.* (2011) investigated the likely exposure of fire fighters and inhabitants to perfluoroalkyl carboxylic acids (PFCAs) as a result of the discovery of PFOA contamination in six water districts within Ohio and West Virginia in the United States and a court-directed class action settlement. In their study they found PFHxS (perfluorohexane sulphonate) levels were highest in the fire fighters and statistically significantly different from that of other employment categories.

In October 2006, the UK Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment released a statement on the Tolerable Intake for Perfluorooctanoic Acid (PFOA) in which it recommended a TDI (tolerable daily intake) of 3 µg/kg bw/day for PFOA be established, based on the range of effects on the liver, kidney, haematological and immune systems. It considered the proposed TDI value is adequate to protect against other potential effects such as cancer. It also stated that, based on the results of the Food Standards Agency 2004 Total Diet Study (TDS) that dietary intakes of PFOA are lower than the recommended TDI, hence estimated intakes of PFOA are not of concern regarding human health.

On 15 October 2009, the UK Food Standard Agency released its Food Survey Information Sheet: 05/09 regarding the survey of fluorinated chemicals in food and stated from its analysis of PFOS, PFOA and related fluorinated chemicals in individual retail samples of fish, offal, meat, eggs, milk, dairy products, bread, cereals, popcorn, vegetables and jams, that PFOS was found most frequently and at the highest concentrations in fish, liver and kidney and not detected in any samples of meat, dairy products, potatoes, potato products, popcorn or other cereals, vegetable or fish oils. PFOA was found mainly at low concentrations in crab and liver. Based on the above results, the estimated average adult dietary intakes in 2007 were 0.01 microgram/kg bodyweight/day for PFOS and 0.01 microgram/kg bodyweight/day for PFOA (upper bound figures), well below the Tolerable Daily Intakes (TDIs) recently set by the European Food Safety Authority of 0.15 and 1.5 microgram/kg bodyweight/day, respectively, for PFOS and PFOA. Therefore the Agency concluded from the survey the results do not raise any concerns for consumer health.

The USEPA is concerned about long-chain PFCs because they are found world-wide in the environment, wildlife, and humans; many also bioaccumulate in wildlife and humans, all are extremely persistent in the environment, and many are toxic to laboratory animals and wildlife, producing reproductive, developmental, and systemic effects in laboratory test animals (as previously discussed above). However, to date, significant adverse effects have

not been found in the general human population but due to the long half-life of these chemicals in humans (years), the USEPA anticipates that continued exposure could increase body burdens to levels that would result in adverse outcomes. Recent results in a study of nearly 6000 children living in the vicinity of a chemical plant reported that children with high levels of perfluorochemicals may reach puberty later than normal (Lopez-Espinosa et al (Env. Sci. Technol. 2011 45, 8160-8166) as discussed by Laura Cassidy, Chemical and Engineering News 89(20), May 16, 2011) and that there may also be links with impulsivity and the ADHD syndrome (Charlie Schmidt, Chemical and Engineering News August 11, 2011 writing about papers by Hofmann et al (Env. Health Perspectives. 2010 118(12), 1762-1767) and Gump et al (Env. Sci. Technol. 2011 45, 8151-8159)).

As part of the USEPA efforts to manage PFCs, USEPA also intends to evaluate the potential for disproportionate impact on children and other sub-populations. Given that human biomonitoring data have demonstrated evidence for PFC exposure in humans with PFCs being found *in utero*, during infancy and during puberty, and that animal studies have shown that the foetus and neonate are sensitive life stages to PFC exposure, the USEPA will also consider effects on the developing foetus and children.

The EPA Office of Pollution Prevention and Toxics submitted a draft risk assessment in 2005 for formal peer review by the Agency's Science Advisory Board (SAB). This draft was preliminary and did not provide conclusions regarding potential levels of concern. The SAB reviewed the information that was available at the time, and suggested that the PFOA cancer data are consistent with the EPA guidelines' descriptor "likely to be carcinogenic to humans." Since their review, additional research has been conducted pertaining to the carcinogenicity of PFOA. EPA is still in the process of evaluating this information and has not made any definitive conclusions at this time (USEPA, 8 October 2010).

The presence of these materials in the environment (in particular in groundwater) is also complicated by their co-occurrence with other pollutants such as jet fuel components, chlorinated solvents and heavy metals.

Fluorotelomers

There are not as many independent pieces of research or studies (i.e., research conducted by independent laboratories or organisations) on the environmental impact of fire fighting foams formulated with fluorotelomers compared to those containing PFOS and PFOA.

Potential degradation products from the new fluorotelomer products and raw materials include the 5:3 acid, PFPeA (perfluoropentanoate) and PFHxA (perfluorohexanoate) depending on environmental conditions – Wang *et al.* (Chemosphere (2011) 82, 853). Nilsson *et al.* (2010) [EST 44,2150] in a study of ski-wax technicians showed that the perfluorocarboxylic acids PFHA, PFOA, PFNA, PFDA and PFUnDA all bioaccumulated, with PFHxA having a relatively short half-life in man compared to other perfluorocarboxylic acids. Martin *et al.* (2003a) did not detect PFHxA in fish tissue in a rainbow trout bioaccumulation study and concluded that PFHxA had negligible bioaccumulation potential. In another rainbow trout bioconcentration study done by Martin *et al.* (2003b), perfluoroalkyl carboxylates with less than seven carbons had insignificant bioconcentration factors and a recent critical review by Conder *et al.* (2008) concluded that PFCAs with seven

or fewer fluorinated carbons are not bioaccumulative. Only recently have there been studies on PFHxA and a better understanding of its toxicology to assess the potential hazards is still required.

As fluorotelomer derivatives based on mainly 6:2 FTS (some older chemistries also have 8:2, 10:2 and 12:2 homologues present) are now being used in fire fighting foams as replacements for PFOS and PFOA, more and more studies have been made in regard to its environmental and human impact. Buck *et. al.* (2011) from DuPont speaking at the 3rd International Workshop on Anthropogenic Perfluorinated Compounds in Amsterdam, The Netherlands, June 15-17, 2011, showed 6:2 FTSA (6:2 fluorotelomer sulphonate, also known as 6:2 FTS, which is the major degradation product from fluorotelomer sulfone and mercaptan chemistry used in telomer-based AFFF) to have low acute aquatic and mammalian toxicity, low risk for acute and chronic toxicity to fish, very different aquatic and mammalian toxicity in comparison to PFOS and PFHxS, and low bioconcentration and dietary biomagnification potential in fish. Korzeniowski *et. al.* (2013) in their toxicology study of 6:2 Fluorotelomer Sulfonate in rainbow trout and rats concluded that 6:2 FTSA has low acute mammalian and aquatic toxicity, represents a low risk for acute and chronic toxicity to fish, bioconcentration and dietary biomagnification potential for 6:2 FTSA in fish are low and 6:2 FTSA is very different in its mammalian and aquatic toxicity in comparison to PFOS and PFHxS. They also stated that despite its widespread detection, little toxicity data is available for PFHxS. It is to be noted that 6:2 FTS is environmentally extremely persistent; however, having said this, 6:2 FTS resulting from the degradation of foam sulfone and mercaptan chemistry will usually be contaminated with at least 8:2 FTS and 10:2 FTS and often even higher homologues as shown by Schultz *et. al.*, 2004).

Wang *et. al.* (2011) showed that the biodegradation of 6:2 fluorotelomer sulphonate in activated sludge of waste water treatment plants (WWTP) was relatively slow and probably due to microbial aerobic de-sulfonation of 6:2 FTS, required for further 6:2 FTS biotransformation and a rate-limiting step in biotransformation by microorganisms of activated sludge in WWTPs. They also concluded that 6:2 FTS is not likely to be a major source of PFCAs and polyfluorinated acids in WWTPs.

However, the degradation of fluorotelomer-based products (which include all raw material building blocks, surfactant and polymeric products, and degradation products that originate from the starting fluorotelomer raw materials, perfluoroalkyl iodides (PFAIs)) constitutes a potential source of PFCAs in the environment; thus n:2 FTCA (fluorotelomer carboxylic acid) and/or n:2 FTUCA (unsaturated fluorotelomer carboxylic acid) have been detected in environmental media and biota, e.g., atmospheric particles (Stock *et al.* 2007; Martin *et.al.*, 2002; Hurley *et.al.*, 2004), indoor dust (Barber *et al.* 2007), precipitation (Loewen *et al.* 2005; Scott *et al.* 2006; Taniyasu *et al.* 2008; Kwok *et al.* 2010; Scott *et al.* 2010), surface waters (Stock *et al.* 2007; Ahrens *et al.*, 2009a; Scott *et al.* 2010; Zushi *et al.* 2011), sediments (Stock *et al.* 2007), WWTP effluent (Sinclair and Kannan 2006; Zushi *et al.* 2011), sewage sludge (Zhang *et al.* 2010), landfill leachate (Huset *et al.* 2011), animal biota (Houde *et al.* 2005; Taniyasu *et al.* 2005; Butt, *et al.* 2007a, 2007b; Furdui *et al.* 2007; Gebbink *et al.* 2009), human breast milk (So *et al.* 2006), and foodstuffs (Ostertag *et al.* 2009). The 7:3 fluorotelomer acid has also been detected in biota (Powley *et al.* 2008; Peng *et al.* 2010; Guruge *et al.* 2011) but perfluorinated and polyfluorinated aldehydes have apparently not yet been found in environmental samples (Buck *et.al* 2011) probably due to their highly reactive nature. Fluorotelomer alcohol has been detected in the aquatic environment and to show potential estrogenic activity (Liu *et.al.*, 2009) but the effects on fish production still remain unknown. Liu *et.al.* (2009) in their study of the effects on zebrafish reproduction exposed to

8:2 FTOH found that the average number of eggs spawned and sperm production were reduced, and thinning of eggshell occurred with reduced protein content and egg diameter. Their results showed that waterborne exposure to 8:2 FTOH caused disruption of sex hormone biosynthesis and impaired reproduction in adult zebrafish which ultimately resulted in decreased hatching rates for the offspring.

Fluorotelomer alcohols (FTOHs) as products of the telomerisation process have been identified as precursors that are potentially significant sources of global contamination by PFCAs (Dinglasan *et.al.*, 2004; Ellis *et.al.*, 2004; Hurley *et.al.*, 2004; Wang *et.al.*, 2005). FTOHs are likely to be released to the environment by degradation of products in which they are incorporated and as fugitive emissions during manufacture and use in the synthesis of polymers (Ellis *et.al.*, 2003a; Dinglasan *et.al.*, 2004; Dinglasan and Mabury, 2006). FTOHs can be oxidised in the atmosphere to produce the corresponding saturated fluorotelomer carboxylic acids (FTCAs) (Ellis *et.al.*, 2004; Loewen *et.al.*, 2005; Wallington *et.al.*, 2006) as well as PFOA (Wallington *et.al.*, 2006), and by microbial degradation in the aquatic environment to yield FTCAs and FTUCAs (fluorotelomer unsaturated carboxylic acids) (Dinglasan *et.al.*, 2004; Wang *et.al.*, 2005). Phillips *et.al.* (2007) assessed the acute toxicity of 4:2, 6:2, 8:2 and 10:2 FTCA and FTUCA using *Daphnia magna*, *Chironomus tentans* and *Lemna gibba* as test species and found in general toxicity increased with increasing fluorocarbon (FC) chain length particularly for telomer acids of \geq C8. FTCAs were generally more toxic than the corresponding FTUCAs and these PFCA precursors are more toxic than PFCAs themselves by some orders of magnitude. In a follow up study, Phillips *et.al.* (2010) carried out a chronic toxicity test using *Daphnia magna* and *Chironomus dilutus* as test species and found 8:2 FTCA to be more consistently toxic than FTUCA for the test species *Daphnia magna* with lethal concentration (LC50s) of 150 and >60 $\mu\text{g/L}$ respectively, and effective concentration (EC50s) for survival and growth at 20 days using *Chironomus dilutus* of 2610 and 1250 $\mu\text{g/L}$ respectively.

8:2 FTOH can be strongly adsorbed to soils (Liu and Lee, 2005) but can also undergo biodegradation in soils (Wang *et.at.* 2009) and bacterial culture (Liu *et.at.*, 2009). Wang *et.at.* (2009) showed that aerobic degradation pathways for 8:2 FTOH in soils were in general similar to those in aerobic sludge and bacterial culture. In their soil biodegradation study of 8:2 FTOH they found 2H-PFOA, PFHxA and $^{14}\text{CO}_2$ indicating that multiple $-\text{CF}_2-$ groups were removed from 8:2 FTOH, and that different FTOH metabolites biodegraded differently and to different end-points, e.g., the 7:3 acid (which maybe a unique metabolite from 8:2 FTOH biodegradation) incubated in aerobic soil did not degrade to PFOA. They also proposed that the ratio of PFOA to the 7:3 acid could be used in evaluating environmental samples to distinguish the potential contribution of 8:2 FTOH biodegradation to the observed PFOA levels versus PFOA originating from other sources; however, future research is still needed to explain the specific mechanisms by which multiple $-\text{CF}_2-$ groups in 8:2 FTOH are aerobically removed through investigations of the biodegradation of known metabolites. Research is still required on anaerobic degradation with a comparison of metabolites and pathways for known aerobic biodegradation pathways to more fully understand the environmental fate of 8:2 FTOH and fluorotelomer-based products under landfill conditions. Likewise, ongoing research and comparable studies to determine the contributions to the presence of PFCAs in the environment and the relative contribution of precursor products from aerobic and anaerobic degradation pathways for perfluoroalkyl sulfonyl compounds is still required (Wang *et. al.*, 2009).

There is still much research to be carried out to evaluate the potential environmental impact of fluorotelomers in fire fighting foams.

Environmental Considerations When Using Fire Fighting Foam

Environmental Acceptance Criteria

It is common for users to talk about the acceptability of fire fighting foams or chemicals in terms of acute toxicity; however, environmental acceptability is not predicated only on acute toxicity to biota and humans but also should and must consider all the following environmental acceptance criteria:

- 1) Persistence in the environment – how environmentally persistent are the perfluorochemicals in fire fighting foams, their degradation products or any other of ingredients, i.e., how long will starting material or degradation products remain in the environment before being destroyed or converted to compounds with minimal impact upon the environment and humans?
- 2) Bioaccumulation – do fire fighting foam ingredients such as perfluorochemicals bioaccumulate in the environment and humans and are they bioconcentrated and biomagnified in the food chain or web?
- 3) Toxicity – how toxic are fire fighting foams ingredients such as perfluorochemicals or glycols and biocides to the environment and humans and at what levels are they toxic enough to cause adverse effects (both acute and chronic) to biota and humans?
- 4) BOD (biological oxygen demand/COD (chemical oxygen demand) – BOD and COD effects caused by fire fighting foams ingredients such as glycols, proteins, hydrocarbon surfactants or other additives should be considered (perfluorochemicals themselves are unlikely to contribute significantly to the BOD/COD because of their extreme chemical and biochemical stability, i.e., they are not oxidised under normal conditions – see below). Although a foam and its ingredients may have low and acceptable acute toxicity levels to aquatic test species if, however, the foam has unacceptable BOD and COD levels, its presence in the aquatic environment can cause acute environmental stress through deprivation of the oxygen necessary for water quality and biota survival or well-being.

Biodegradation is a process reflecting the ability of microorganisms to decompose pollutant chemicals such as contained in fire fighting foam. Several methods exist for determining biodegradation, for example, the United Nations Organisation for Economic Cooperation and Development (OECD) method for measuring biodegradability of industrial chemicals in water (OECD 301A) which uses the ratio of BOD₂₀ to COD as a measure of biodegradation. The method is a quick screen for obtaining an initial measure of biodegradability. The closer the ratio is to one, the greater is the biodegradability of the material. Rapid degradation and the associated high oxygen demand, however, can also have a greater short term impact upon the aquatic environment than slower degradation associated with reduced oxygen stress.

Standard methods of oxidation used for the determination of chemical oxygen demand (COD) - also known as theoretical oxygen demand or ThOD – use acid potassium dichromate as the oxidising agent and a titrimetric method to estimate the oxygen equivalents used. Acid potassium dichromate has several limitations as an oxidising agent: (i) any nitrogen in the sample goes only so far as ammonia NH_3 as there is not full nitrification to nitrate NO_3^- - this

means that a correction has to be applied particularly in samples containing large amounts of protein, e.g. FP and FFFP foams; (ii) perfluoroalkyl carbon atoms will not be oxidised due to the stability of the C-F bond (as previously mentioned) – full mineralisation of C-F compounds requires much more drastic oxidising conditions typically involving photo-catalysed or metal-catalysed persulphate treatment. All of this means that, under the standard analytical conditions used for COD determination because fluoroalkyl chains make no apparent contribution to the oxygen demand, just because the BOD approaches 100% COD this does not indicate that a fluorochemical-containing foam concentrate is completely biodegradable. And this discrepancy between measured COD and theoretically oxidisable carbon becomes even greater as one moves from a 6% concentrate to a 3% and then to a 1% concentrate because of increasing amounts of fluorochemical in the preparation.

The persistence criteria for EPA’s final rule for TRI reporting (Toxics Release Inventory (TRI), under section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA) is shown below (USEPA 1999):

	Considered Persistent	Considered Very Persistent
Half-life in water, soil, and sediment	Half-life \geq 2 months (\geq 60 days)	Half-life $>$ 6 months ($>$ 180 days)
Half-life in Air	Half-life $>$ 2 days	

Bioaccumulation potential is a measure of the absorption and concentration of a chemical within a living organism, and is measured using parameters such as BCF or Bioconcentration Factor, octanol/water partition coefficient ($\log K_{ow}$) and water solubility data. The use of $\log K_{ow}$ and physical-chemical properties to predict the potential for bioaccumulation is based, in general, on the assumption that the hydrophobic and lipophilic interactions between compound and substrate are the main mechanisms governing partitioning. This assumption has been shown to hold for non-polar or lipophilic and slightly polar organic chemicals but is known not to apply to the highly fluorinated materials such as are used in fire fighting foam. Due to perfluorination the carbon-fluorine chains become both oleophilic and hydrophobic. In addition, functional groups attached to the perfluorinated chain (e.g., a charged moiety such as sulphonic acid) can impart hydrophilicity to part of the molecule. Hydrophobicity is unlikely to be the sole driving force for the partitioning of perfluorinated substances to tissues because the oleophobic repellency opposes this partitioning process (Kannan *et. al.*, 2001). Perfluorinated substances are also intrinsically polar chemicals because fluorine, a highly electronegative element, imparts polarity by induction. Thus, perfluorinated substances have combined properties of oleophobicity, hydrophobicity, and hydrophilicity over different portions of the same molecule. Lipid normalizing of concentrations in organisms for perfluorinated substances may not be appropriate since these substances appear to preferentially bind to proteins in liver and blood rather than accumulating in lipids.

Measures of bioaccumulation (bioconcentration factors (BCFs), bioaccumulation factors (BAFs), biomagnification factors (BMFs) and trophic magnification factors (TMFs)) may be used as indicators of either direct toxicity to organisms that have accumulated PFOS or indirect toxicity to organisms that consume prey containing PFOS (via food chain transfer).

The USEPA guidelines for BCF under the Toxic Substances Control Act (TSCA) is that a substance is considered to be not bioaccumulative if it has a bioconcentration factor (BCF) less than 1000, bioaccumulative if it has a BCF from 1000-5000 and very bioaccumulative if it has a BCF greater than 5,000.

Traditional bioaccumulation measurements focus on the storage of chemicals in fatty tissues of organisms. Fluorosurfactants as discussed above have been found to bioaccumulate in liver and blood in humans and animals, however, the USEPA model for bioaccumulation does not predict this as it is based upon accumulation in fatty tissues. Thus the USEPA is revising its bioaccumulation model. In Europe the criteria for assessing bioaccumulation under Annex VIII of the REACH regulations have already been modified to take account of this problem.

Toxicity testing and analysis focus on the biota most likely to be affected and the toxicological pathway that will cause the worst or unacceptable effects. In the case of fire fighting foam, aquatic toxicity is the main area of concern and the main pathways for toxicity are through ingestion, absorption and inhalation. Aquatic toxicity is an indicator of the relative toxicity of a chemical or compound in water and is determined using a series of tests for acute (short term) or chronic (long term) toxicity with results commonly expressed as EC50 (effective concentration for an effect to be seen in 50% of the species tested), or LC50 (lethal concentration causing death for 50% of the species tested). When conducting aquatic toxicity testing for fire fighting foams for use in Australia, the test should preferably use Australian aquatic indicator species in addition to the standard internationally agreed species for comparative purposes, for both freshwater and the marine environment where appropriate, including but not limited to dermersal, benthic and pelagic test species; toxicity testing should be carried out for neat foam concentrate as well as for finished foam at the diluted end-use concentration (i.e., at the recommended concentration for use) in accordance with test protocols such as OECD 203. Foam active or make-up ingredients other than fluorosurfactants and hydrocarbon surfactants should also be tested. All toxicity testing should be carried out by approved certified test laboratories, not by the manufacturer themselves or by uncertified laboratories or consultants.

The toxicity data are then compared to a standard toxicity reference scale to determine their potential impact and also evaluated based upon use-specific conditions. There are several such toxicity reference scales of which the US Fish and Wildlife Service Acute Toxicity Rating Scale as also used by the OECD (Table 1 below), is the most commonly used and generally accepted within the industry (note the *caveat* given in the original publication this scale is highly situation specific and should not be used as a planning tool or guidance for relative toxicity without consulting a qualified toxicologist).

Table 1 – US Fish and Wildlife Service Acute Toxicity Rating Scales

Relative Toxicity	Aquatic EC50 or LC50 (mg/l)
Super toxic	<0.01
Extremely toxic	0.01 – 0.1

Highly toxic	0.1 - 1
Moderately toxic	1 - 10
Slightly toxic	10 - 100
Practically Nontoxic	100 - 1000
Relatively harmless	>1000

Most commercially available foam concentrates lie within the least toxic categories of this scale (>100mg/l) based on standard test species. In order to put acute aquatic toxicities into context, e.g., (i) FP and FFFP foams lie in the Relatively Harmless category; (ii) in general AFFFs lie spread across the Relatively Harmless to Practically Non-toxic categories with MilSpec and other high performance AFFF foams having slightly greater aquatic toxicity and falling into the Practically Non-toxic category; (iii) fluorine-free foams range from being close to the Relatively Harmless/Practically Non-toxic borderline to close to just either side of the Practically Non-toxic/Slightly Toxic borderline depending on manufacturer and performance specification; (iv) Class A foams and many synthetic foams all fall within the Slightly Toxic category (note, however, that Class A foams are used dispersively in huge quantities but at very low concentrations (high dilution ratios) and (v) commercial catering detergents (i.e., washing up liquid) often fall into the Highly Toxic category.

In order to highlight chemicals that may be chronically toxic to fish, the USEPA has developed a PBT screening tool or PBT Profiler that provides estimates of the persistence, bioaccumulation, and chronic fish toxicity potential of chemical compounds. It is designed to be used in situations where no data are available. In order to help interested parties make informed decisions on a chemical's PBT characteristics, the PBT profiler automatically identifies chemicals that may persist in the environment and bioaccumulate in the food chain. The criteria used in the USEPA New Chemicals Program (1993) are:

	Low Concern	Moderate Concern	High Concern
Fish ChV (mg/l)	> 10 mg/l	0.1 - 10 mg/l	< 0.1 mg/l

BOD and COD are both pertinent and useful indicators for evaluating potential impact upon the aquatic environment caused by a chemical. BOD (biochemical oxygen demand) is the amount of dissolved oxygen in a body of water used for microbiological degradation within a specified time period whereas COD (chemical oxygen demand) measures the maximum amount of dissolved oxygen necessary to oxidise susceptible organic compounds completely (note failure with C-F containing compounds) in the water. Although COD represents the ultimate total oxygen requirement attainable for a particular pollutant, the rate at which the BOD develops may be a better measure of acute oxygen stress for the environmental compartment. For example, a very high BOD₅ (say 70% of COD) will produce more oxygen stress than a BOD₅ that is just 40% of COD, for identical COD values.

The result of a BOD₅ test indicates the amount of water-dissolved oxygen (expressed as milligrams oxygen per litre of water) consumed by microbes incubated in darkness for five days at an ambient temperature of 20°C. The higher the BOD value, the higher is the amount

of pollution in the test sample. For contaminants that cannot be oxidised biologically, chemical oxygen demand (COD) method is used. Again note the failure of COD with high nitrogen content or perfluoro-compounds.

The 20 day BOD test is the common and recommended BOD test for wastewater, however, for fire fighting foams the BOD time period used may be as long as 28-30 days. When compared to the normally accepted wastewater BODs and CODs, all fire fighting foam concentrates currently have high and unacceptable BODs.

Most applications of COD determine the total, i.e., dichromate oxidisable, amount of organic pollutants found in surface water (e.g., lakes and rivers), groundwater or wastewater, making COD a useful measure of water quality.

High oxygen demand can remove all of the oxygen from the water and cause fish and plant kills in addition to aquatic toxicity effects upon other aquatic fauna. Many government agencies impose strict regulations and guidelines regarding the maximum biochemical oxygen demand allowed in wastewater before it can be returned to the environment, e.g., the UK Environmental Agency Typical BOD Guide (Table 2) and Australian water quality BOD guidelines (Table 3).

Table 2 – UK Environmental Agency Typical BOD Guide

Typical BOD values	mg oxygen /l
Natural rivers	0.5 – 5.0
Crude sewage	200 – 800
Treated sewage	3 – 50
Poultry waste	24,00 – 67,000
Silage liquor	60,000
Dairy waste	300 – 2,000
Milk	140,000
Brewery waste	500 – 1,300
Orange juice (unsweetened)	80,000
Paper mill effluent	100 – 400
Typical fire fighting foam concentrate	350,000
Diluted 3% – 6 %	50 – 100 times sewage BOD

Table 3 - Summary of the recommended water quality guidelines for BOD (ANZEC Guidelines for Fresh and Marine Water 2000)

Group	Guideline mg/l	Comments	Reference
Recommended guidelines	<15	freshwater BOD5	Schlotfeldt & Alderman 1995
	<40	freshwater COD5	Schlotfeldt & Alderman 1995
	ND	saltwater BOD5	
	ND	saltwater COD5	
General	<15	freshwater BOD5	Schlotfeldt & Alderman 1995
	<40	freshwater COD5	Schlotfeldt & Alderman 1995
Freshwater fish	<10	rainbow trout BOD	Forteach pers. comm.
	<12	freshwater species BOD	DWAF 1996
	<30	rainbow trout COD	Forteach pers. comm.
	<5	salmonids BOD	Svobodova <i>et. al.</i> 1993
	<10	salmonids COD	Svobodova <i>et. al.</i> 1993
Marine fish	<10	BOD5	Swindlehurst pers. comm.
Brackish water fish	<20	BOD5	Swindlehurst pers. comm.
Freshwater crustaceans	<10	BOD5	Swindlehurst pers. comm.
Marine crustaceans	<10	BOD5	Swindlehurst pers. comm.
Edible bivalves	<10	BOD5	Swindlehurst pers. comm.
Non edible bivalves	<10	BOD5	Swindlehurst pers. comm.
Gastropods	<10	BOD5	Swindlehurst pers. comm.

From the above two tables, it can be seen that BOD is an important criterion to be considered when fire fighting foams are used or discharged into the environment for the reasons mentioned above.

Remediation and Groundwater Contamination

Remediation of soil and groundwater contaminated by perfluorochemicals in fire fighting foams is a growing issue in Australia and in many other countries. Contamination of groundwater due to the manufacture of fluorochemicals and the use of fire fighting foams containing perfluorochemicals is now well documented, e.g., in the State of Minnesota, USA, where the 3M Company used to manufacture perfluorochemicals, as well as at airports and at former US military fire fighting foam training sites. There have been many studies reported of perfluorochemicals in surface and groundwater as discussed above.

Currently in Australia there are still no landfill acceptance criteria or contamination assessment trigger values for perfluorochemicals such as PFOS, PFOA and fluorotelomer 6:2 FTS. In Australia environmental agencies, consultants and practitioners commonly use the USEPA and the Minnesota Department of Health guidelines for water quality and contamination screening of groundwater and soil contamination by perfluorochemicals.

The Minnesota Department of Health (MDH) has established Health Risk Limits (HRLs) for four PFCs which are: for PFOS 0.3µg/l; for PFOA 0.3µg/l; and Health Based Values (HBVs) for PFBA (Perfluorobutanoate) 7µg/l; and for PFBS (Perfluorobutane Sulphonate) 7µg/l. HBVs are criteria that MDH considers safe for human consumption over a lifetime. According to MDH the only real difference between an HRL and HBV is that an HRL is promulgated through a formal rule-making process (in August 2007) while an HBV is not. MDH began developing these drinking water criteria before the USEPA released their guidelines for PFOS and PFOA but consulted regularly with EPA regarding their work. Once the EPA guidelines were available MDH Health Risk Assessment staff reviewed the information used by USEPA and determined there was nothing that warranted any further refinement of MDH criteria for these compounds. The USEPA Office of Water (OW) Provisional Health Advisories contain guidelines of 0.4µg/l for PFOA, and 0.2µg/l for PFOS for drinking water. MDH has not set a drinking water standard for 6:2 FTS and currently is not developing one. Their Health Risk Assessment staffs have perfluorohexane sulphonate (PFHxS) on their work plan to develop a health based value for drinking water but currently there are insufficient health risk studies to set a value.

The UK Environment Agency has stipulated that the maximum concentration of PFOS in groundwater abstractions used for drinking water should remain below 1µg/l; if the concentrations of PFOS in groundwater are above 1µg/l further investigation should be made to protect the groundwater resource. It also stipulated that PFOS levels in fresh surface waters should not exceed 1µg/l (annual average) after initial dilution and, where possible, detectable emissions should be prevented; if the PFOS concentration in surface water is above 1µg/l (spot sample) further investigation and the potential need for action to reduce inputs by the polluter must be assessed. For saltwater, the PFOS level should not exceed 2.5µg/l (annual average) after initial dilution especially if there are significant discharges to shellfishery areas.

The Minnesota Pollution Control Agency (MPCA) also has soil reference values (screening criteria) for residential settings: PFBA 77mg/kg; PFOA 2.1mg/kg; and PFOS 2.1mg/kg. For its Superfund Program, the USEPA residential soil screening level for PFOA is 16mg/kg and PFOS 6mg/kg. MPCA has also established state-wide surface water criteria of 1mg/l for PFBA and site-specific surface water criteria for Pool 2 of the Mississippi River: 7ng/l PFOS and 2,700ng/l PFOA.

The UK Environment Agency has stipulated that for sewage sludge disposal, i.e., if sewage sludge is spread on the land as agricultural top-dressing, the PFOS concentrations should not exceed 39µg/kg wet-weight or 46µg/kg dry-weight (based on 15% moisture in the soil and mixing of the sludge with the soil) for the protection of soil organisms. If this is breached the sewage sludge should be disposed of by high temperature incineration at 1100°C.

Current Legislation and Policy

Australia

NICNAS

NICNAS (National Industrial Chemicals Notification and Assessment Scheme) is an Australian Commonwealth (equivalent to Federal in the US) government body responsible for the risk assessment of chemicals used in or imported into Australia. It has issued four alerts regarding PFOS and its related substances as well as related PFAS-based chemicals (Alerts No.1 – July 2002, No.2 – April 2002, No.5 – February 2007 and No.8 – December 2008).

In April 2009, NICNAS conducted a national survey to collect information relating to the production, importation, stocks held and use of PFOS, PFAS and their related substances, and products/mixtures containing these substances, in Australia. Some of the survey findings are listed below:

- Overall there was an increase in PFAS and PFOS imports into Australia compared to previous surveys, e.g., in the 2007 survey over 14 tonnes of PFAS were imported into Australia with PFOS accounting for 1.3 tonnes (8.9%), whereas in the 2006 survey approximately 8 tonnes of PFAS were imported into Australia with PFOS accounting for 0.76 tonnes (8.6%).
- There were significantly increased imports of PFAS and PFOS chemicals in the metal plating industry and of PFOS in the aviation industry. On the other hand, no imports of PFAS chemicals for surface treatments occurred in 2007 compared to half a tonne of imports in 2006. Imports for the other sectors of industry showed less significant variations.
- Stocks of fire fighting foam containing PFOS continued to exist although there were no imports and existing stocks were reduced by a quarter since the last survey. The survey data indicated that imports of PFAS including PFOS increased for industrial applications and declined or ceased for consumer applications and for fire fighting foams. In the latter case, respondents reported a move towards telomers and shorter chain length fluorinated sulphonates (mainly C4 and C6 chain lengths) or perfluorobutane sulphonates (PFBS).²
- Imports of PFOS for applications such as aviation and metal plating and to a small extent for photography and photolithography are likely to continue as there are no viable replacements yet.
- These findings are consistent with other international reports. The OECD survey in 2004 on the production and use of PFAS, PFOS, PFOA and related substances indicated that products containing PFOS were still being manufactured and imported by many countries for use in the fire-fighting, metal plating, photographic, semiconductor and aviation industries.

²: but not the C4 for fire fighting foams; in addition it is very unlikely that any of the fire fighting foams were C6 compliant as there are very few companies worldwide with C6 EPA compliant products! PFBS is not used in fire fighting foams. When the 3M Company introduced PFBS-based fluorosurfactants post-PFOS it was decided that these C4 compounds would not be available for dispersive product use such as fire fighting foams or indeed for consumer products such as paints and varnishes.

- Possible overestimates could occur if a quantity of import was reported by the importer as well as reseller or user. These uncertainties, however, do not detract from the valuable findings of the survey.

In October 2009, NICNAS released an Existing Chemicals Information Sheet on Options for Disposal of Perfluorooctane Sulphonate (PFOS) Waste in which it comments on the various State's and Territory's disposal capability for PFOS (NICNAS, 2009) but no statements were made regarding State policy on the use or disposal of fire fighting foams containing perfluorochemicals.

PFOA is not manufactured in Australia or imported as the base chemical. Imports of polymers containing PFOA have virtually ceased, dropping from 27.5 tonnes in 2003 to approximately 20 kg in 2004 following co-regulatory activity between NICNAS and the industry.

On 20 May 2004, Australia ratified Article 3 of the UN Stockholm Convention which requires parties to the Convention to take into account POPS characteristics when conducting assessments on new and existing chemicals. The POPS characteristics are persistence, bioaccumulation and potential for long-range environmental transport, and include adverse effects on human health and the environment.

In 2009, PFOA was added to Annex B of the UN Stockholm Convention; however, Australia has yet to ratify the Stockholm Convention as a signatory party (see discussion below under Stockholm Convention).

Department of Defence

The Australian Department of Defence has a policy for the procurement and use of AFFF (Aqueous Film Forming Foam (AFFF) Procurement and Use Interim Policy Version 1, August 2008) in which it states the minimum requirements for the Department of Defence and its contractors to follow when purchasing AFFF products. In the policy, the Department of Defence states the following:

- More environmental friendly fire fighting foam products to be sought.
- Need to comply with its Defence Environmental Guidelines for Management of AFFF Products, June 2007.
- Must be suitable for Class B fires such as hydrocarbons or fuel fires.
- Aims to minimise the use of AFFFs preferring their use only for real and emergency fire fighting purposes.
- Fire fighting foam suppliers must supplying the following information:
 - Surfactants data.
 - Toxicology data such as EC50, LC50 or LD50.
 - Persistence/biodegradation data – must be highly degradable in freshwater within the first week, with a performance of at least 99 % after 4 weeks.³

³ This requirement effectively excludes ALL AFFF-type foams because of the fluorochemical content and the degradation products not being biodegradable! Also the requirement for a high BOD in the first week, i.e., a high BOD5, will result in high oxygen stress for the receiving aquatic environment.

- MSDS data.
- Must be properly stored.
- Must be managed so that it is NOT released into the environment, to prevent land, air and water pollution, during all stages of the lifecycle (including foam used for training).
- AFFF-contaminated waste water must not be allowed to enter stormwater or sewerage.

Airservices Australia

Airservices Australia is moving away from using fire fighting foams containing perfluorochemicals and is in the process of retiring its AFFF (*pers. comm.* Dr. Craig Barnes, Airservices Australia, 2011).

Metropolitan Fire Board, Melbourne, Victoria (MFB)

MFB does not have a formal policy position on foam use; however, it has selection criteria for choosing fire fighting foams. MFB when selecting fire fighting foams will take into consideration the health impact upon fire fighters and any potential for environmental contamination. Since AFFF became unpopular and expensive to dispose of, MFB has evaluated various other foam formulations and have moved to using fluorine-free foams (*pers. comm.* Chris Watt, Assistant Chief Fire Officer, MFB, 2010).

Australian State Environmental Departments

Currently the Queensland Department of Environment and Heritage Protection would be the first Australian environmental department to have a formal written policy in its Procedural Guide Draft 2.15 – *Managing Contaminated Fire Water* - to categorically state that it does not allow fluorinated foams contain bio-accumulating persistent organic pollutants (POPs) as defined under the *Stockholm Convention* to be released to the environment and that these must be contained and disposed of properly. Other environmental departments including the Western Australia Department of Environment and Conservation have yet to have a formal written policy or position on fire fighting foams with perfluorochemicals similar to that recently released by the Queensland Department of Environment and Heritage Protection.

USA

In 2000, the 3M Company, the principal global producer of PFOS and the only producer of PFOS and PFOS-related compounds in the USA decided voluntarily to cease global production of both PFOS and PFOA by the end of 2002. The USEPA followed up this voluntary phase out of PFOS with Significant New Use Rules (SNURs) under the Toxic Substances Control Act (TSCA) Section 5 in 2000, 2002 and 2007. TSCA Section 5 provides authority for the USEPA to review and regulate the manufacture, importation and

processing of new chemicals, and to regulate significant new uses of existing chemicals that may change or increase the exposure of humans and the environment to these fluorochemicals. These rules restrict the reintroduction into the market of perfluoroalkyl sulphonates (PFAS). The manufacture or importation of these chemicals for any other use would require prior review by the USEPA. The few uses not excluded by this regulation are for use in hydraulic fluids, semiconductors, imaging films, and use in intermediate processing solely for the three foregoing processes – also use in plating processes to produce electronic devices and use as a fume/mist suppressant in plating baths.

In January 2006, the USEPA launched a global 2010/15 PFOA Stewardship Program to phase out PFOA and PFOA-related chemicals including potential PFOA precursors by the end of 2015. Eight major companies that use or manufacture PFOA and related chemicals committed to reduce facility emissions and product content of PFOA and related chemicals by 95 per cent by no later than the end of 2010, and to work toward eliminating emissions and product content by the end of 2015. The eight companies participating in the Program are Arkema, Asahi, BASF Corporation (previously Ciba), Clariant, Daikin, 3M/Dyneon, DuPont and Solvay Solexis. Companies have indicated to the USEPA that they are on track to meet the 2015 goals.

On December 30, 2009, USEPA published a chemical action plan for long-chain perfluorinated chemicals (PFCs). The chemical action plan summarises available hazard, exposure and use information; outlines risks that long-chain perfluorinated chemicals may be present and identifies the specific steps that the USEPA is taking to address these concerns with opportunities for input from stakeholders.

Perfluorinated chemicals (PFCs) according to the USEPA definition comprise two sub-categories: perfluoroalkyl sulphonates (PFAS) and perfluoroalkyl carboxylic acids (PFCA).

The PFAS sub-category includes perfluorobutane sulphonic acid (PFBS), perfluorohexane sulphonic acid (PFHxS), perfluorooctane sulphonic acid (PFOS), other higher homologues, and their salts and precursors.

The PFCA sub-category includes perfluorohexanoic acid (PFHxA or C6), perfluorooctanoic acid (PFOA, sometimes called C8), other higher homologues, and their salts and precursors. Some of those potential PFCA precursors include chemicals known commercially as fluorotelomers.

In order to manage long-chain PFCs, the USEPA may use the Toxic Substances Control Act (TSCA) Section 6 for rulemaking to either ban or restrict the manufacture (including import), processing, and use of these chemicals. Rulemaking under TSCA allows the USEPA to expand the reach of its three Significant New Use Rules (SNURs) that it promulgated over the past decade, as well as its 2010/15 PFOA Stewardship Program, to further reduce exposure to LCPFCs (long chain PFCs) by addressing their use in products from sources other than the eight companies participating in the Stewardship Program.

The PFAS SNURs apply only to new manufacture and import, not to existing stocks of PFAS, and as a result PFAS compounds in AFFF are still being used in the USA. However, manufacture and import of new PFOS-based surfactants are no longer permitted in the USA except for any existing stocks; the fire-fighting industry in the USA has fully transitioned to non-LCPFC alternatives and are working on improving control measures to limit environmental releases during application.

The USEPA is committed to work with companies to eliminate long-chain PFCs from emissions and products under the 2010/2015 PFOA Stewardship Program, to continue to evaluate alternatives under EPA's New Chemicals Program and to collaborate with other countries on managing PFCs.

In 2010, USEPA published a Final Rule that amended the Polymer Exemption Rule to exclude from eligibility polymers containing as an integral part of their composition, except as impurities, certain perfluoroalkyl moieties consisting of a CF₃ group or longer perfluorinated chain length. This exclusion includes polymers that contain any one or more of the following: PFAS; PFCA; fluorotelomers; or perfluoroalkyl moieties that are covalently bound to either a carbon or sulfur atom where the carbon or sulfur atom is an integral part of the polymer molecule. The rule became effective in January 2012.

As described above, the USEPA has taken steps to investigate further PFOA and related chemicals as well as to reduce their emissions and use in products. However, given the scientific uncertainties, the USEPA has not yet made a determination as to whether PFOA poses an unreasonable risk to the public, and there are no steps that the USEPA currently recommends that consumers should take to reduce exposure to PFOA.

Canada

In 2004, DuPont Canada, the University of Trent and Environment Canada jointly organised a Workshop on the Environmental Fate of Fluorotelomer-Based Polymers to discuss the scientific aspects regarding the environmental fate of fluorotelomer-based polymers and their degradation products. The workshop focussed on the science of fluorotelomer-based substances but did not address their toxicology, nor did it consider regulatory or policy issues. The general aim of the workshop was to establish a better understanding of the environmental fate of fluorotelomer-based polymers and their degradation products. In the workshop agreement was reached that fluorotelomers have an impact upon the environment due to their bioaccumulation, persistence and toxicity (**Jimmy – reference needed for this statement**).

In December 2005, Health Canada and Environment Canada proposed temporary prohibitions on the introduction of four new polymers containing fluorinated carbon chains based on the toxicological effects of their breakdown products, perfluorocarboxylic acids (PFCAs).

In February 2006, Health and Canada Environment Canada published a position paper "Perfluorinated carboxylic acids (PFCAs) and precursors: A proposed action plan for assessment and management" and a Gazette Notice was published in June 2006 to highlight the effects of PFCAs upon the environment.

In the same year of 2006, Environment Canada released a comprehensive report regarding the concentrations of PFOS in air, water, sediment and biota, and their impact upon the environment and human health. It concluded that PFOS, its salts and its precursors, are entering the environment in a quantity or concentration, or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity.

In 2008, Environment Canada began to regulate and prohibit the manufacture, use, sales and offer for sale and import of PFOS into Canada.

On September 30, 2010, Environment Canada added four new fluorotelomer-based substances to the Canadian Environmental Protection Act, 1999, Toxic Substances Schedule 1 (Canada Gazette Vol. 144, No. 21, 2010).

On October 30, 2010, Environment Canada posted its decision to regulate long-chain perfluorocarboxylic acids (PFCAs) in the Canada Gazette (Vol.144, No. 44) to include perfluorocarboxylic acids (linear or branched) which have the molecular formula $C_nF_{2n+1}CO_2H$ (where $8 \leq n \leq 20$) and their salts be added to Schedule 1 of the Canadian Environmental Protection Act, 1999. The PFCA sub-category includes perfluorooctanoic acid (PFOA, sometimes called C8), other higher homologues, and their salts and precursors. Potential PFCA precursors include chemicals known commercially as fluorotelomers, for example, the fluorotelomer sulphonate 8:2FTS giving rise to PFOA.

UK (United Kingdom)

In 2006, the UK Environment Agency released an interim Policy on the Disposal of Firewater Containing PFOS (Policy No. 32-06, 2006); in this document it highlighted concerns over PFOS being bioaccumulative, persistent and toxic, and said that it should be phased out in fire fighting foams.

In 2007, the UK Environmental Agency published a Policy on the disposal of liquid effluent containing Perfluorooctane Sulphonate (PFOS) providing the following advice and guidelines:

- The UK Environment Agency will use its available powers to prevent, and where this is not possible, to minimise the emissions of PFOS to the environment, and progressively reduce and ultimately phase out the discharge of PFOS to controlled waters.
- The preferred disposal option for liquid effluent containing PFOS is high temperature incineration at 1100°C.
- Groundwater - seek to ensure that the maximum concentration of PFOS in groundwater abstractions used for drinking water remains below 1µg/l, and even where there is no immediate risk to the quality of drinking water sources, and if the concentration of PFOS in groundwater is above 1µg/l, further investigation should be made leading to remedial action to protect the groundwater resource.
- Freshwater – PFOS levels in fresh surface waters should not exceed 1µg/l (annual average) after initial dilution and, where possible, measures should be taken to prevent detectable emissions, and if the PFOS concentration in surface water is above 1µg/l (spot sample) further investigation and the potential need for action to reduce the input by the polluter must be assessed.
- Saltwater – PFOS levels should not exceed 2.5µg/l (annual average) after initial dilution, and if discharges to waters in the vicinity of a designated shellfishery are significant, the Food Standards Agency (FSA) must be notified.
- Discharge to sewer - to progressively reduce and ultimately phase out the discharge of PFOS to sewer.

- Sewage sludge disposal - to progressively reduce and ultimately phase out the release of PFOS to the environment via sewage sludge, and if sewage sludge is spread on the land, the PFOS concentrations should not exceed 39 µg/kg wet weight, or 46 µg/kg dry weight (based on 15% moisture in the soil and mixing of the sludge with the soil) for the protection of soil organisms. If this is breached the sewage sludge should be disposed of by high temperature incineration at 1100°C.
- Air emissions - point source emissions from the incineration of PFOS-containing material should be consistent with the relevant air quality guidelines. Incineration of PFOS will produce hydrogen fluoride and the EPAQS short-term guideline for hydrogen fluoride of 0.2 ppm (0.16 mg/m³) as a 1 hour average should be met⁴. Ash should be disposed of according to the relevant waste criteria. Incineration below 1100°C may not destroy all of the PFOS. A worst case assessment should be made of particulate deposition using estimates of the total PFOS load. If resultant soil deposition rates are likely to approach 15,000µg/m², the UK Environment Agency will assess the risks to human health in consultation with relevant bodies. Care will also be needed to ensure no harm can result from disposal of scrubber wash waters and ash.

In June 2007 the Drinking Water Inspectorate issued revised guidance as to the acceptable levels of PFOS in drinking water. This guidance was based on advice from the Health Protection Agency and is a tiered approach, with thresholds at 0.3, 1 and 9µg/l.

In 2008, the Department of Communities and Local Government (DCLG) published part of the Fire and Rescue Manual in which Chapter 3.7 deals with fire fighting foam. In that chapter, the UK Environment Agency highlighted the following:

- Class A and B foam concentrates have extremely high BOD, and even when diluted to 3–6% solution for use (Class A foam concentrates are usually used at 0.5% w/v dilution or less), will still have a BOD of 50–100 times the strength of untreated sewage. This will lead to de-oxygenation of any receiving water body.
- The surfactants and the other components are acutely toxic to aquatic life in varying degrees and this toxicity is usually but not always of lesser environmental significance than the BOD.
- A particular problem with protein-based foams is their potential to break down into ammonia, which is toxic to aquatic life.
- Concern about PFOS due to its extreme persistence in the environment; additionally it is bioaccumulative and has toxic properties.
- UK is abiding by the EU Directive 2006/122/EC to restrict the marketing and use of PFOS-based foams (see discussion under EU) and also to permit an exemption from the Directive to allow PFOS-based foams that were placed on the market before 27 December 2006 to be used until 27 June 2011.
- The UK government will enact legislation to bring into force the EU Directive which will be enforced by its environment agencies.
- Under current EU and domestic UK legislation there is an absolute prohibition on the discharge of fluorosurfactant-containing foams to groundwater.

⁴ It is technically possible, however, to remove HF from flue gases by scrubbing using CaCO₃ (calcium carbonate) or CaO(H₂O)_n (quicklime) thus producing CaF₂ (calcium fluoride), which is environmentally neutral as it is the original mineral source for the fluorine in fluorochemicals.

- The UK Environment Agency had previously promoted a voluntary ban on the use of PFOS containing foams via its Fire and Rescue Services Circular 40/2006.
- Environmental effects of film-forming foams currently on the market contain non-PFOS-based fluorosurfactants are currently being studied by manufacturers, and the UK Environmental Agency may or may not proceed to make similar controls as for PFOS-containing foams depending on the outcome of their research.
- Due to the high BOD and potential toxicity issues, every effort should be made to prevent fire fighting foam entering surface and groundwater during emergency incidents and always during testing or training activities.
- Although discharge of fire fighting foam or firewater containing foam to a sewage treatment works during an incident can be a viable disposal option, however, suitability of this disposal route will depend on the capacity of the drainage system, the size of the sewage treatment works, the type and volume of foam and the presence of any other pollutants within the firewater or foam solution, as the introduction of foam into a treatment facility may disrupt the biological process and allow untreated sewage and foam into the receiving watercourse. The presence of significant amounts of detergent in the incoming flow will also present physical difficulties to treatment works due to excessive foaming, especially where pumping is necessary.
- Foam used during training events must not be allowed to cause pollution and foam training on open land (unmade ground) may lead to ground or surface water pollution and should be prohibited unless agreed with environment agencies. For these reasons, purpose-made training foams should be used for Class B fire training as they usually have lower BODs and do not contain fluorosurfactants⁵.

⁵ As pointed out in §1.4.3 of Volume 2 of the UK Government's DCLG Fire and Rescue Manual, there has always been a Statutory Defence in the United Kingdom protecting the Fire Service if it causes pollution during operational activities, for example, by discharging foam contaminated fire water run-off. In England and Wales this Statutory Defence under Section 89 of the Water Resources Act (England and Wales) 1991 provides a defence against prosecution based on three criteria, all of which must be in place for the defence to succeed. These criteria are:

- (i) *The entry is caused or permitted, or the discharge is made **in any emergency in order to avoid danger to life or health**;*
- (ii) *That person [the incident commander] takes all steps that are reasonably practicable in the circumstances for minimising the extent of the entry or discharge and of its polluting effects; and*
- (iii) *Particulars of the entry or discharge are furnished to the Environment Agency as soon as reasonably practicable after the entry occurs.*

Similar arrangements that differ in legally detailed wording are in place in Scotland and Northern Ireland. In England and Wales newer legislation - the Environmental Permitting Regulations 2010 - contains similar criteria for a statutory defence against causing pollution in an emergency where human life or health is at risk. Additionally, however, there have also been Memoranda of Understanding (MOUs) and Protocols between the UK Local Government Association (LGA), representing local Fire Authorities, and the UK Environment Agency (such as the 2002 Protocol) outlining the procedures to be followed when foam is discharged at an operational incident, stressing the importance of the criterion "...in any emergency in order to avoid danger to life or health...", as well as the need to inform the Environment Agency of the discharge or entry into controlled waters as soon as reasonably practicable. Notably there is no Statutory Defence for causing pollution of controlled waters as a result of discharging foam for training or maintenance purposes nor indeed operationally if human life or health are not at risk.

Likewise, in Western Australia, there is also a statutory defence as in Section 75 of the Environmental Protection Act 1986 which allows for discharges or emissions in emergencies from premises; however, unlike the situation in the UK "emergency" is not defined in the Act.

UK policy on fire fighting foams with perfluorochemicals is determined by:

- EU Directive 2006/122/EC (see above and discussion under EU).
- Groundwater Regulations 1998 (SI 1998:2746) which prohibits the discharge of organohalogens to groundwater (replaced by the Environmental Permitting Regulations 2010 and the implementation of the EU Water Framework Directive and its Groundwater Daughter Directive, which also require Member States to control or prohibit discharge of organohalogens to groundwater).
- The Water Industry Act 1991 which deals with ‘trade effluent’ discharges to sewer with an offence of discharging without or in breach of consent quality and quantity conditions, with charges which can be levied.

The UK Environmental Permitting Regulations SI 0675 2010 which transpose the EU Groundwater Directive 1980 (80/68/EEC hereafter GWD), the EU Water Framework Directive 2000 (EC/60/2000 WFD) and EU Groundwater Daughter Directive 2006 (EC/118/2006 hereafter GWDD) into UK law under the principle of subsidiarity. The changes from the requirements of the GWD to the GWDD involve a period of transition. This is necessary partly because the GWD remains in force until it is repealed in December 2013 and meanwhile runs in parallel with the new Directive.

- One of the most significant parts of the GWDD as far as fire fighting foams are concerned is contained in Article §6.1(b) in which Member States are obliged to take all measures necessary to prevent the discharge of non-hazardous pollutants to groundwater where concentrations may rise over time, i.e., the pollutant is environmentally persistent, especially for indicative pollutants mentioned in Annex VIII to the WFD. Annex VIII (1) which refers specifically to “...*organohalogen compounds and substances which may form such compounds in the aquatic environment...*”, i.e., all fluorochemicals.

Currently there is no specific restriction, ban or policy on using PFOA containing foams; however, foams containing organofluorine, i.e., fluorosurfactants or fluoropolymers, must not be discharged into the groundwater per the Groundwater Regulations 1998 (SI 1998:2746) which prohibits the discharge of organohalogens to groundwater and in UK fluorine-free foams are supported (*pers.comm.* Roger Harman, UK Environment Agency 2011).

Germany

PFOS import, its use and manufacture are banned and PFOA is not used in German/European fire fighting foams, and the current Germany position on PFCs for fire fighting is as follows:

- Use as little PFCs as possible.
- Not to use PFC foam for training.
- If PFC foam is used, fire fighters must be aware of the environmental consequences and impact.
- To collect and treat fire fighting water contaminated with PFCs.
- PFC-containing foams are allowed to be used only in exceptional cases where there is no alternative (e.g., tank fires).
- Per- and polyfluorinated chemicals replacing PFOS in fire fighting foams are not environmentally friendly alternatives.

Due to the persistent, bioaccumulative and toxic properties of PFOA Germany and Norway are going to submit a proposal to identify PFOA as a substance of very high concern according to the European Chemicals Regulation REACH Art. 57 (c) and (d), to the European Chemicals Agency (ECHA) in January 2013. If the Member State Committee agrees to the proposal PFOA will be taken up into the Candidate List. The inclusion of a substance in the Candidate List obliges the manufacturer or importer to inform the European Chemicals Agency (ECHA) and consumers if products contain more than 0.1 % (w/w) of the substance.

Because of the widely dispersive use of PFOA in numerous consumer products together with low fractions of PFOA in these products (usually less than 0.1%, so that provision of information requirements and obligations on the manufacturers or importers are not met) further measures are necessary.

Subsequently, Germany together with Norway are currently working on a proposal to restrict the EU-wide marketing and use of PFOA which will be submitted to the ECHA in 2013.

Norway

In 2007, the former Norwegian Pollution Control Authority or SFT (now named the Climate and Pollution Agency, KLIF) released a survey of PFOA in Norway which showed that although perfluorinated products are extremely versatile and are used in a variety of industrial and consumer applications and products, some of these perfluorinated products, however, contain or release perfluoroalkyl carboxylic acids (PFCAs), among them perfluorooctanoic acid (PFOA) which has been well documented as being persistent and widely spread in man and the environment (Norway SFT Report TA-2354/2007). Among the polyfluorinated products are PFOA-precursors such as 8:2 FTS or 8:2 FTOH which can degrade to PFOA in the environment. PFOA is a carcinogenic and a reproductive toxicant. It is a national goal in Norway that the discharges of PFOA should be significantly reduced by 2010 and completely eliminated before 2020.

On 23 March 2007, Norway banned PFOS in fire fighting foams by means of its Products Regulation Section 2-9 and EU REACH Annex XVII Entry 53 (which will be replaced by the European POP Regulation, Commission Regulation (EU) No 757/2010). The EU Regulation came into force on 27 June 2008 and also included a ban on textiles and impregnating agents containing PFOS. Norway is co-operating closely with the German Federal Environmental Protection Agency (Umweltbundesamt - UBA) to impose stricter regulations on PFOA (perfluorooctanoic acid), with the aim of banning PFOA impregnation in sports clothes and blankets by 2016 (Chemical Watch, 2011).

Norway has proposed a national ban on PFOA in consumer articles. Norway believes there are no specific legal regulations/total harmonisation requirements in the EEA chemicals regulations for PFOA that hinder their proposed regulation. It is proposed that PFOA should be prohibited in consumer products with an upper limit value of 0.0001 per cent by weight (1 ppm) and 1 microgram per square metre in textiles and coated material, due to concerns that PFOA poses serious human health and environmental risks since it been found everywhere in the environment and in human blood samples around the world. The proposed limit value in textiles will prevent placing textiles containing PFOA on the market.

The Climate and Pollution Agency has an action plan to achieve Norwegian reduction targets for PFOS and PFOA, to continue to map out other perfluorinated substances in order to assess their risks to health and the environment, and to survey the types of perfluorinated substances found on the Norwegian market. The action plan will be revised in 2012 (*pers. comm.* Ingunn Myhre, Climate and Pollution Agency (KLIF formerly SFT) Norway, 2012).

The requirement for incineration of PFOS-containing fire fighting foams is contained in the Norwegian Regulations relating to restrictions on the use of chemicals and other products hazardous to health and the environment (Product Regulations - being updated Jan/Feb 2012). Section (2-9) reads - "*Fire-fighting foam containing PFOS or PFOS-related compounds in a concentration equal to or higher than 0.005 % by weight shall be delivered to an authorised facility for destruction.*"

The Norwegian Government has notified the World Trade Organisation (WTO Notification G/TBT/N/NOR/17/Rev.1) regarding the use of PFOA, and the regulation is still being considered by the Ministry of the Environment. There is no schedule set yet as to when this work will be finished or when the potential regulations will enter into force (*pers. comm.* Henrik H. Eriksen, Deputy Director, Section for Chemicals and Waste, Ministry of the Environment, Norway, 2012)

EFSA – EU Food and Safety Authority

In 2008, the European Union's European Food and Safety Authority published a report – "*PFOS, PFOA, and Their Salts. Scientific Opinion of the Panel on Contaminants in the Food Chain (CONTAM)*" which commented on the levels of PFOS and PFOA found in the human food chain and the associated human health risks. The report highlighted the following:

PFOS:

- Exposure comes from both food and non-food sources and precursors.
- Fish seems to be an important source of human exposure to PFOS; concentrations of PFOS in fish are almost invariably higher than PFOA concentrations and its concentration in liver is consistently higher than those in fillet.
- Shown to bioaccumulate in fish and has a kinetic bioconcentration factor estimated to be in the range 1000 – 4000.
- Drinking water is estimated to contribute less than 0.5% of the indicative exposure.
- Risks more critical for children as the possible pathways of non-food human exposure to PFOS have been estimated to decrease when moving from childhood into adulthood.
- Following absorption, PFOS is only slowly eliminated and therefore accumulates in the body.
- PFOS shows moderate acute toxicity. In subacute and chronic studies the liver was the major target organ and developmental toxicity was also seen.
- PFOS induced liver tumours in rats, apparently due to a non-genotoxic mode of action; however, epidemiological studies in PFOS-exposed workers have not shown convincing evidence of an increased cancer risk.

- The very limited epidemiological data available for the general population do not indicate a risk of reduced birth weight or gestational age.
- Indicative dietary exposure of 60ng/kg /body-weight per day is below the TDI of 150ng/kg body-weight per day but that the most highly exposed people within the general population might slightly exceed this TDI.
- The CONTAM Panel considers it unlikely that adverse effects of PFOS are occurring in the general population.

PFOA:

- Exposure comes from both food and non-food sources and precursors.
- Fish seems to be an important source of human exposure to PFOA. Concentrations are almost invariably lower than PFOS concentrations and PFOA has been shown to bioaccumulate in fish but probably less than for PFOS.
- Like PFOS children are more at risk.
- Drinking water is estimated to contribute less than 16% to the indicative exposure.
- PFOA is readily absorbed and its elimination is dependent on active transport mechanisms which vary between different species and between sexes in some species.
- PFOA shows moderate acute toxicity.
- In sub-acute and chronic studies, PFOA affected primarily the liver and can cause developmental and reproductive toxic effects at relatively low dose levels in experimental animals.
- It increased tumour incidence in rats, mainly in the liver.
- Epidemiological studies in PFOA-exposed workers do not indicate an increased cancer risk.
- The CONTAM Panel established a TDI for PFOA of 1.5µg/kg body-weight per day by applying an overall UF of 200 to the BMDL10, and noted that the indicative human average and high level dietary exposure for PFOA should be 2 and 6ng/kg body-weight per day, respectively, well below the TDI of 1.5µg/kg body-weight per day.
- The CONTAM Panel considered it unlikely that adverse effects of PFOA are occurring in the general population, but noted uncertainties with regards to developmental effects.
- Finally the CONTAM Panel recommended that further data on PFAS levels in food and in humans would be desirable, particularly with respect to monitoring trends in exposure.

European Union (EU)

In December 2005, the European Commission (EC) issued a proposal for a Directive to restrict the use of PFOS in carpets, textiles, clothing and other items.

Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006 amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws,

regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulphonates) and restricted the marketing and use of PFOS-based foams.

The above Directive aims to restrict the marketing and use of PFOS in order to reduce the risks to health and the environment from these substances by setting the following limits:

- PFOS must not be placed on the market or used as a substance or constituent of preparations in a concentration equal to or higher than 0.005% by mass.
- PFOS must not be placed on the market in semi-finished products or articles, or parts thereof, in a concentration equal to or higher than 0.1% by mass calculated with reference to the mass of structurally or microstructurally distinct parts that contain PFOS, or for textiles or other coated materials, if the amount of PFOS is equal to or higher than $1\mu\text{g}/\text{m}^2$ of the coated material.

However, the ban on the use of PFOS did not apply to producers from outside EU. For new products, i.e., depending on national legislation, it is possible for producers to use PFOS for the production process in the country of origin and export their products to the EU but these products will have to comply with the limits regarding the marketing of PFOS and products containing PFOS.

An exemption from the Directive allows PFOS-based foams that were placed on the market before 27 December 2006 to be used until 27 June 2011, i.e., the EU Environment Directive determined that foam concentrate containing PFOS shall not be used or stored after 27 June 2011.

In 2010, the EU released its EU-POP Regulation (EC) 850/2004 whereby it:

- Bans the production, supply and use of PFOS with certain exceptions for use in:
 - Photoresists or anti-reflective coatings for photolithography processes.
 - Photographic coatings applied to films, papers or printing plates.
 - Mist suppressants for non-decorative hard chromium (VI) plating and wetting agents.
 - Hydraulic fluids for aviation.
- Bans the production and supply of PFOS above 0.001 % by weight (10mg/kg) in fire fighting foams.
- Allows no more production of new PFOS fire fighting foam stocks.
- Mandates that any existing stocks cannot be used after 27 June 2011.
- Requires that remaining PFOS foams must be managed as waste and treated.
- The EU has also promulgated certain Directives which contain provisions affecting the way in which any fluorochemicals are used dispersively because they all count as *organohalogen*s, where contamination of the aquatic environment may result. The EU Groundwater Directive 1980 (80/68/EEC hereafter GWD), the EU Water Framework Directive 2000 (EC/60/2000 WFD) and EU Groundwater Daughter Directive 2006 (EC/118/2006 hereafter GWDD) require controls or prohibit discharge to groundwater of organohalogen or substances that can give rise to them by obliging Member States to take all measures necessary to prevent increasing concentrations of pollutants in groundwater. The 1980 GWD remains in force until it is repealed in

December 2013 at which point the new Water Framework Directive (WFD) and its Groundwater Daughter Directive (GWDD) come into force.

- One of the most significant parts of the GWDD as far as fire fighting foams are concerned is contained in Article §6.1(b) in which Member States are obliged to take all measures necessary to prevent the discharge of non-hazardous pollutants to groundwater where concentrations may rise over time, i.e., the pollutant is environmentally persistent, especially for indicative pollutants mentioned in Annex VIII to the WFD. Annex VIII (1) refers specifically to "...organohalogen compounds and substances which may form such compounds in the aquatic environment...", i.e., all fluorochemicals.
- The Groundwater Daughter Directive (GWDD) requires the discharge of non-hazardous but persistent pollutants to bodies of groundwater to be prevented or controlled. The significance of Article §6.1(b) is that persistence, with the risk of increasing concentrations over time, is enough to trigger requirements for control/prohibition of discharge under the Directive – even if the pollutant is non-hazardous, i.e., does not trigger regulatory toxicity or bioaccumulation criteria.

OECD

The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 30 industrialised countries in North America, Europe and the Asia-Pacific region, as well as the European Commission, meets to coordinate and harmonise policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised committees and working groups composed of member countries' delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's workshops and other meetings. Committees and working groups are served by the OECD Secretariat, located in Paris, France.

In 2000, OECD developed a Hazard Assessment of PFOS and Its Salts Report to document information on the environmental and human health hazards of perfluorooctane sulphonate (PFOS). It recommended that perfluorooctane sulphonate (PFOS) warranted further work as sufficient information existed to show that PFOS is persistent, bioaccumulative and toxic to mammalian species.

In 2006, the OECD released the results of the survey on the Production and Use of PFOS, PFOA, PFAS, PFCA, their Related Substances, Chemicals and Products/Mixtures Containing these Substances.

Also in 2006, the OECD held a workshop on PFCs and their precursors as well as publishing a report of an OECD Workshop on Perfluorocarboxylic Acids (PFCAs) and Precursors in 2007 in which a number of key recommendations were made to the OECD, government, industry and end-users, such as adopting a stewardship program to reduce the use of PFCs and their precursors, application of basic principles of Green Chemistry to new product development and further studies such as addressing bioaccumulation and biomagnification potential in wildlife other than fish, as well as studies of toxicokinetics, growth, development, hepatic effects, tumorigenicity and other endpoints.

In 2009 (OECD 2011b), the OECD conducted another survey similar to that done in 2006 and reported a number of key findings in their conclusion such as that the most commonly reported use of products containing perfluorinated chemicals appears to be in the production of water/oil repellent products. No common uses across all study PFC groups were noted except for antireflective coating products for photolithography that used PFOS, PFAS or PFOA products. Related substances were not reported to be used in fire fighting products and very small quantities of perfluorinated chemicals were released to air or water systems compared to landfill or off-site transfer for incineration. It was also recognised that some shorter chain alternatives are persistent, and as more information on toxicity of these chemicals becomes available they could be included in future OECD surveys.

In 2009, the OECD held another workshop in Geneva where participatory countries, industry, environmental groups, intergovernmental organisations and academia explored opportunities to reduce exposure to, as well as making a transition from, perfluorooctyl sulphonate (PFOS), perfluorooctanoic acid (PFOA), PFOS and PFOA precursors and related higher homologue chemicals. The Workshop discussions and key findings are summarised below:

- PFOS and PFOA are globally distributed in the environment and humans and have long half-lives in humans that are measured in years. As a result of changes in manufacturing and use, major reductions in the concentration of PFOS and PFOA in human blood have been measured in the USA and some European countries. There is additional ongoing research to learn more about sources, fate and pathways of exposure to PFCs.
- A dramatic decline in PFOS production volume occurred from 2004-2006; however, volumes of PFCA precursors increased.
- The various stewardship policies of the participating countries aimed at withdrawing PFOS from the market were discussed.
- PFOS alternatives and the transition away from PFOS were discussed by the participants, in particular issues of performance, toxicity, persistence and bioaccumulation in the environment and humans.
- Listing of PFOA on Stockholm Convention Annexes.

Stockholm Convention on Persistent Organic Pollutants (POPs)

In 2001, an international environmental treaty, the Stockholm Convention on Persistent Organic Pollutants, was signed to eliminate or restrict the production and use of persistent organic pollutants (POPs). The Stockholm Convention became effective from May 2004.

In June 2005, Sweden proposed a global ban on PFOS and its related substances and for these compounds to be listed in Annex A to the Stockholm Convention on Persistent Organic Pollutants. Previously, both Sweden and Britain had filed for a national ban on PFOS with the European Commission (EC) and had urged the EC to pursue an EU-wide ban. Consequently, the POPs Committee undertook a risk management evaluation of PFOS and recommended to the Conference of the Parties (COP) of the Stockholm Convention that PFOS acid, its salts and PFOS fluoride, should be listed in either Annex A or Annex B of the Convention.

In May 2009, the Stockholm Convention was amended to ban nine new chemicals, and the production and use of PFOS, its salts and perfluorooctane sulphonyl fluoride (POSF), were restricted under Annex B. This ban came into force on 26 August 2010. Parties to the Convention and observers were invited to submit information on alternatives to the use of perfluorooctane sulphonic acid (PFOS) to the POPs Review Committee by 9 January 2012. Australia as Party to the Convention has yet to ratify the May 2009 Stockholm Convention Annex B as it is still considering its position (*pers. comm.* Director NICNAS, Dr Marion Healy, 2011).

The Stockholm Convention on Persistent Organic Pollutants commits governments to reducing, and where feasible, eliminating the production and environmental release of chemicals that are classified as persistent organic pollutants (POPs). Originally, there were twelve chemicals listed in the Convention: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene, polychlorinated biphenyls, dioxins, furans and hexachlorobenzene (HCB).

Australia ratified the entire Convention and the first 12 chemicals listed in the Convention in May 2004. It is the Australian Government which enters into Treaties on behalf of Australia following appropriate consideration of the impacts by Parliament and relevant ministers. The Australian Government works in partnership with the state and territory governments to implement mutual obligations under the Stockholm Convention.

Perfluorooctane sulphonic acid (PFOS), its salts and perfluorooctane sulphonyl fluoride (POSF) were listed in Annex B of the Convention in 2009. As mentioned above Australia is now considering whether it will ratify the addition of PFOS to the Convention (i.e., whether it will ratify the amendment to the Convention to add these chemicals to Annex B). Perfluorooctanoic acid (PFOA) is a different chemical and is not presently listed in the Convention.

The responsible Australian Government agency for Stockholm Convention matters is the Department of Sustainability, Environment, Water, Population and Communities (DSEWPaC). DSEWPaC is the agency leading the Australian Government's process for consideration of the potential treaty action to add new chemicals such as PFOS.

DSEWPaC has engaged a consultancy firm to undertake work which aims to:

- develop an accurate and up to date profile of the use of PFOS by Australian industry in articles and products and in chemical formulations;
- consider feasible domestic implementation options that could achieve goals around consumption, use and end of life management of PFOS, that are consistent with the requirements of the Stockholm Convention (and assess their likely efficacy); and
- to undertake a cost/benefit analysis (CBA) of the feasible domestic implementation options.

DSEWPaC will use the above information to assist with drafting a regulation impact statement and National Interest Analysis, both of which are required as part of Australia's treaty making processes and which must be tabled before the Joint Standing Committee on Treaties.

State and Territory governments have a crucial role in managing the handling and disposal of PFOS foam and contaminated material. The Australian Government and State and Territory governments will continue to work in partnership in order to implement Australia's obligations under the Convention. In particular, DSEWPaC will work with State and Territory governments to develop suitable options for implementing measures that would enable Australia to meet the requirements of the listing of PFOS in the Stockholm Convention.

United Nations Environment Programme (UNEP)

On February 12-13, 2009, the UNEP hosted an International Workshop on Managing PFCs and Transitioning to Safer Alternatives in order to provide opportunities for reviewing PFC developments since the Organisation for Economic Co-operation and Development (OECD) Workshop on Perfluorocarboxylic Acids (PFCAs) and Precursors in 2006 was convened to discuss risk reduction programs for PFOS, PFOA, PFOS and PFOA precursors, and related higher homologue chemicals and the use of safer alternatives. The workshop was also held in order to discuss mitigating and addressing sufficiently the risks posed by these chemicals and the associated emerging policy issues.

Highlights of the Workshop were as follows:

- There is no known environmental degradation of PFOS and PFOA, which are among the ultimate degradation products of PFOS-related and PFOA-related chemicals, making these chemicals some of the most persistent known. PFOS and PFOA are globally distributed in the environment and humans and have long half-lives in humans that are measured in years.
- Additional ongoing research is needed to learn more about the sources, fate and pathways of exposure to PFCs, as well as to know more about reactive PFC intermediates as regards potential toxicity, to explore the properties of perfluorinated phosphate acids (PFPAs) and other per- and poly-fluorinated chemicals, and for research on degradation of fluorinated polymers.
- Proposals to list PFOS and perfluorooctanesulphonyl fluoride (POSF), the primary intermediate for synthesis of PFOS and PFOS-related substances, under either Annex A or B of the Stockholm Convention to be considered at the Conference in May, 2009 by the Parties.
- Notably feedback showed a dramatic decline in production volume of PFOS from 2004-2006, while volumes of PFCA precursors increased.
- Risk management activities undertaken by a number of governments to reduce the use of PFOS and PFOS-related substances and recognition of exemptions or derogations for certain essential uses where alternatives may not exist, e.g.,
 - USEPA is conducting research on telomer biodegradation, toxicology and pharmacokinetics, as well as analytical techniques.
 - Canada showcased how assessments to date of new notified substances with alternative chemistries showed that these were not suspected to be toxic.
 - Australia showed how safe handling and user information provided in Material Safety Data Sheets (MSDS) and the results of a hazard assessment with

potassium perfluorobutane sulphonate (PFBS), a four-chain length carbon compound, were shared.

- The European Commission reviewed how their current restrictions were being transferred to its REACH regulations and its PFOA risk assessment research programme.
 - Japan has conducted extensive environmental monitoring and added PFOS to its Pollutant Release and Transfer Register (PRTR) for annual reporting.
 - China has experienced increased production of PFOS as a result of cessation of PFOS production in the USA and European markets, and while there is no control for existing substances registered on its inventory, it is implementing EU requirements for PFOS in certain applications.
- Alternatives to PFOS and PFOS-related substances and progress in this area were reported.

United Nation's Economic Commission for Europe (ECE)

With the coming into force of the 1998 Protocol on Persistent Organic Pollutants (POPs) in October 2003, the Executive Body for the Convention established a Task Force on POPs at its twenty-first session in December 2003 which was led by Canada and the Netherlands.

In December 2005, the Parties to the Convention LRTAP Working Group agreed that PFOS should be considered as a persistent organic pollutant (POP) and explored management strategies through its Working Group on Strategies and Review.

In September 2008, parties to the above Working Group in its session on Options for Revising the Protocol on Persistent Organic Pollutants made a number of amendments related to PFOS such as the definitions and exemptions to be included or the several proposed definitions:

- European Union (EU) - PFOS to include the 96 congeners (perfluorooctane sulphonates $C_8F_{17}SO_2X$ ($X=OH$, metal salt, halide, amide or other derivatives including polymers) [in concentrations higher than 0.005 per cent by mass].
- United States - to define PFOS as perfluorooctane sulphonic acid $C_8F_{17}SO_2X$ ($X=OH$, CAS No. 1763-23-1).
- To adhere to the decision of POPRC-3/5 of the Persistent Organic Pollutants Review Committee under the Stockholm Convention pertaining to perfluorooctane sulphonic acid (CAS No. 1763-23-1), its salts and perfluorooctane sulphonyl fluoride (CAS No. 307-35-7), which may be revisited in time with possible changes negotiated under the Stockholm Convention.

Proposals for restricted uses were proposed by the following parties:

EU proposal - exemptions for the following uses and the production related to these uses:

- a. Photo-resists or anti-reflective coatings for photolithography processes;
- b. Photographic coatings applied to films, papers, or printing plates;

- c. Mist suppressants for non-decorative hard chromium (VI) plating and wetting agents for use in controlled electroplating systems;
- d. Hydraulic fluids for aviation; and
- e. Fire fighting foams that have been placed on the market before the ban can be used until 27 June 2011.

(ii) United States (supported by Canada) proposal - exemption for:

- a. Use as an anticorrosion additive in fire-resistant phosphate ester aviation hydraulic fluids;
- b. Use as a component of a photo-resist substance, including a photo acid generator or surfactant, or as a component of an anti-reflective coating, used in a photo-microlithography process to produce semiconductors or similar components of electronic or other miniaturised devices;
- c. Use in coating for surface tension, static discharge, and adhesion control for analogue and digital imaging films, papers, and printing plates, or as a surfactant in mixtures used to process imaging films;
- d. Use as a component of an etchant, including a surfactant or fume suppressant, used in the plating process to produce electronic devices;
- e. Use as a mist/fume suppressant in metal finishing and plating baths, e.g., hard chrome plating, decorative chromium plating, chromic acid anodizing, nickel, cadmium, or lead plating; metal plating on plastics; and alkaline zinc plating; and
- f. Use as an intermediate to produce chemical substances for hydraulic fluids used in aviation, semiconductor manufacturing, and photographic coatings.

(iii) Canadian proposal – exemptions for chromium electroplating, chromium anodizing and reverse etching; electrodes for nickel-polytetrafluoroethylene plating; and etching of plastic substrates prior to their metallisation.

(iv) Norwegian proposal - add conditions that stockpiles of fire fighting foam containing more than 0.005% PFOS by weight to be identified, collected and destroyed.

Restricted uses of PFOS shall be reassessed no later than two years after the entry into force of the Protocol.

Conclusions

From the above review of available literature, information and documents, as well as dialogue with various agencies and organisations in Australia, USA, UK, Norway and Germany, the following conclusions and key findings are made:

1. Perfluorochemicals are not found naturally in the environment and are man-made.
2. Perfluorochemicals are persistent in the environment and do not easily biodegrade due to their stable chemical structure, i.e., due to the strength of the C-F bonding making this class of chemicals environmentally extremely persistent. Once PFOS is present in the environment it does not undergo any further chemical, microbial or photolytic degradation or breakdown, but PFOS precursors can degrade to PFOS in the environment. Once PFOA is in the environment it is persistent and not known to undergo any further abiotic or biotic degradation under relevant environmental conditions.
3. Many perfluorochemicals are bioaccumulative in both terrestrial and aquatic biota and humans.
4. Perfluorochemicals have both acute and chronic impact upon both aquatic and terrestrial biota and humans. Effects upon biota include pathological and histopathological effects including hepatocellular effects. Perfluorochemicals have been detected in humans; however, according to the USEPA significant adverse effects have not been found to date in the general human population but due to the long half-life of these chemicals in humans (years), the USEPA anticipates that continued exposure could increase body burdens to levels that would result in adverse outcomes. Given that human biomonitoring data have demonstrated that evidence of PFC exposure in humans is found *in utero*, during infancy, and during puberty, and that animal studies have shown that the foetus and neonate are sensitive life stages for PFC exposure, the USEPA will also consider further effects to the developing foetus and children. The USEPA believes that PFOA is "likely to be carcinogenic to humans" and that further information is still required to categorise it as a carcinogen.
5. Alternatives to fire fighting foams with fluorochemicals such as fluorine-free fire fighting foams are now commercially available on the market and are in their 3rd or 4th generation.
6. Formulations containing pure short chain C6 fluorotelomers are now being developed for use in fire fighting foams to replace fluorochemicals such as PFOS and to limit the possibility of fluorotelomer degradation yielding perfluorocarboxylic acids such as PFOA and higher homologues. Current data indicate that C6-fluorotelomer breakdown products are of relatively low toxicity and bioaccumulative potential.
7. Canada, all EU Member States led by UK, Norway and Germany, have taken measures to phase out PFCs used in fire fighting foams by banning the production, importation, use and storage of PFOS-based products as from 27 June 2011. However, PFAS compounds in AFFF are still being used in the USA. The manufacture and import of new PFOS-based surfactants is no longer permitted in the USA. Except for any existing stocks, the fire-fighting industry in USA has fully transitioned to non-PFOS alternatives and is working on improving control measures to limit environmental releases after application. Furthermore there is a transition underway to shorter chain derivatives for many products (see above) in response to the US EPA PFOA Stewardship Program.
8. Various countries have taken steps to restrict the use of PFOA. Norway and Germany are moving to restrict the use of PFOA by legislation in 2012. Environment Canada decided to regulate PFCAs including perfluorocarboxylic acids (linear or branched)

and their salts, by adding them to Schedule 1 of the Canadian Environmental Protection Act, 1999. The PFCA sub-category includes perfluorooctanoic acid (PFOA, sometimes called C8), other higher homologues, and their salts and precursors. Some of the potential PFCA precursors include fluorotelomers. In the USA, the USEPA has taken steps to further investigate PFOA and related chemicals as well as to reduce their emissions and use in products. However, given the scientific uncertainties, the USEPA has not yet made a determination as to whether PFOA poses an unreasonable risk to the public, and there are no steps that the USEPA currently recommends that consumers should take to reduce exposure to PFOA. In Australia both Commonwealth and State agencies have not yet made any move to restrict or to legislate against the use of PFOS and PFOA other than to forewarn of its impact upon the environment and humans. In 2009, PFOA was added to Annex B of the UN Stockholm Convention; however, Australia has yet to ratify the Stockholm Convention as a signatory party.

9. Some agencies in Australia have moved away from using fire fighting foams with fluorochemicals such as Airservices Australia, the Metropolitan Fire Board Victoria and the Queensland Fire and Rescue Service.
10. Many agencies overseas have clear policies which encourage or mandate the non-use of fire fighting foams containing fluorochemicals, such as the national authorities in the UK, Norway and Germany.
11. Many agencies forbid the use of fire fighting foams containing fluorochemicals for training purposes, requiring special "training" foams to be used. Also fire fighting foams with fluorochemicals must not be discharged into the environment causing pollution, e.g., in UK the Environment Agency instructs fire services that fire fighting foams used during training must not be discharged to the environment. This policy has also been adopted in Australia by the Australian Department of Defence. In Germany the policy is not to use fire fighting foams containing PFCs.
12. The Queensland Department of Environment and Heritage Protection would be the first environmental department in Australia to have a formal written policy not to allow fluorinated foams containing bio-accumulating persistent organic pollutants (POPs) as defined under the Stockholm Convention to be released to the environment and to demand that foam-contaminated run-off must be contained and disposed of properly.

Recommendations

Based upon the above conclusions and findings the following recommendations are proposed:

1. Choice of Foams

If practical, and for best environmental practice, the preferred choice of fire fighting foam should not contain fluorochemicals. However, it must be stressed that any fire fighting foam chosen for operational use must be “fit-for-purpose”, preferably having been tested by the end-user as part of due diligence during the procurement process, and must have relevant recognised approvals or certifications such as UL162, EN1568, ICAO level A/B/C, etc. Some agencies in Australia have already implemented policies to reduce the use of fire fighting foams containing fluorochemicals, e.g., Airservices Australia and the Australian Department of Defence advocate the use of more environmentally friendly fire fighting foams and also aim to minimise the use of AFFF preferring its use only for certain ARFF purposes, whilst the Victorian MFB Melbourne and Queensland FRS are now using fluorine-free fire fighting foams.

2. PFOS and PFOA

Fire fighting foams containing PFOS should no longer be used for the reasons of bioaccumulation, persistence and toxicity and high BOD; the holding of stocks or use of these fire fighting foams has already been banned in a number of countries, especially in the European Union, such as the UK, Norway and Germany. New production or importation of PFOS-based foams is not permitted in the USA. Australia does not yet have legislation or regulations to restrict their use and has so far only issued warnings about the impact upon the environment and human health via agencies such as NICNAS. Only a few agencies in Australia have categorical written statements or policies advising that PFOS should no longer be used in fire fighting foams, e.g., the Australian Department of Defence categorically states in its Aqueous Film Forming Foam (AFFF) Procurement and Use Interim Policy. Version 1 - August 2008 that suppliers of fire fighting foams must not have PFOS, PFAS or PFOA surfactants present in the foam.

3. Fluorotelomers (mainly 6:2 FTS)

The US EPA is not particularly concerned with fluorotelomer fluorosurfactants, in particular those based on 6:2 FTS, as these eventually partly degrade to PFHxA (perfluorohexanoic acid) and PFPeA (perfluoropentanoic acid), which are of low toxicity, low biopersistence and are not bioaccumulative. However, as research is still being carried out on the impact of fluorotelomers, the use of fire fighting foams containing fluorotelomers and their manner of application must be considered in order to reduce unnecessary impact upon the environment and the human population to ALARP levels. Although available research has shown that these materials have low toxicity and bioaccumulative potential, their environmental acceptability should not only be based upon acute toxicity testing but also based upon bioaccumulation in fauna and the persistence of degradation products in the environment as well as any BOD/COD related effects upon the aquatic environment, which are significant for any foam.

4. Fluorine-free Foam

Although fluorine-free fire fighting foams do not contain fluorochemicals, their environmental acceptability should not be only based upon acute toxicity testing but also based upon any possible bioaccumulation in fauna, persistence in the environment and BOD/COD effects upon the aquatic environment; although in this case bioaccumulation and persistence are unlikely to be significant unless unusual additives are present.

5. Other synthetic foams

Their use in Western Australia should only be approved after further environmental testing (see discussion below).

6. Environmental Testing

As discussed above there needs to be a holistic approach to testing fire fighting foams for these to be considered environmentally acceptable, and not just based upon acute toxicity measurements. Hence fire fighting foams should be tested for the following to determine their overall impact upon the environment.

- Bioaccumulation
- Persistence
- Toxicity (acute and chronic)
- BOD/COD

The above holistic approach criteria would allow approving agencies and users to better determine environmental acceptability of fire fighting foams and to gauge both the short and long term environmental effects.

It must be emphasised that all of the ingredients making up a fire fighting foam and not only the fluorochemical components must be environmentally acceptable. It is also important to test and evaluate fire fighting foams not only for the neat product, i.e., the foam concentrate, but also to consider all the ingredients which may have the potential to cause adverse or unacceptable environmental impacts.

Appropriate testing standards and methodologies such as those accepted and recognised in Australia, the USA, Canada and OECD countries should be adopted when assessing and determining environmental acceptability for the use of fire fighting foams and should be conducted by an independent laboratory or organisation.

6.1 Bioaccumulation and Persistence

Fire fighting foam Material Safety Data Sheets (MSDS) must include bioaccumulation and environmental persistence data derived from accepted and recognised best practice using Australian, USEPA or OECD methods or tests conducted by an internationally certified test

house laboratory in order to demonstrate that the fire fighting foams have ALARP bioaccumulation and persistence risks to the environment.

6.2 Toxicity

Toxicity testing should be conducted against standards and methodologies such as those accepted and recognised in Australia, the USA, Canada and OECD, by an independent laboratory or organisation. Australian or test species equivalent should include fresh water and marine test species, for example:

a 48hr acute (immobilisation) test using a freshwater species, e.g., the daphnid *Ceriodaphnia dubia* (using USEPA 2002 method) or Australian or equivalent test species;

72-hr micro-algal growth inhibition (cell yield) tests using, e.g., freshwater alga *Selenastrum capricornutum* (using USEPA Method 1003.0) or Australian or equivalent test species;

96-h fish imbalance tests using a freshwater fish species, e.g., Rainbow fish *Melanotaenia splendida splendida* (based on OECD Method 203) or Australian or equivalent test species;

72-h micro-algal growth inhibition tests using *Isochrysis aff. galbana* or *Nitzschia closterium* (based on USEPA Method 1003.0 and Stauber *et. al.* 1996 for the National Pulp Mills Research Program) or Australian or equivalent test species;

96-hour acute toxicity tests using juvenile tiger prawn *Penaeus monodon* (based on USEPA OPPTS 850.1045), or the amphipod *Melita plumulosa* should tiger prawns not be available or Australian or equivalent test species;

96-hr fish Imbalance tests with larval marine fish (species depending on availability) (based on USEPA 1993 and OECD Method 203) or Australian or equivalent test species.

6.3 BOD/COD

Fire fighting foam MSDSs must provide BOD/COD data using accepted and recognised best practice Australian, USEPA or OECD methods with measurements made by an internationally accredited test house laboratory with suitable quality control protocols in place (original certificates to be provided) to show that the fire fighting foams have ALARP risk to the environment.

7 Fire Fighting Training

Following general practice by various agencies in Australia and overseas (see above discussion under Current Legislation and Policy) foams with perfluorochemicals (including fluorotelomers) should not be used. If any foams, including training foams, are used for training or maintenance purposes, the fire-water run-off must be fully contained and not be discharged into the environment (e.g., water bodies, creeks, soils, etc.); spent fire fighting foams containing fluorochemicals must be disposed of at approved treatment facilities or premises (note: this is not the preferred option).

8 Operational Use during Fire Fighting

If fire fighting foams containing perfluorochemicals including fluorotelomers are used during fire fighting, foam-contaminated run-off water must not be discharged to the environment but must be contained or confined by bunding or other means followed by cleanup (if at all possible given operational circumstances at the incident), and removed as soon as possible to prevent it affecting environmental targets such as biota, water bodies, creeks, soils, etc.

As discussed in the above review of the use of fire fighting foams with fluorochemicals, the common recommended management requirements are as follows:

- Must be managed so that these are NOT released into the environment, to prevent land, air and water pollution, during all stages of the lifecycle;
- Must NOT be allowed to enter stormwater or sewerage.

If fire fighting foams containing fluorochemicals have to be used under those circumstances exempted in the USA and OECD countries (as discussed above in Current Legislation and Policy) and there are clear, defensible and credible safety reasons for their use, the fire fighting water run-off must not be allowed to enter the environment but must be fully contained, confined and disposed of at approved treatment facilities or premises. Enforcing authorities often permit the uncontained use of fire fighting foam under emergency conditions defined as when human life or health is to be protected but not otherwise.

9. Containment, Confinement, Disposal and Treatment

Fire fighting foams and run-off water contaminated with fluorochemicals must be contained, confined and appropriately disposed of and treated (such as by thermal incineration if deemed suitable and appropriate) in accordance with required legislation and regulations.

As currently there are no landfill acceptance criteria or contamination assessment trigger values for fluorochemicals (such as PFOS, PFOA and fluorotelomer 6:2 FTS) in Australia, it is recommended that in the interim the USEPA and the Minnesota Department of Health guidelines for water quality and contamination screening for groundwater and soil be adopted.

Glossary

ALARP

As low as reasonably practical.

Bioconcentration

Is defined as the process leading to a higher concentration of a substance in an organism than in the environmental media to which it is exposed (after WHO, 1979) - International Union of Pure and Applied Chemistry, 1993.

Bioconcentration factor (BCF)

Is defined as the ratio of a contaminant concentration in biota to its concentration in the surrounding medium (water). At long exposure times (equilibrium), the BCF also equals the ratio of the uptake constants (Mackay, 1982; Nowell et. al., 1999).

Bioaccumulation

Is defined as the accumulation of chemicals in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, and pore water in the sediment – US Environmental Protection Agency, 2000;

or as:

the progressive increase in the amount of a substance in an organism or part of an organism which occurs because the rate of intake exceeds the organism's ability to remove the substance from the body – International Union of Pure And Applied Chemistry, 1993.

Bioaccumulation Factor (BAF)

Is defined as the ratio of the contaminant in an organism to the concentration in the ambient environment at a steady state, where the organism can take in the contaminant through ingestion with its food [*all possible routes of exposure - dietary, dermal, respiratory*] as well as through direct contact – US Environmental Protection Agency, 2010.

Biomagnification

Biomagnification (also known as Trophic Magnification) is the process by which chemical concentrations increase with trophic level in a food chain and results from the trophic level transfer of a chemical through the diet from a lower to a higher trophic level.

Fluorochemical

A general non-specific term used to describe broadly all organic chemicals containing the element fluorine and carbon; specifically, the term is used most commonly to describe small (1-8 carbon length) fluorinated molecules which are most often used for refrigeration, as fire suppression agents and as specialty solvents. Some fluorochemicals are potential precursors for PFOA, PFOS, PFCAs and/or PFASs.

Fully fluorinated (or perfluorinated)

A fully fluorinated or perfluorinated chemical is one in which all the carbon-hydrogen bonds in a chain have been replaced by carbon-fluorine ones. All fully fluorinated chemicals are man-made. Examples include perfluorooctanoic acid (PFOA) and perfluorooctane sulphonate (PFOS).

Fluorinated chemical

A general, non-specific, term used synonymously with fluorochemical.

Fluorotelomer alcohol

A general term which describes a class of alcohols of general structure, for example, $F(CF_2CF_2)_nCH_2CH_2OH$, where n is an integer.

Fluorinated (organic) polymer

A general term used to describe a polymer which has a hydrocarbon backbone (polyamide, polyester, polyurethane, etc.) to which is appended a fluorinated carbon chain, also known as a fluorinated alkyl chain; an example would be a polymer such as $-[CH_2CH(C(O)OCH_2CH_2(CF_2)_8F)]_n-$.

Fluorinated (organic) surfactant

A term to describe a surface-active, low molecular weight (MW <1000) substance which contains fluorinated carbons; the term Fluorosurfactant is non-specific but often used synonymously; an example is $F(CF_2)_6CH_2CH_2SO_3-NH_4+$.

Fluoropolymer

A term which describes a highly fluorinated polymer made by joining together monomers containing fluorinated carbon chains. PFOA is currently used in the manufacturing process for most fluoropolymers. Examples of fluoropolymers include DuPont Teflon® brand non-stick coatings on cookware; the membranes that make Gore-Tex® waterproof, breathable clothing; fire-resistant casings for plenum cable; fire and chemical-resistant tubing; and plumbing thread sealant tape.

Fluorotelomer

See telomer.

Fluorosurfactant

A non-specific, general term used to describe a surface-active, low molecular weight (MW <1000) substance in which carbon atoms bear fluorine in place of hydrogen.

PFAS - perfluoroalkyl sulphonate.

PFAC - perfluoroalkyl carboxylates: synonymous with PFCA.

PFBA – perfluorobutanoate.

PFBS - perfluorobutane sulphonate.

PFCs – perfluorochemicals.

PFCA- perfluoroalkyl carboxylic acids and synonymous with PFAC.

PFOA - perfluorooctanoic acid.

PFOS – perfluorooctane sulphonate.

POPS - persistent organic pollutants.

Perfluorochemicals (PFCs)

Are a family of man-made chemicals that have been used for decades to make products that resist heat, oil, stains, grease and water. Common uses include non-stick cookware, stain-resistant carpets and fabrics, coatings on some food packaging (especially microwave popcorn bags and fast food wrappers), as components of fire-fighting foam, and some industrial applications. Some of the chemicals in the PFC group are perfluorooctane sulphonate (PFOS; $C_8F_{17}SO_3^-$), perfluorobutane sulphonate (PFBS; $C_4F_9SO_3^-$), perfluorooctanoic acid (PFOA; $C_7F_{15}CO_2H$), perfluorobutanoic acid (PFBA; $C_3F_7CO_2H$), and perfluorohexane sulphonate (PFHxS; $C_6F_{13}SO_3^-$). The chemical structures of PFCs make them extremely resistant to breakdown in the environment. Perfluorochemicals as a class of compounds include all fluorinated chemical substances containing a perfluorinated moiety anywhere within the molecule, for example, N-methyl-perfluorooctanesulphamidoethanol (N-Me-FOSE), 6:2 fluorotelomer sulphonate (6:2 FTS), or fluoropolymers. The fluorotelomer fluorosurfactants 1157 and 1183 are classified by the manufacturer as perfluoroalkyl betaines and amine oxides, respectively.

Precursor

A chemical which can be transformed to produce another chemical. For example, some residual monomer chemicals from the telomer manufacturing process, such as telomer alcohols and telomer iodides, are PFOA precursors because they may remain in the final product and can be transformed into PFOA.

REACH

Registration, Evaluation, Authorisation and Restriction of Chemical substances is a European Community Regulation on chemicals and their safe use (EC 1907/2006). The law entered into force on 1 June 2007.

Telomer (or Fluorotelomer)

A fluorinated compound produced by a specific polymer-making process called telomerisation. Fluorotelomers consist of a perfluorinated (i.e., perfluoroalkyl) moiety, usually C6 or C8, terminated by a CH_2-CH_2 group. Telomers are not technically perfluorinated because not all of the carbon-hydrogen bonds are replaced with carbon-fluorine ones: the telomer terminates in a CH_2CH_2 group. Most telomers are relatively small polymers and are used in surface treatment products to impart soil, stain, grease and water resistance to carpets, textiles, paper, stone and leather. Some are used as high performance surfactants in products that must flow evenly, such as paints, coatings, cleaning products, fire-fighting foams for use on liquid fuel fires, or the extremely thin engineering coatings used in semiconductor manufacture.

Go to USEPA glossary at <http://epa.gov/oppt/pfoa/pubs/glossary.html> for other terms.

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