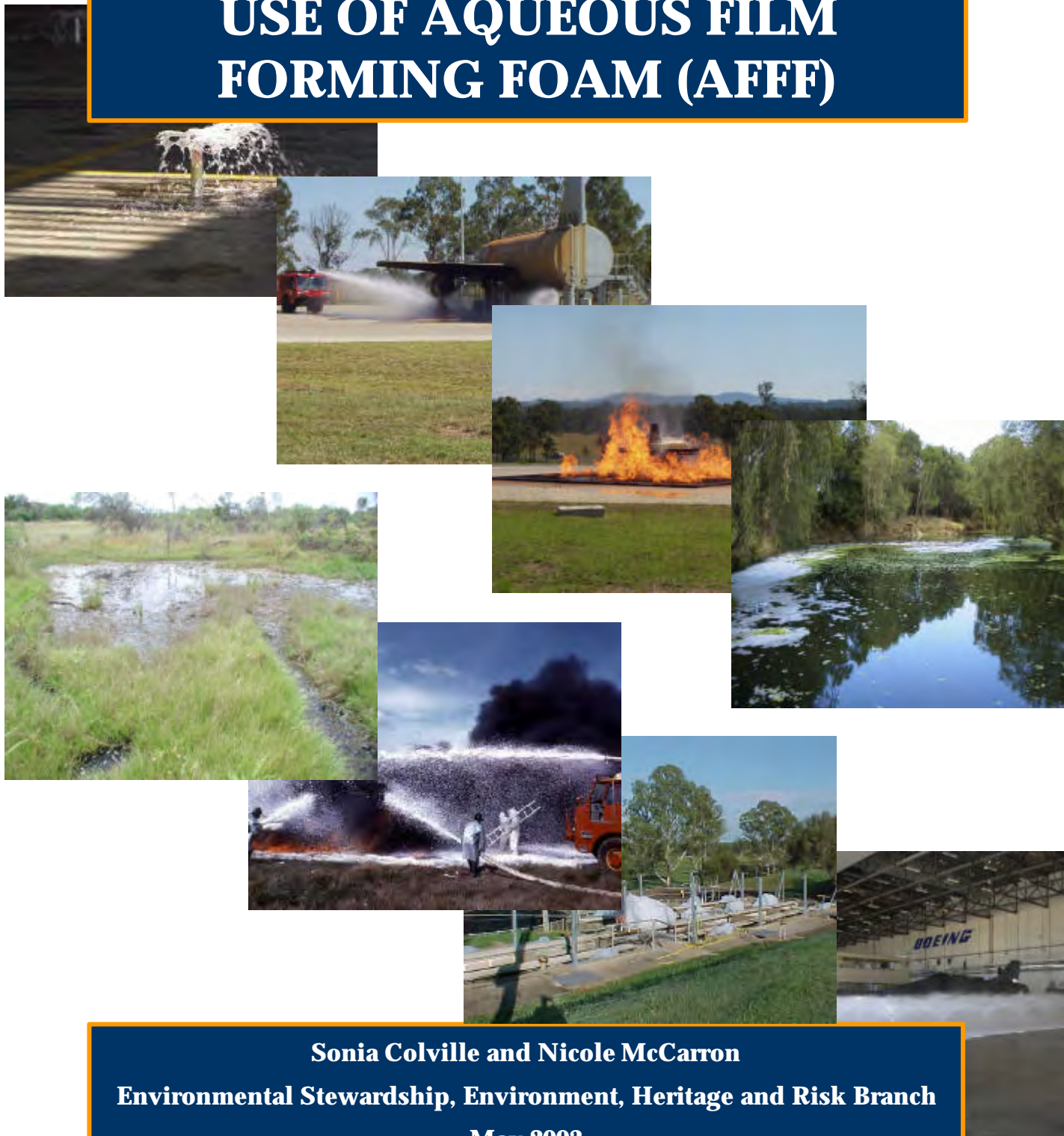


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ENVIRONMENTAL ISSUES ASSOCIATED WITH DEFENCE USE OF AQUEOUS FILM FORMING FOAM (AFFF)



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May 2003

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Executive Summary

The purpose of this report is to provide a general overview of environmental issues associated with Defence use of Aqueous Film Forming Foam (AFFF).

Fire fighting foams, such as AFFF, are used primarily to control fires involving flammable liquids such as fuel and oil. AFFF suppresses fire by producing a film over the fuel/oil fire that effectively starves the fire of oxygen. Defence uses AFFF across many of its facilities (e.g. hangars, fuel farms, ships, crash crews), in fire control systems, the testing and maintenance of these systems, and in fire fighting training.

In many cases the AFFF foam solution is discharged to sewage system or to a holding tank under controlled conditions without incident. However, pollution incidents have occurred across Defence establishments as a result of unintentional foam discharges (e.g. accidental spillage or leaks), and intentional foam discharges (e.g. fire fighting equipment testing and training). Some of the AFFF related environmental incidents across Defence include the contamination of stormwater drainage systems and off-site contamination of local streams and dams resulting in fish kills (Figure 1, URS, 2002, pers. com. Defence personnel; Defence AFFF survey results). Because of the propensity for AFFF to foam (as designed) the pollution of waterways is highly visible. In addition to environmental harm, such obvious pollution incidents have the potential to seriously damage Defence's reputation as an environmental manager and good corporate citizen.



Figure 1. Accidental release of AFFF foam waste-water into a watercourse is a known environmental hazard (near RAAF Amberley, Queensland).

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Defence currently uses the AFFF product manufactured by the 3M company. Although there are general environmental issues associated with most fighting foam use (e.g. it's ability to deplete oxygen in aquatic environments causing fish kills), researchers have also recently identified some specific environmental concerns associated with the use of AFFF manufactured by the 3M Company (3M 2001a; OECD 2002). This AFFF product has been found to contain non-biodegradable fluorosurfactants that are environmentally persistent (does not break down), bioaccumulative (accumulates in living tissue) and toxic (EPA 2001; OECD 2002). A number of case studies in the literature indicate that the repeated usage of AFFF at sites where discharge has been inappropriately contained and disposed of, has lead to the contamination of soil, groundwater, and surface waters (Levine et al. 1997; Moody & Field 1999; Moody & Field 2000; OECD 2002). Furthermore, these fluorosurfactants have not only been found to bioaccumulate in fish and mammals, but also in humans (OECD 2002; USEPA 2003). Due to environmental concerns, 3M will discontinue the production of this AFFF product in 2003 (3M 2003; Schaefer 2002), and any users of this product, such as Defence, will need to determine a suitable replacement product. Currently, Defence Materiel Organisation (DMO) is developing a new DEF(AUST) standard for the replacement AFFF product, in which the environmental aspects of product use and stewardship will be addressed. Until a suitable product has been identified some interim measures may need to be undertaken to minimise the release of AFFF to the environment, such as in restricting AFFF use for essential purposes only.

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Table of abbreviations

3M – 3M Company Incorporated (producers of AFFF used by Defence)
AFFF - Aqueous Film Forming Foam
AFFF-AR – Alcohol Resistant Aqueous Film Forming Foam
ASH – Air-Sparged Hydrocyclone System
BOD – Biological Oxygen in Demand
COD – Chemical Oxygen in Demand
DFFEC - Defence Fire Fighting and Equipment Committee
DMO – Defence Materiel Organisation
EC₅₀ – Concentration Effecting 50% of the test population
EPA – Environment Protection Agency
FFFP - Film Forming Fluoroprotein Foam
FFFP-AR - Alcohol Resistant Film Forming Fluoroprotein Foam
FP – Fluoroprotein Foam
HMFSI - HM Fire Service Inspectorate
LC₅₀ – Lethal Concentration killing 50% of the test population
MPFE – Manual of Fire Protection Engineering
MSDS – Material Safety Data Sheet
NFESC - Naval Facilities Engineering Service Centre, US Defense
NICNAS – National Industrial Chemical Notification and Assessment Scheme
NOSCH –National Occupation Health and Safety Commission
OECD – Organisation for Economic Co-operation and Development
PFOS – Perfluorooctane Sulfonate
PFOA - Perfluorooctanoic Acid
S – Synthetic Detergent

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Key Findings

The key findings of this investigation are:

1. Defence uses Aqueous Film Forming Foam (AFFF) product produced by the 3M company. This AFFF product contains non-biodegradable fluorosurfactants (specifically perfluorooctane sulfonate (PFOS) and perfluorooctanic acid (PFOA)) that are environmentally persistent, bioaccumulative and toxic to animals and humans. Both PFOS and PFOA have been implicated with a variety of cancers and toxic health effects in humans that have had long term exposure to products containing PFOS/PFOA. 3M are ceasing the production of this AFFF product in 2003, and Defence will have to source an alternative product. Appropriate drainage, containment and disposal of foam waste-water will still be required for any replacement foam product. (p.20)
2. Current Defence AFFF use and waste management practices are inconsistent and generally fall below the best practice of other national and international organisations. (p.40,44)
3. Across many Defence facilities AFFF waste-water is not appropriately collected or disposed of. Based on these past and current practices there is a risk that PFOS/PFOA has contaminated Defence land as well as neighbouring properties, creeks, dams, and reservoirs. (p.44)
4. There is no Australian Regulatory Actions in place that specifically encompass the use and disposal of products containing PFOS/PFOA, although regulations are currently being developed by the Australian National Industrial Chemical Notification and Assessment (NICNAS). (p.27)
5. On 30th April 2003, NICNAS released an alert recommending that PFOS/PFOA products such as AFFF be restricted to essential use only, and that AFFF foam should not be used for fire training/testing purposes (p. 20,45).
6. Defence Materiel Organisation (DMO) are currently producing new DEF(AUST) standards in anticipation of a replacement AFFF product. AFFF waste-water handling in Defence is also currently being reviewed for the next amendment of the Manual for Fire Protection Engineering (MFPE). The findings in this report are being considered as a part of the MFPE review process (p. 45).

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Key Recommendations

The key recommendations in this report are:

1. Defence should aim to meet the best practice of AFFF management methods used by other national and international organisations. (p.28,45)
2. Defence will need to revise it's AFFF practices (use/handling/disposal) and update its infrastructure to appropriately manage AFFF waste-water. (p.45)
3. Defence should take appropriate measures to ensure that fire fighting foam concentrate/foam solution/waste-water is not disposed of on soil or grass, and does not reach streams, creeks, wetlands, dams, groundwater or storm-water drains. (p.13)
4. A more comprehensive study may be necessary to identify and assess Defence site-specific environmental risks and personnel health effects relating to AFFF use and management. (p.20,41)
5. If environmental and health risks are to be minimised, the AFFF replacement product should not contain PFOS/PFOA. Until a suitable product has been identified some interim measures may need to be undertaken to minimise the release of AFFF that contains PFOS/PFOA to the environment. Where no adequate containment of AFFF is available, AFFF use should be restricted. (p.45)

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1. Introduction

This report was conducted as a part of a Graduate rotation with the Environmental Stewardship Directorate within Corporate Services and Infrastructure. This report addresses some of the environmental issues resulting from the use and management of Aqueous Film Forming Foam (AFFF). The investigation was limited to the review of reports and literature, communications with relevant Defence personnel, communications with outside organisations that use AFFF, Defence AFFF survey results, and visual observations. The report provides a general overview of Defence AFFF use and management. This is not an exhaustive review of the fire fighting capability or environmental issues associated with each fire fighting foam product available.

The Defence Environmental Strategic Plan 2002-2005 is built around the vision that “Defence will be a leader in sustainable environmental management to support Australian Defence Force capability to defend Australia and its national interests”. This strategic plan also emphasises that environmental management in Defence is the responsibility of all personnel, both ADF and civilians, and that Defence must comply with Commonwealth environmental legislation, particularly the *Environment Protection and Biodiversity Conservation Act 1999* (EPBC Act). Bound by the EPBC Act, Defence needs to consider whether any activity could be an action that has, will have, or is likely to have a significant impact on the environment, with the aim of minimising environmental risks (section 28).

The use and accidental or intentional release of Aqueous Film Forming Foam (AFFF) onto soil and grass, into stormwater drains, creeks, and dams has the potential to cause significant environmental impact. AFFF is used in fire suppression systems and equipment in hangars, ships, submarines, fuel farms, and on crash crew vehicles. AFFF foam is regularly released during the testing of fire fighting systems and equipment, and during fire fighting training. Environmental concerns about the possible uncontrolled and inappropriate use and management of AFFF during equipment testing and fire fighting training lead to the tasking of this report. A number of environmental incidents involving the release of AFFF and off-site contamination of local streams and dams resulting in fish kills have been reported.

AFFF products not only deplete oxygen from aquatic environments causing fish kills, but the AFFF product used by Defence has also been found to

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contain fluorosurfactants that are environmentally persistent, bioaccumulative and toxic to animals and humans. The environmental and health concerns associated with the fluorosurfactants heightens the need for Defence to identify and improve on current AFFF management practices, and mitigate environmental and health risks associated with these practices.

The AFFF product currently used by Defence is being taken off the market, so there is a need for Defence to determine a suitable replacement product. A part of this product replacement process is acknowledging that there is a need for Defence to use an effective fire fighting product that saves lives and property, whilst considering the environmental and health risks.

With the above in mind, and in line with the scope of the investigation, this report aims to:

- Identify the potential environmental issues associated with the use of fire fighting foams, particularly those associated with the use of AFFF.
- Identify potential health and safety issues.
- Identify best practice in managing AFFF use and minimising environmental contamination by AFFF waste-water.
- Identify areas across Defence that use AFFF, and how AFFF waste-water is managed, contained and disposed of.

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2. Fire fighting foams, environmental and health issues

2.1 Fire fighting foams

Fire fighting foams have been developed primarily to control hazards posed by liquid fuel fires (Figure 2.1). The bubbles formed by fire fighting foam solution forms a blanket that floats on the surface of flammable liquids, suppressing the release of vapour and suffocating the fire, and cooling the fuel surface (Figure 2.2).



Figure 2.1. Crash crew extinguishing fire using fire fighting foam (source: RAAF Image Gallery)



Figure 2.2. Activated AFFF foam sprinkler system test forming a foam blanket on the hangar floor.

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Foams are supplied as concentrates, which must be mixed with water to form the 'foam solution'. Foam solution usually contains 6%, 3% or 1% of the concentrated foam product. The percentage values indicate the dilution factor required to make the 'foam solution'. For example to make 100 litres of 'foam solution' you can either mix three litres of 3% AFFF concentrate with 97 litres water, or you can mix six litres of 6% concentrate to 94 litres water. This foam solution is then passed through specialised foam fire fighting equipment that mixes air into the foam solution. The mix of foam concentrate, water and air creates the 'finished' fire fighting foam solution that is used to fight fires. The performance of the 'finished' fire fighting foams depends on the foam-making equipment, type of foam concentrate, the type of fire and fuel involved, tactic of foam application, rate of foam application, the quality of water used to mix with the foam concentrate, and length of pre-burn (HMFSI 2000).

Foams are generally classed into either protein based foams or synthetic based foams. Both protein based and synthetic based foams are used on fires that involve flammable liquids, liquidizable solids, oils, greases, tars, oil based paint and lacquers (Class B fires). Both foam types can also be used to assist in the extinction of fires that involve solid materials usually of an organic nature such as wood, cloth, paper, rubber, and many plastics (Class A fires).

Protein foam (P) concentrate is generally made from plant or animal matter with other chemical additives for stability, freeze protection, corrosion prevention, and protection from bacterial decomposition. Protein foam needs to be sprayed to cover the fuel surface (Hague 2002). Fluoro-protein Foam (FP), Film Forming Fluoroprotein Foam (FFFP) and Alcohol Resistant FFFP (FFFP-AR) concentrates are similar to protein foam but they have a fluorinated surfactant additive, which allows them to form a thin film by spreading quickly across the surface of the fuel to prevent formation of vapour (Hague 2002). Alcohol resistant foam concentrate is used to protect water-soluble fuels or other fuels that destroy FFFP or AFFF (Hague 2002).

Synthetic based foams include Aqueous Film Forming Foam (AFFF), Alcohol Resistant AFFF (AFFF-AR), and synthetic detergent (S). The synthetic foam concentrates are based on fluorinated surfactants that allow it to spread quickly across the fuel surface to form a thin vapour suppressing layer (Hague 2002).

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There are a number of companies that manufacture these foams (e.g. 3M, Ansul, Angus Fire, Orion, Chemguard). The quality of these fire fighting foams vary from manufacturer to manufacturer. The quality of a single foam product from the manufacturer, can also vary. The specific formulations of these fire fighting foams are usually not known outside the companies that produce them (Moody & Field 1999).

2.1.1 Aqueous Film Forming Foam (AFFF) – a synthetic foam

AFFF foams are among the most popular fire fighting foams used to suppress fuel and oil fires because of their effectiveness and ease of application. In the United States, the US Military use 75% of AFFF produced for use in the US, and municipal (oil refineries, fire departments), hydrocarbon processing industries and others use the remaining 25% of AFFF produced (Moody & Field 2000). The proportion of AFFF in Australia used by Defence is unknown, however it is feasible to assume that Defence is one of the major users of AFFF in Australia. Currently, Defence holds more than 325,000 litres of AFFF concentrate (pers. com. John Barwick, Defence Engineering, Policy and Planning). Other users of AFFF in Australia include Air Services Australia (for use at civilian airports, hangars and crash crews), and some country and state fire authorities (mainly for vehicle and industry fires). Defence uses AFFF manufactured by the 3M company.

AFFF was first developed in the 1960s to prevent fire damage and re-ignition of fires involving flammable liquid fuels (Moody & Field 2000). The AFFF concentrates are themselves mostly water, with other components such as fluorosurfactants, glycol ethers and ethylene or propylene glycol (Sheinson et al. 2002). When stored under the conditions recommended by the manufacturer, most foam concentrates should last at least ten years (HMFSI 2000). The fluorocarbon and hydrocarbon surfactants in AFFF lower the surface tension, making it easier for the foam solution to spread over the fuel, while the synthetic foaming agents in AFFF allow the formation of foam. Together these additives enable AFFF to form a foam blanket with a very thin vapour sealing film.

AFFF is considered to have low to medium expansion properties (HMFSI 2000). When activated, low expansion foam solution forms a foam film that is approximately 4 to 20 times its original solution volume, while medium expansion foams increase by 20 to 200 times, both suppressing a fire with only a small amount of finished foam product (Hague 2002; HMFSI 2000; Reese 1995). High expansion foams expand by about 1,000 times their original solution volume and require a couple of feet of foam to expand

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around obstacles to smother a fire (Hague 2002; HMFSI 2000; Reese 1995). Also, low expansion foams can be projected over reasonably long distances and heights making them suitable in many situations, while high expansion foams can not be projected any appreciable distance (HMFSI 2000).

AFFF is less viscous than the other foam types (as mentioned in section 2.1), meaning that it can flow more easily through the pipes and spraying nozzles of fire fighting equipment (HMFSI 2000). Both AFFF and FFFP have similar fire fighting characteristics, the main difference is that AFFF is slightly quicker at extinguishing flames and controlling a fire than FFFP (HMFSI 2000; Scheffey et al. 1995). Also AFFF can be applied at lower rates than FFFP (Scheffey et al. 1995).

According to HMFSI (2000), AFFF foams tend to have the following characteristics:

- useable foam can be produced with minimal working;
- flows quicker than protein and fluoroprotein foams over liquid fuel surfaces, quickly resealing breaks in the foam blanket and flowing around obstructions. This often results in very quick fire knockdown and extinction;
- suitable for subsurface injection, where the foam is introduced beneath the surface of fuel fire; and
- the foam is moderately resistant to mixing with a fuel during application (i.e. moderate resistance to fuel contamination).

AFFF foams also have the following disadvantages:

- poor at sealing against hot objects;
- poor foam blanket stability and very quick foam drainage times (i.e. rate at which foam solution drains out of finished foam (Magrabi et al. 2002). Quick drainage time indicates that the foam loses its water content quickly, rendering it vulnerable to high temperature and hot surfaces;
- poor burn-back resistance (i.e. ability of a foam blanket to resist destruction from direct contact with heat and flames);
- poor vapour suppression (ability to prevent fuel vapour percolating through the foam film); and
- unsuitable for use with polar fuels (i.e. refers to liquid fuels that have a permanent electric discharge and are usually able to dissolve in water, such as alcohol. Polar fuels destroys standard foams.)

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Finding:

- Defence is probably a major user of AFFF in Australia, and currently holds more than 325,000 litres of AFFF concentrate manufactured by 3M

2.2 Environmental considerations associated with fire fighting foam use

Many foam products such as AFFF, were developed in the 1960s, before environmental issues were clearly understood (Moody & Field 1999). Since then, fire fighting foams have been found to have a negative impact on the environment (e.g. can remove oxygen from aquatic environment in turn killing aquatic fauna). The environmental effects of fire fighting foam pollutants are generally considered in terms of their toxicity and their biodegradability. How much of an impact fire fighting foam has on the environment depends on the total volume of foam concentrate that is released into the environment.

The most obvious environmental incidents occur where the foam waste-water has reached aquatic environments causing fish kills and disrupting ecosystem function (Hamilton et al. n.d.; Labat-Anderson 1996; McDonald et al. 1996; Minshall & Brock 1991). Such environmental incidents are commonly reported in areas where fire fighting foams are set up as fixed systems (e.g. in hangars), sites where fire fighting equipment is tested (e.g. crash crew vehicle testing), and at areas set aside for fire fighting training (HMFSI 2000; Moody & Field 1999; Orion 2000). Such fixed foam systems, equipment testing sites and training facilities exist across many of Defence's bases. These locations are frequently exposed to the use of foams during the testing of fire fighting foam systems and equipment, and therefore there is a higher risk of accidental release of foam waste-water into the environment, particularly where the foam waste-water is inappropriately collected, contained and disposed of. Such environmental incidents have been reported across Defence, where waste-water has reached dams and creeks on nearby properties and caused fish kills (Refer to Figure 2.3 Defence AFFF survey results; Defence environmental incident reports; pers. com. Defence personnel; URS 2002).

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Figure 2.3 Foam waste-water contaminates an off-base water course following accidental release (RAAF Amberley).

Environmental problems commonly associated with a fire fighting foam relate to it's:

- toxicity;
- biodegradability;
- chemical additives e.g. nutrients, heavy metals, ethylene glycol based solvents, and fluorosurfactants; and
- sewage treatment plant incompatibility (Orion 2000)

2.2.1 Toxicity

Due to the enormous variation among different foam categories, as well as differences between manufacturers, the toxicity of fire fighting foams vary widely. In general, the protein based foams are found to be least toxic, whilst the synthetic AFFF foams most toxic (approximately 12,500 times more toxic than FFFP) (AF n.d.; HMFSI 2000; Roy n.d.). Most foam manufacturers undertake and present their own toxicity tests results.

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Toxicity tests are generally conducted on a variety of organisms that represent key links in the food chain. In aquatic environments such tests are conducted on algae, protozoa, crustacea, and fish. The toxicity effects of fire fighting foams to aquatic organisms are usually due to the surfactants they contain, which lower the surface tension of water, therefore depleting the ability of water to carry oxygen for aquatic organisms (McDonald et al. 1996; Poulton n.d.). Although many of the test organisms, such as aquatic invertebrates, are considered to be of low economical and recreational importance, they are critical to the function of the food chain that supports higher trophic levels such as birds and fish, and eventually humans.

As the range and type of test specimens vary widely, so to does their susceptibility to the effects of the fire fighting foam pollutants. The aquatic toxicity of the substance is usually measured in terms of its LC₅₀ or EC₅₀. The lethal concentration of the substance in water at which 50% of the test specimens die within a fixed time period is described as the LC₅₀, while EC₅₀ is the lethal concentration of the substance in water at which 50% of the test specimens are affected in some way (e.g. behavioural problems, growth) within a fixed time period (Walker et al. 2001). For 3M's AFFF (FC-3003), after 96 hrs of exposure to concentrations greater than 1000mg/L, AFFF was found to kill 50% of the Fathead minnow fish (*Pimephales promelas*) population (96hr LC₅₀>1000mg/L) (3M 2001a).

2.2.2 Biodegradability

Many manufacturers indicate that their fire fighting foams are biodegradable (this does not include foams that contain fluorosurfactants, see section 2.3). Biodegradability of a substance is a measure of how quickly it is broken down by micro-organisms (mostly bacteria) in the environment. Bacteria in the environment will break down and eat the substance, extracting oxygen from the surrounding water as they do so. Biodegradability is determined by the amount of oxygen used by micro-organisms to break down a substance. There are two measurements required to determine biodegradability, chemical oxygen in demand (COD) and biological oxygen in demand (BOD).

COD is the total amount of oxygen required by micro-organisms to degrade a set amount of organic material (in this case the foam concentrate). The lower the COD, the less oxygen that is stripped from the environment. BOD is the amount of oxygen consumed by aquatic microorganisms in a specified number of days (usually 5 or 28) when trying to break down any organic

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material found in foam concentrate (HMFSI 2000). Biodegradability is often calculated by dividing BOD, for a given time period, by the COD, expressed as the percentage (Chemguard n.d.). Foams with a BOD₅:COD ratio greater than 50% are generally considered to be highly biodegradable (AF n.d.).

Initially, high biodegradability (i.e. a high BOD:COD ratio) was considered desirable, however, the more rapidly the foam is degraded the more oxygen is required from the surrounding aquatic environment. The rapid depletion of oxygen has the effect of asphyxiating aquatic organisms. As most foams are highly biodegradable (e.g. 3M's AFFF product is BOD₂₀:COD is 85%, 3M 2001a) there is a risk that if foam concentrate/foam solution/waste-water finds its way into streams, creeks, wetlands, it could cause oxygen depletion in these aquatic environments with serious consequences to aquatic organisms (Walker et al. 2001).

2.2.3 Other environmental issues

The chemicals added to fire fighting foams vary widely due to the enormous variation in foam types and differences between manufacturers (Erten-Unal et al. 1997). Some of the chemicals that may be added to foam concentrates include corrosion inhibitors, preservatives, stabilisers, and anti-freeze chemicals, many of which have been identified as potential environmental pollutants (Levine et al. 1997; Moody & Field 2000; Orion 2000; Roy n.d.). Ethylene glycol based solvents such as glycol ether are used in some AFFF products, and are classified as toxic and hazardous by the US EPA (Roy n.d.). Some AFFF products contain alkyl phenol ethoxylate which can cause reproductive changes in fish (Roy n.d.). Corrosion inhibitors (e.g. tolyltriazole used in 3M's AFFF product) have been shown to persist in the environment (Moody & Field 2000). Fluorosurfactants used in some foam products, like 3M's AFFF, are not fully biodegradable and can persist in the environment (refer to section 2.3). Protein based foam products sometimes contain heavy metals (e.g. zinc) that can accumulate in living tissue and cause significant health problems in animals and humans (Orion 2000).

Some foam products contain phosphate and/or nitrates, that act as fertilizers, promoting excessive growth of weedy plants and algae that can choke out other flora species and reduce ecosystem biodiversity (Chemguard n.d.). Although most protein based foams contain more of these 'fertilizing' substances than synthetic foams, these nutrient loads are generally quite low (Orion 2000). However, in terrestrial environments the nutrient content of

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foams is great enough to initiate the invasion of weedy plant species and cause a reduction of native plant species richness (Larson & Newton 1996). 3M's information sheets do not mention whether or not it's AFFF product contains any 'fertilizing' substance (3M 2001a).

Findings:

- Fire fighting foams have been found to have a negative impact on the environment (e.g. can remove oxygen from aquatic environment in turn killing aquatic fauna).
- Environmental incidents have been reported across Defence, where waste-water has reached dams and creeks on nearby properties and caused fish kills.
- The specific environmental effects of foams differ between product type and manufacturers. Usually environmental information such as toxicity and biodegradability can only be obtained from the manufacturer.
- Biodegradability (measured as BOD:COD) indicates how rapidly a foam can degrade. The more rapidly a foam degrades the more oxygen is required from the surrounding environment, with the depletion of oxygen having the effect of asphyxiating aquatic organisms.
- As most fire fighting foams are highly biodegradable there is a significant risk that if foam concentrate/foam solution/waste-water found its way into streams, wetlands or dams, it could cause oxygen depletion in these aquatic environments with potentially serious consequences to aquatic organisms.
- Some fire fighting foam products can contain environmentally damaging additives such as fluorosurfactants and heavy metals.

Recommendations:

- Take appropriate measures to ensure that fire fighting foam concentrate/foam solution/waste-water does not reach streams, creeks, wetlands, dams or storm-water drains.
- Obtain environmental information from the manufacturer of the foam product. This should include specifics on what chemicals are found in the foam, and what level of environmental risk each chemical may pose.

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2.3 Environmental and health considerations associated with 3M's AFFF – the AFFF product currently used by Defence

Recent studies have shown that many AFFF products not only have some of the general environmental biodegradation and toxicity issues mentioned above (section 2.2) but also contain environmentally persistent fluorosurfactants that can accumulate in body tissue. These fluorosurfactants are found in 3M's AFFF product, which is currently used by Defence.

AFFF foams decompose in the environment to a certain extent, however, the surfactants used in AFFF always leave behind a residue of fluorosurfactants (fluorinated carbon chains) (Moody & Field 2000). These fluorosurfactants have been found to persist in soil and in ground water around sites where AFFF has been used on grass or soil surfaces, with the possibility of these substances transporting/leaching to areas surrounding the contaminated sites (Levine et al. 1997; Moody & Field 1999). As many Defence facilities have indicated that AFFF concentrate/foam solution/waste-water is deposited onto grass and soil surfaces and into storm-water drains (Defence AFFF survey results), it is possible that these on-base AFFF disposal locations, as well as any neighbouring off-base properties that storm-water run-off flows onto, could be contaminated by AFFF residues. A contaminated site refers to a "site at which hazardous substances occur at concentrations above background levels and where assessment indicates it poses or is likely to pose and immediate or long term hazard to human health or the environment" (ANZECC Guidelines for the Assessment and Management of Contaminated Sites, 1992).

Fluorosurfactants are essential ingredients in AFFF concentrate as they have the capability of producing aqueous solutions of sufficiently low surface tension to permit the formation an aqueous film on hydrocarbon fuels (Moody & Field 2000). Fluorinated surfactants behave both hydrophobic (water repelling) and oleophobic (oil repelling) characteristics (Moody & Field 2000). This behaviour coupled with the low surface tension allows the aqueous film to spread over and seal the surface of the fuel, extinguishing the flames and preventing the flammable liquids from evaporating. It is these properties that make AFFF a superior foam fire fighting agent (HMFSI 2000). However, these properties also enable the surfactants to move with surface water into aquatic systems or leach through soil, eventually reaching groundwater or migrate to surface waters such as creeks, farm dams or

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reservoirs (Levine et al. 1997; Moody & Field 1999; URS 2002).

Fluorosurfactants used in AFFF are produced by the process of electrochemical fluorination, also known as Simon-cell chemistry (FFFC n.d; Moody & Field 2000). During the electrochemical fluorination process the substance to be fluorinated is dissolved in hydrofluoric acid and an electric current is passed through the media, all hydrogen molecules are replaced with fluorine, and perfluorinated molecules result (Moody & Field 2000). Alternate AFFF surfactant formulations are synthesized by telomerization. Although these telomer based surfactants were thought to be less toxic they are also highly fluorinated, and thus may also be environmentally persistent and bioaccumulative (Sheinson et al. 2002). Currently fluorosurfactants produced by either the electrochemical or telomerization process are being scrutinised by the US Environmental Protection Agency (Sheinson et al. 2002).

AFFF products containing fluorosurfactants are only partly biodegradable. As the specific formulations AFFF are not known outside the companies that manufacture them (Moody & Field 1999), the environmental implications and biodegradability of AFFF is complicated, and the extent to which AFFF components and pollutants in AFFF waste-water biodegrade is quite varied. The general composition of 3M's AFFF consists of water, butyl carbitol (diethylene glycol monobutyl ether), fluoroalkyl surfactants (fluorosurfactants), and synthetic detergents (refer to Table 2.1) (3M 2001a; EPA 2001; Moody & Field 2000).

Table 2.1. Chemical composition of 3M's Light Water (FC-203CF) AFFF

Chemical Name	% of Total Composition
Water	69.0 - 71.0
Diethylene glycol butyl ether (butyl carbitol)	20.0
Amphoteric fluoroalkylamide derivative	1.0 – 5.0
Alkyl sulfate salts	1.0 – 5.0
Perfluoroalkyl sulfonate salts (PFOS)	0.5 – 1.5
Triethanolamine	0.5 – 1.5
Tolyltriazole (corrosion inhibitor)	0.05

Source: Moody and Field (2002)

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The biodegradable part of AFFF foam is butyl carbitol (Moody & Field 2000). Butyl carbitol has a high BOD value, so as it breaks down it consumes a lot of oxygen. The consumption of oxygen may influence the biological/chemical/geological conditions of groundwater and surface waters by driving anaerobic systems and causing the asphyxiation of aquatic fauna (refer to section 2.2.2) (Moody & Field 2000). The alkyl sulfate hydrocarbon surfactants present in some AFFF formulations are considered biodegradable under aerobic and anaerobic conditions. The non-biodegradable part of AFFF consists of a fluorosurfactants as well as some corrosion inhibitors (Moody & Field 2000). As a whole, virtually nothing is known about the biodegradation of this complex AFFF mixture and any synergistic effects of AFFF components on different environmental conditions (subsurface soil/water or surface waters).

The fluorosurfactants that have currently received much attention are those specifically associated with perfluorooctyl sulfonate (or perfluoroalkyl sulfonate salts - PFOS) and related telomers such as perfluorooctanoic acid (PFOA) (3M 2001a; EPA 2001; Moody & Field 1999; Moody & Field 2000; USEPA 2003). Telomers are man-made chemicals produced by a process that utilizes the ability of certain chemicals to link together into chains (EPA 2003). The PFOS/PFOA compounds represent a very unique chemistry whose toxicity is likely to be influenced by the presence of different perfluorinated carbon chains and functional groups (refer to Appendix 1, OECD 2002).

PFOS, and PFOA, are found in 3M's AFFF product (3M 2001a; 3M 2003; EPA 2001; Moody & Field 2000). PFOS and PFOA, and possibly other related telomers, have been found to be environmentally persistent, bioaccumulative and toxic (EWG 2003; FFFC n.d; Lee 2003; OECD 2002; USEPA 2003; WalkiWisa n.d.). Because of this, in 2002 the US EPA has forced products containing PFOS/PFOA off the market (EWG 2003). Although PFOS/PFOA based chemicals are not currently manufactured in Australia, products containing PFOS/PFOA are still being used in Australia (NICNAS 2003).

PFOS/PFOA are persistent, bioaccumulative and toxic to mammalian species (OECD 2002; USEPA 2003). PFOS has been shown to bioconcentrate in fish, marine mammals and fish-eating birds, and of low to moderate toxicity to aquatic organisms, and acutely toxic to frogs and honey bees (OECD 2002). The studies by Moody and Field (1999, 2000) indicate that repeated AFFF usage at set sites across US Defense bases had lead to PFOS/PFOA contaminated groundwater. Other studies indicate that PFOS is persistent in soil and sewage sludge (OECD, 2002, Levine et al., 1997). PFOS has also been

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found in blood and livers of fish and surface waters across Japan (Taniyasu et al. 2002). Both PFOS and PFOA have been found in blood samples of the general human population, with some levels of PFOA in children above the level that cause serious toxicity in laboratory studies (EWG 2003; Lee 2003; OECD 2002; USEPA 2003; WalkiWisa n.d.). Both PFOS and PFOA have been implicated with a variety of cancers and toxic health effects in humans that have had long term exposure to products containing PFOS/PFOA (EWG 2003; OECD 2002; USEPA 2003). All of these factors indicate that the repeated uncontrolled or poorly managed use of AFFF products that contain PFOS/PFOA is cause for major environmental and health concern (OECD 2002; USEPA 2003). If PFOS/PFOA contaminated water is purposely or accidentally deposited onto grass, soil or into stormwater drains (such as what is commonly occurring across Defence) it can easily leach through soil or migrate to surface waters such as creeks and farm dams and reservoirs. From these points it could easily contaminate drinking water used by humans and farm stock. Based on the current use and management of 3M's AFFF product across Defence, it is possible that PFOS/PFOA could be contaminating Defences' own facilities and also neighbouring off-base properties (Defence AFFF survey results). Defence should consider undertaking site testing (e.g. collection of water and soil samples) to determine if its facilities are contaminated by PFOS/PFOA and the extent of the contamination, and also consider establishing monitoring wells in areas where AFFF is repeatedly used and released (beyond the scope of this study).

Because of the issues associated with PFOS/PFOA the Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS) released an alert on 30th April 2003 recommending that PFOS/PFOA products such as AFFF be restricted to essential use only, and that AFFF foam should not be used for fire training/testing purposes (NICNAS 2003).

The relationship between PFOS and PFOA is complicated. 3M's AFFF product contains both PFOS and PFOA (3M 2001a; 3M 2002; 3M 2003; EPA 2001; OECD 2002; Reicher 2000). According to the latest 3M report released 13th March 2003, PFOS would be generated through biotic degradation (e.g. by microorganisms) of AFFF, but PFOA would be formed instead of PFOS under abiotic conditions during the last step of the degradation pathway (3M 2003). However, the chemical structure of PFOA is so similar to PFOS (also too many similarities in toxicity and health effects) that more comprehensive investigations are needed (EWG 2003; WalkiWisa n.d.).

The fact that these fluorinated surfactants, as well as other AFFF components, co-occur with priority pollutants in AFFF waste-water (e.g. jet

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fuel components and chlorinated solvents) complicates studies on their fate and effect in the environment (Moody & Field 2000). Although much is known on effects of PFOS/PFOA compounds alone, especially under laboratory conditions, little is known about the occurrence, transport, biodegradation, and toxicity of the mix of fluorinated surfactants, AFFF mixtures, and co-occurring pollutants in the environment. Currently more information is needed to sufficiently identify the fluorinated surfactants present in commercial AFFF, and the environmental behaviour of the AFFF mixtures and complexities associated with AFFF waste-water. Defence should consider facilitating industry partnerships into researching the behaviour of AFFF mixtures and AFFF waste-water as they may occur in the Australian environment.

2.3.1 AFFF Health Hazards

3M's Light Water (FC-3002, FC-3034) AFFF used by Defence is classed as being 'hazardous' according to Worksafe Australia Criteria (Chemwatch - <http://dsmachem.dcb.defence.gov.au/>, National Occupation Health and Safety Commission (NOSCH)).

The general health hazards associated with fire fighting foams, as outlined by Chemwatch and 3M (2001a) include:

- eye irritation;
- skin irritation ;
- inhalation may cause central nervous system depression (headache, dizziness, drowsiness) and sore nose and throat; and
- ingestion may cause irritation to the gastrointestinal tract (3M 2001a).

Safety requirements when using AFFF include:

- do not breathe gas/ fumes/ vapour/ spray;
- wear gloves;
- wear eye/ face protection;
- wash hands after use; and
- immediately take off all contaminated clothing.
- Clean the floor and all objects contaminated by this material using water (3M 2001a).

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More detailed information on health hazards and safety requirements associated with a specific foam product are in Material Safety Data Sheets (MSDS) provided by the foam manufacturer. Currently 3M's MSDS does not mention that it's AFFF product contains PFOS/PFOA, only that they may contain fluorosurfactant, and that there are no known health effects if the AFFF concentrate is used as intended and instructed in the MSDS.

2.3.1.1 PFOS/PFOA

PFOS and PFOA are toxic to humans, and both have been implicated with a variety of cancers (EWG 2003; OECD 2002; USEPA 2003). Once PFOS or PFOA makes it way into the human body (via food contaminated when touched by unwashed hands, in drinking water, breathing in foam vapour), elimination from the body is slow. As PFOS/PFOA have the potential to be absorbed and remain in the body for long periods of time, and accumulate with repeated exposures (EWG 2003; Lee 2003; OECD 2002; USEPA 2003; WalkiWisa n.d.), it is extremely important to follow the safety instructions indicated in MSDS's for use of AFFF (e.g. by wearing PVC gloves, safety foot wear, full body overalls, and safety glasses/chemical goggles). It has been observed that some Defence personnel and contractors are not implementing these safety precautions. Defence personnel and contractors have been observed to place their bare hands in the foam solution during the rinsing out of fire fighting vehicles foam systems after drills, and during foam sprinkler maintenance (Figure 2.4 pers. com, pers. obs.). Defence Health Service Branch has been made aware of these observations.



Figure 2.4 Current practices for managing exposure to AFFF by Defence leave a lot to be desired. Here foam samples are collected during a test, but without protective clothing.

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Findings:

- Defence currently uses AFFF product that contains non-biodegradable fluorosurfactants (PFOS/PFOA) that are environmentally persistent, bioaccumulative and toxic to animals and humans.
- PFOS is acutely toxic to frogs and honey bees. Both PFOS and PFOA have been implicated with a variety of cancers and toxic health effects in humans that have had long term exposure to products containing PFOS/PFOA.
- In 2002 the US EPA forced products containing PFOS/PFOA off the market.
- The repeated uncontrolled or poorly managed use of AFFF products that contain PFOS/PFOA is cause for major environmental and health concern. There is the risk that poor AFFF management practices across some of Defence's facilities may have resulted in PFOS/PFOA contaminating of soil, surface water and groundwater, both on and off base. Furthermore, the biodegradable part of AFFF consumes a lot of oxygen as it breaks down. The consumption of oxygen may influence the biological/chemical/geological conditions of groundwater and surface waters by driving anaerobic systems and causing the asphyxiation of aquatic fauna.
- Little information is known on how the fluorosurfactants in AFFF and other pollutants in the waste-water (e.g. oil and fuels) co-occur and behave in the environment.
- NICNAS is recommending that PFOS/PFOA products such as AFFF be restricted to essential use only, and that AFFF foam should not be used for fire training purposes.
- The use of personal protective equipment when handling AFFF is not consistent across Defence.

Recommendations:

- Defence should consider undertaking site testing (e.g. collection of water and soil samples) to determine if its facilities are contaminated by PFOS/PFOA and the extent of the contamination, and also consider establishing monitoring wells in areas where AFFF is repeatedly used and released.
- Defence should consider restricting the use of AFFF across its facilities in accordance to NICNAS recommendations.
- Defence should consider facilitating industry partnerships into researching the behaviour of AFFF mixtures and waste-water as they may occur in the Australian environment.

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3. Fire fighting foam waste-water management Best Practice

The main issues associated with fire fighting foam waste-water management are based around how it is collected, contained and disposed of. As the issues surrounding PFOS/PFOA were only recently identified, as yet there are no regulatory actions that specifically encompass the use and disposal of products containing PFOS/PFOA. NICNAS is currently developing Australian Regulatory Actions, while the US EPA hazard assessment is yet to be publicly released (OECD 2002). Some Commonwealth Legislation and Government regulations relating to fire fighting, waste, and environment legislation and guidelines that may be of relevance to the disposal of AFFF are included in Appendix 2.

Although there is no specific design guidance that provides a reasonable approach to handling AFFF discharges that contain PFOS/PFOA, best practice in the management of AFFF products have been identified by international and national companies/departments that regularly use AFFF (e.g. US Defense, UK Defence, Air Services Australia, Australian Country and Rural Fire Authorities). AFFF handling and disposal recommendations have also been made by the companies that produce AFFF (e.g. 3M, Angus Fire, Ansul, Orion, Chemguard), and by environmental consultants (e.g. URS, GHD). These management practices have been primarily developed for areas where AFFF systems are fixed (e.g. hangars) or locations where AFFF is frequently used (e.g. fire equipment testing sites, fire training sites). Under these conditions AFFF waste-water can be appropriately collected and contained, and disposed of via a sewage plant or by incineration (Figure 3.1). Ideally the management system should be designed to contain the most probable worst case AFFF discharge (maximum discharge likely to occur in a non-catastrophic event).

The following AFFF waste management best practice is based on the information collected from US Defense, UK Defence, Air Services Australia, Australian country and rural fire authorities, producers of AFFF, and environmental consultants reports. It applies to testing, training and exercising involving AFFF products. It is recognised that catastrophic events requiring property loss will inevitably result in AFFF release (to some extent) to the environment. In such instances the effects of that exposure may require remediation.

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Testing, training and exercising with AFFF

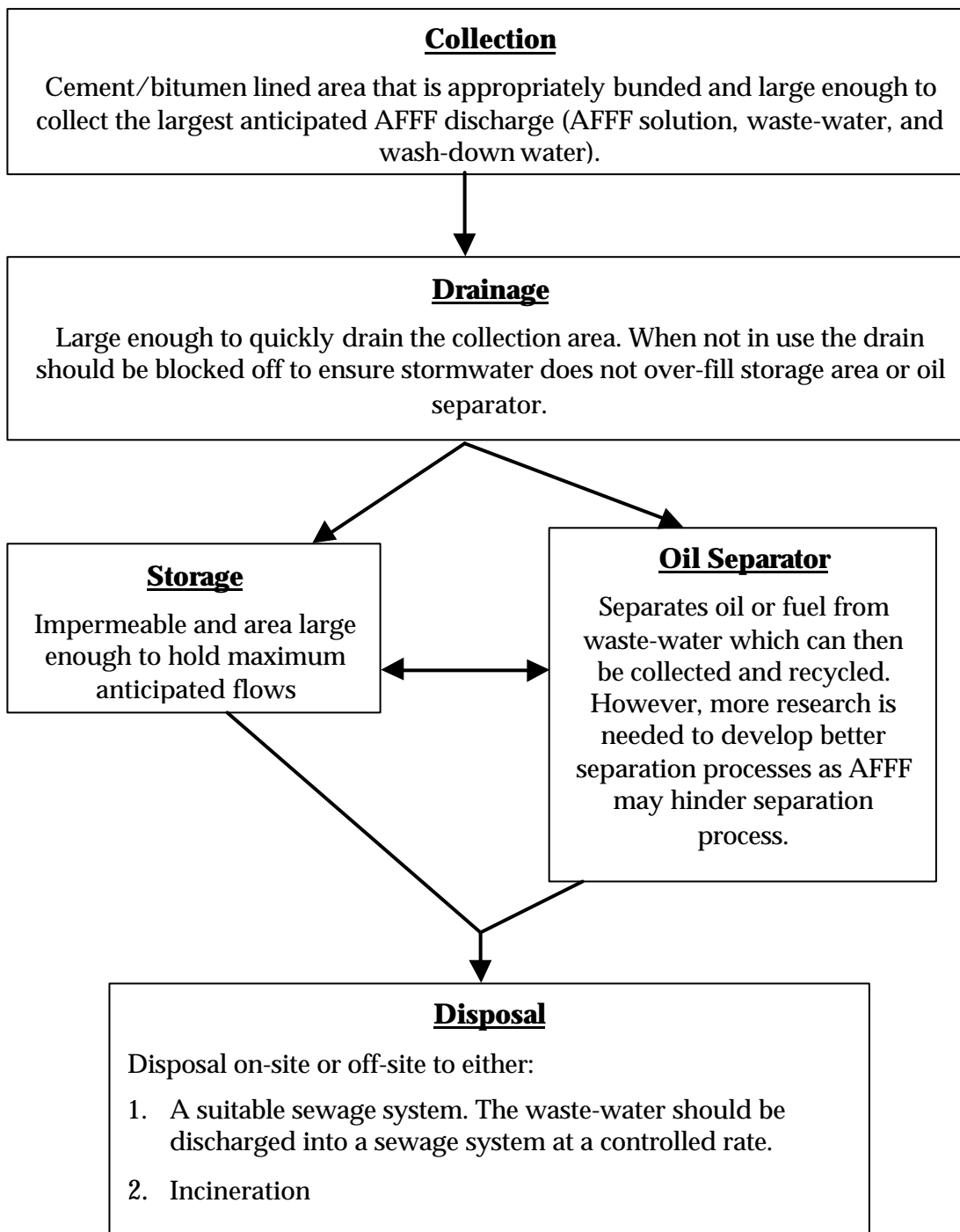


Figure 3.1. Flow diagram of AFFF waste management best practice (based on the information collected from US Defense, UK Defence, Air Services Australia, Australian country and rural fire authorities, producers of AFFF, and environmental consultants reports). Waste management practices must be in accordance with relevant legislation and regulations (depending on the State/Territory) (Appendix 2).

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3.1 Collection and Drainage

Any area where AFFF foam is or may be released should have spill controls that enable containment and treatment of foam waste-water. All surfaces and equipment in contact with AFFF and AFFF waste-water should be “washed down” until no visible AFFF or foam residue remains. The ground surface of these release and wash down areas should be non-porous (e.g. cement, bitumen) and should cover an area larger than the furthest reaches of the AFFF foam discharge. These areas may also need to be bunded (pers. com. UK Defence). The ground surface should slope towards drains to restrict spread of fuel or AFFF waste-water, and enable the AFFF waste-water to drain into pipes to a liquid waste storage area or oil separator. The floor drainage system configuration and size of piping must take into consideration the hydraulic demands placed on the system.

3.2 Storage

The collected waste should be stored in an impermeable tank/pond (underground tank, above ground tank, or in a collection pond).

The minimum capacity of a storage tank should be adequate to handle anticipated maximum flows i.e. based on producing the largest discharge (during system testing, accidental release of AFFF from overhead system). Underground tanks should be located so that gravity flow can be utilized, while above ground tanks require the waste-water to be pumped into them.

Open ponds should be designed to contain both worst-case discharge as well as allow for rainfall event (i.e. based on the greatest 24 hours rainfall event in a 5 year period (USACE 1997). When the open ponds are not being used, valving and piping should be provided to drain off rainwater to the sewage system. However, for open ponds there is always a risk of any collected AFFF waste-water overflowing into the environment. Another problem with open ponding is that birds and frogs may use the ponds. Open ponds are used by Air Services Australia to collect AFFF waste-water however, they have had issues with a threatened frog species establishing in one of their ponds (pers. com. Air Services Australia Environmental Officer). If possible, open ponds should be managed to restrict access by fauna (e.g. using netting or synthetic liners).

3.3 Oil Separators

Oil separators can be included as part of the drainage system prior to storage, or en route from one storage area to another. Oil separators are

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installed to intercept oil or fuel spilled on to ground. Separating systems are basically holding tanks that provide sufficient detention time to allow the oil, which is lighter than water, to rise to the top of the separator for removal. The collected oil and fuel can sometimes be recycled for re-use (pers. com. UK Defence). Oil and fuel products need to be removed as they can inhibit the sewage plant treatment process, with many operators refusing to accept sewage with any of these products above small threshold limits (USACE 1997). Separators are sized for a designated flow rate which is generally based on maximum anticipated spill (if on route from one storage point to another, discharge into and out of the separator can be regulated).

Unfortunately there has been some issues with AFFF waste-water affecting the oil separation process, with many separators requiring constant repairs or replacement (pers. com. Defence personnel, pers. com. UK Defence). The fluorosurfactants used in AFFF can sometimes allow the water and fuel/oil to mix, restricting oil/fuel separation, while any foam forming on top of the waste surface restricts the rising of the oil/fuel to the surface (USACE 1997), both processes hindering the removal of the oil from the waste surface. If the oil/fuel is not properly removed prior to placement in storage ponds, the oils can erode the bitumen lining of the ponds enabling AFFF waste-water to leak into the groundwater (pers. com. Defence personnel).

So far, there have been very few advancements in the oil/fuel separation process. An Australian company, Adtech Environmental, have produced a filtration system (ANJAN technology) that can treat AFFF waste-water. This ANJAN system is currently being used by the US Defense at Base Camp Pendleton. The US Defense Air Force Research Laboratory and Advance Processing Technologies Incorporated have developed the Mobile Air-Sparged Hydrocyclone (ASH) reactor technology to effectively remove more than 80% of AFFF, emulsified oil, fuel and grease from waste-water (reduce AFFF concentrations to levels in waste-water generally acceptable for treatment by sewage plants) (NFESC 2002).

3.4 Disposal

Most reports distinctly state that fire fighting foam waste-water should not be disposed of into watercourses, soils, or foul stormwater drains without the prior consent from the local environmental authority (3M 2001a; AF n.d.; BFPSA 2001; HMFSI 2000; Labat-Anderson 1996; USACE 1997). There are two main methods of disposing of the stored AFFF waste-water, through a sewage treatment plant or by incineration. These disposal methods can be either undertaken via a metered drainage system into a suitable local

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sewage facility, collected and removed by waste collection facility, or treated on-site via water treatment plant or by incineration.

3.4.1 Sewage

The most common, and currently the best, disposal solution of AFFF waste-water is via sewage plant treatment (3M 2001a; 3M 2001b; AF n.d.; Chemguard n.d.; Darwin et al. 1995; Moody & Field 2000; NFESC 2002; Roy n.d.; Walker et al. 2001). As long as the receiving sewage plant operators are aware of the discharge, processes can be modified to ensure effective treatment. It is imperative to liaise with local sewage plant operators prior to disposing of any fire fighting foam waste-water because:

- problems with excess foaming can disrupt sewage treatment operations;
- problems with high BOD and COD levels can disrupt sewage treatment operations;
- possibility of some foam solution killing the bacteria cultures used in some waste-water treatment facilities disrupting sewage treatment operations; and
- the level of sewage treatment operation determines the quality of water discharged from the sewage works (3M 2001b; Darwin et al. 1995; Erten-Unal et al. 1997; Moody & Field 1999). This is a concern when sewage systems discharge poorly treated waste to watercourses, oceans and creeks.

If too much fire fighting foam is discharged to a waste-water system at one time, excess foaming may occur (Figure 3.2). Excess foaming results in aesthetic and operational problems in sewers and waste-water treatment facilities, and can cause the shutdown of these facilities (Darwin et al. 1995; Moody & Field 2000; Roy n.d.). Excess foaming in discharges also alarms the community, and clearly flags that discharges are contaminated with chemical residues irrespective of the degree of environmental risk. Another concern for waste-water treatment facilities is that incoming foam waste-waters have high BOD and COD load (Erten-Unal et al. 1997; Moody & Field 2000). Incoming waste with high BOD and COD load may be beyond the treatment capability of the facility, particularly if the microbes/bacteria cultures used by the sewage facility are already inhibited by excess foaming. Although microbe/bacteria can tolerate concentration of 100:1 (100 parts water to 1 part foam), some AFFF foams and residual fuel and other combustion products that are often a part of AFFF waste-water can kill these cultures (Moody & Field 2000).

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Figure 3.2. Excess foaming caused by AFFF waste at RAAF Amberley water treatment facility. (The excess foaming is not due to any fault of the sewage treatment plant operator.)

Also, if sewage plant operators are unaware of the disposal of foam waste-water into their sewage system, and the plant is unable to appropriately treat the waste-water, the release of this partly ‘treated’ water may inadvertently contaminate the receiving surface waters (Walker et al. 2001). This is particularly relevant to the occurrence of PFOS/PFOA contaminated AFFF waste-water (OECD 2002). It is therefore imperative to contact the local waste authority (or on-site sewage operator) to determine suitable foam waste-water disposal methods, and if any pre-treatment or dilution is required depending on the concentration of the foam, type of foam, volume of waste-water, and if the waste-water contains other substances such as oil or fuel. In cases where oil separation was ineffective (see section 3.3), the waste may need to be assessed to determine if volatile flammable materials are present at hazardous concentrations and whether or not they pose an explosion hazard (i.e. meet sewer codes).

3M suggests that AFFF foam waste-water be released into sewage system in a controlled manner, at a rate of 50ml of AFFF waste-water per litre of sewage flow (URS, 2002). Some sewage operators (Australia and world-

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wide) will only accept fire fighting foam waste-water at a rate of 1ml of foam waste-water per litre of sewage flow (NFESC 2002), and some will only accept foam waste-water that has been pre-treated (Chemguard n.d.). Several pre-treatments such as precipitation, coagulation, adsorption on activated carbon, and ultrafiltration are being evaluated for the treatment of AFFF waste-water before dispensing it to a waste-water treatment facility (e.g. ANJAN technology, ASH system, section 3.3), however few world-wide pre-treatment strategies are being implemented (Moody & Field 2000).

3.4.2 Incineration

A licensed hazardous waste contractor can incinerate AFFF waste. Due to occasional oil separation issues (section 3.3) the UK Defence contracts a waste specialist to recover fuel/foam emulsions and incinerate it (pers. com. UK Defence). Incineration of AFFF waste-water may produce toxic fumes of nitrogen oxides and hydrogen fluorides or perfluorobutylenes (3M 2001a). 3M however believe that as the fluorochemical content of its AFFF product is very low, these toxic by products do not pose a hazardous risk. In all cases, high temperature incineration must be in accordance with legislation/regulation for the disposal of contaminated waste. It is unlikely that incineration will provide a solution to environmental issues associated with AFFF use in Defence in the short term.

Findings:

- The main issues associated with fire fighting foam waste-water management are based around how it is collected, contained and disposed of.
- There are currently no regulatory actions in Australia that specifically encompass the use and disposal of AFFF foams or products containing PFOS/PFOA.
- Most reports distinctly state that fire fighting foam waste-water should not be disposed of into watercourses, soils, or stormwater drains.

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Findings (cont.):

- Best management practice for AFFF waste-water, as indicated by reports and literature, include the appropriate collection and containment of AFFF waste-water, and disposal via a sewage treatment plant or by incineration.
- There has been some issues with AFFF waste-water affecting the oil separation process, with many separators requiring constant repairs or replacement.
- AFFF waste-water is commonly disposed of via sewage treatment plant. However, if too much foam is discharged at one time, it can result in operational problems and shutdown of treatment facilities. This could also result in poorly treated waste-water inadvertently contaminating the receiving waters (creeks, streams, oceans).

Recommendations:

- AFFF waste-water management system should be designed to contain the most probable worst case AFFF discharge, to minimise the risk of any AFFF waste-water reaching watercourses, soil, or stormwater drains.
- The management of AFFF across Defence should meet the best practice methods used by others, as indicated in reports (manufacturer recommendations, US Defense, UK Defence, consultants' reports) and in scientific literature.
- If open ponds are used to store AFFF waste-water they should be managed to restrict access by fauna (e.g. using netting or synthetic liners).
- It is imperative to contact the local waste authority to determine suitable waste disposal methods and if any pre-treatment or dilution is required.

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4. AFFF use within Defence

Defence currently uses both 3% and 6% AFFF concentrates produced by 3M, although 3M are no longer manufacturing this AFFF product. Defence primarily uses AFFF to save lives and property from the risk of fuel fires. AFFF is used in hangars, on crash crew vehicles, fuel farms, and on ships. According to NICNAS Defence is the largest holder of AFFF in Australia (pers. com. Dr Jane Weder, NICNAS). Defence holdings of AFFF concentrate have been estimated to be greater than 325,00 litres (pers. com. Defence personnel). This could supply some Defence facilities for 1 to 5 years (e.g. crash crews) or up to 10 years (e.g. hangars) (pers. com. John Barwick, Defence Engineering, Policy and Planning).

In the past AFFF was managed by the Defence Fire Fighting and Equipment Committee (DFEFC). Currently the responsibility for AFFF, fire fighting and fire fighting equipment, materials and standards are widely dispersed, and no organisation has responsibility for the overall coordination of all related activities (AMPST1A & STANCOORD 2003). Possibly as a result of this, the use and management of AFFF across Defence facilities is not uniform. Some Defence documents that may be relevant to the use and management of AFFF across Defence facilities are included in Appendix 2. It must be noted that the Defence Materiel Organisation is currently producing new DEF(AUST) standard for AFFF to replace DEF(AUST) 5603 and DEF(AUST) 5639. This new DEF(AUST) should aid in the AFFF replacement product selection process.

There have also been a few reports of environmental incidents across Defence establishments as a result of unintentional foam discharges (e.g. accidental spillage or leaks) and uncontrolled intentional foam discharges (e.g. foam sprayed onto grass). Because of the environmental and health issues associated with AFFF, particularly relating to PFOS/PFOA contamination (sections 2.2 and 2.3), there is a need to identify if any of Defence's AFFF management practices are cause for concern. An internal investigation was conducted in order to gain a better understanding on how AFFF is used and how the waste-water is collected, stored and treated across Defence facilities, and whether or not these management practices fall within the best practice of other organisations (section 3). Some of this information is expressed in following sections (sections 4.1.1 to 4.1.5). This investigation only provided a broad overview of AFFF use across Defence.

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4.1.1 Aircraft hangars

AFFF systems are used in aircraft hangars to help suppress potential fuel fires, particularly in hangars that house fuelled aircraft. Fuel spills present the greatest potential risk of fire within an aircraft hangar.

The main hanger fire suppression methods include:

- a) portable/mobile fire equipment such as fire extinguishers and foam proportioning devices attached to fire hose reels;
- b) low level foam systems such as pop-up sprinklers and/or oscillating foam monitors (Figures 4.1– 4.2); and
- c) overhead fire suppression systems (Defence 2000). Overhead fire suppression systems (water/foam) have been installed in aircraft hangars where two or more fuelled aircraft are housed and passive fire separation is not available (Defence 2000).



Figure 4.1. A pop-up sprinkler on the floor of a hangar, a few seconds after the foam system was activated.

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Figure 4.2. An activated pop-up sprinkler foam system

Defence Aircraft hangars generally have fixed AFFF systems (Figure 4.2, either pop-up systems or overhead systems) plus AFFF extinguishers. The fixed AFFF systems are tested annually to 5 yearly. Any AFFF sprayed on a hanger floor is collected on cement floors and drained into grates or traps located inside the hanger, and into underground holding tanks (Figure 4.3).



Figure 4.3. AFFF waste-water drainage grates located inside the hangar

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However, in some instances hangers do not contain appropriate collection systems and the foam waste-water flows out of the hangar door and into bunded areas outside the hangar (Figure 4.4) where it can be collected in a sump. The waste collected in the sump is sometimes removed by waste contractors. Less than half of the Defence bases dispose of the stored AFFF waste-water to sewer or waste contractors. In many cases the stored AFFF waste-water is disposed of onto grassed areas to evaporate or it is released into stormwater drains. The disposal of AFFF waste-water in this manner could possibly lead to the contamination of soil, surface water and groundwater. Just under half of the facilities investigated indicated the occurrence of AFFF related environmental incident.



Figure 4.4. Temporary bunding outside a RAAF Amberley hanger in preparation of foam discharge during the testing of a hangars AFFF system.

4.1.2 Crash crews and fire training exercises

4.1.2.1 Crash crews

Crash rescue crews respond to runaway and terminal aircraft accidents and need to be in a state of operational readiness. Crash crews generally test the equipment on their fire fighting vehicles on a weekly basis. They also undertake testing whenever they obtain a new vehicle, or a vehicle comes out of the vehicle workshop. This testing is required to ensure that their systems are in good working order, in readiness of a fire emergency. Any testing site

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must be no further than three minutes drive away from the crash crew fire station.

Fire fighting vehicles can carry approximately 20-50 litres AFFF concentrate. The concentrate is mixed with water to the appropriate concentration by the vehicles systems, to create working AFFF foam solution. To test the equipment on these vehicles the sprayer system is initiated until AFFF foam solution formation is consistent. This can take anywhere from one to five minutes, depending on the vehicles foam system and operator's decision to cease spraying. About half of the bases with fire fighting crews spray the foam into special purpose built facilities (Figure 4.5), the other half spray the foam onto grassed areas. It can take up to a couple of days for the physical form of the foam to collapse in cold weather, while in hot weather it takes approximately three hours (pers. com. Defence personnel). Also, the grassed areas have been known to re-foam after heavy rain (pers. com. Defence personnel).



Figure 4.5. An example of a purpose built crash crew vehicle testing/fire training facility at a RAAF Williamtown.

AFFF is not highly corrosive so AFFF products usually do not contain special corrosion inhibitors (note that 3M's AFFF product does contain a corrosion inhibitor, see Table 2.1). However, as AFFF contains surfactants it is more searching than water (i.e. it is able to find its way into areas that it shouldn't), which could damage fire fighting equipment and systems (HMFSI 2000). For this reason the AFFF working solution and AFFF concentrate remaining in the vehicles pump system requires to be flushed with water (sparged) after using AFFF (pers. com. Defence personnel). This waste-water is generally

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released onto cement or bitumen, with run-off flowing into grassed depressions, storm water drains, or sewage drains (Figure 4.6).



Figure 4.6. Foam waste-water leaking from a collection pit drain within Defence land (RAAF Amberley).



Figure 4.7. An unlined AFFF waste-water evaporation pond at RAAF Tindal. Source: URS (2002).

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Of the waste-water that is collected, it is often spread onto grassed areas or into ponds for evaporation (Figure 4.7). It appears, however, that many of these evaporative ponds are unlined possibly allowing AFFF pollutants (PFOS/PFOA) to infiltrate into soil and groundwater, particularly in areas with sandy soils, or where the water table is high (URS 2002; pers. com. Defence personnel). Also, the ponds have been known to overflow onto surrounding areas after heavy rain (URS 2002; pers. com. Defence personnel). Even so, only a couple of AFFF related environmental incidents have been reported across Defence. Only a few Defence facilities collect their waste and send to sewage (via an oil separator), or have a contractor dispose of it in the appropriate manner.

4.1.2.2 Fire Training

Portable and manual AFFF systems are also used during fire training exercises. A fire training exercise consists of flooding a fire pit (Figure 4.8) or other purpose built facility (Figures 4.9-4.10) with flammable liquids e.g. jet fuel, igniting the fluids, and subsequently extinguishing the fire with fire fighting agents (pers. com. Defence personnel). In some cases the facility used for crash crew vehicle testing is also used for fire training exercises (Figure 4.5). The disposal options for AFFF waste-water is similar to crash crew vehicle sites (section 4.1.2.1.), with AFFF waste-water discharge into a waste-water treatment facility or directly onto the ground adjacent to the training facility.



Figure 4.8. An example of a hot fire training pit at RAAF Williamtown. This pit does not have any controls to prevent spillage of fuel or AFFF flowing onto surrounding soil/grass areas.

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Figure 4.9. An example of a fire training facility at RAAF Amberley. The mock aircraft is on a porous fire tray (approximately 10m by 10m) that allows the collected foam water to drain into an underground pit. Any foam spray outside the fire tray remains in the environment.



Figure 4.10. An example of FA-18 fire simulation at RAAF Security and Fire School. The fire training facilities at this school are considered to be one of the most advance facilities in Australia.

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Training foams

Many companies produce environmentally friendly training foams, with an existing 3M Training Foam product currently being used by some Defence facilities (GHD 2002). This foam can be used with conventional fire fighting foam extinguishers for cold training exercises (without fire) and for hot training exercises. Some Defence personnel indicated that fire training foams do not realistically portray AFFF's properties, and can not be sprayed from the fire fighting equipment in the same manner as AFFF (e.g. training foam can not be projected as far as AFFF). Also, this product can not be used in a real emergency fire fighting situation as it is not film forming and allows fuel to re-light (GHD 2002). Although this product does not contain any PFOS/PFOA, it can disrupt sewage system operation if too much is released (in a similar manner to other fire fighting foams, section 3.4.1). Overall the environmental risks posed by training foams are minimal, although discharges of any foam chemicals to water courses presents Defence with problems of perception and community relations. Discharge is considered contrary to Defence environmental policy.

Training foams could not be used to test fire fighting foam systems on fire fighting vehicles because it could compromise the operational readiness of the fire fighting crew. The foam systems would need constant flushing between using fire training foam, and the system holding AFFF for operational readiness requirements.

4.1.2.3 RAAF Security and Fire School

The RAAF Security and Fire School at Amberley, Queensland, is considered to be one of the most advanced in Australia (GHD 2002). The training site consists of three large cement pads (greater than 27m in diameter, based on the turning circle of the fire fighting vehicles), each with a different simulation (Boeing 737 (Figure 4.11), FA-18 fuel spill (Figure 4.10), and a two storey building).

A computer control centre regulates the nature and size of the LPG based fires across all three pads. This computer system also monitors AFFF discharge and waste treatment. Approximately 2,000 to 3,000 litres of working foam solution are used per training session. All the used AFFF water is collected on the pads, flows into underground drains and pipes, and into a lined AFFF collection pond (Figure 4.12). The drainage system pipes have a splitter so the water can be diverted to the water collection pond when the pads are not in use, or when only water is used to suppress fires. These lined ponds primarily rely on evaporation, however, when full, some

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of the AFFF waste-water is pumped (at a set rate) into the sewer system. The water in the water collection pond is recycled. Overall this system cost about \$10.5 million to develop. Unfortunately, the school is not close enough to RAAF Amberley for it to be used by the crash crews for their weekly testing of their vehicle's foam systems.



Figure 4.11. Boeing 737 fire training simulation.



Figure 4.12. AFFF collection pond (left) and water collection pond (right).

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Although this system is superior than most other systems, there are a few small issues regarding AFFF waste-water being left in the drainage pipes. If the AFFF waste-water is not sparged from these pipes, the water in the water collection pond can become contaminated (pers. com. Defence personnel). Also, if the AFFF pond is full and the sewage pump breaks down, the AFFF waste-water is allowed to overflow into an earthen gully. Furthermore, there is no fauna access prevention at these ponds.

4.1.3 Ship-borne AFFF systems

Navy ships and some submarines are fitted with AFFF fixed systems, designed to provide a secondary method of extinguishing fires beyond the control of primary, portable fire fighting appliances (Defence 1996). These automatic fire suppression systems are tested monthly.

If the AFFF system is activated while the ship is at sea, the waste-water is either discharged straight into the ocean or collected in an oily waste tank. If it is collected in the oily waste tank, the amount collected depends on operational requirement and availability of storage space at the time of the incident. On return to base the collected waste is pumped out via oil separators to a Defence base sewage treatment plant. If the AFFF system is activated when the ship is docked, the AFFF waste-water is pumped directly out into the base's treatment plant.

For submarines, if the automatic fire suppression system or annually operated foam cannons are used at sea the waste is discharged into the ocean. The waste cannot be stored on board submarines due to buoyancy requirements of submarines. If the system is activated while docked (such as during monthly testing), the waste is pumped via an oil separator to base sewage treatment plant. The environmental issues associated with the release of AFFF waste-water into the ocean has been identified by the US Defense Department. The US Defense are currently working on a preventive maintenance system procedure to separate AFFF from bilge water and minimize AFFF discharges into the environment via bilge water (NDCEE 2002). However, as AFFF systems would only be used during an emergency, and due to the huge dilution factor when AFFF waste is disposed of in the ocean, the impact on ocean life is likely to be minimal.

The AFFF waste-water released into the base's treatment facility first passes through an oil separator. As discussed in section 3.3, the AFFF reduces the capacity of the separator to separate out the oily waste. This allows oil into

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the ponds that erodes the bitumen lining, allowing waste-water to leach into the ground (pers.com. Defence personnel).

4.1.4 Fuel farms

Most Defence based fuel farms have sealed direct injection AFFF systems. These systems are tested monthly to annually. When a system is activated, most sites collect any AFFF waste-water in bunded areas. A few fuel farms have contractors collect and dispose of the waste-water, most however, dispose of the waste-water into storm-water drains or onto areas for evaporation.

4.1.5 Other

AFFF extinguishers have also been used in for wildfire suppression. Under these circumstance the AFFF would only be discharged in a fire emergency with the location of AFFF discharge being ill-defined.

Findings:

- The use and management of AFFF across Defence facilities is not uniform, and there is no Defence organisation with the responsibility for the overall coordination of fire related activities.
- There have been a few reports of environmental incidents across Defence establishments.
- Only a few Defence facilities collect and store their AFFF waste-water and have a contractor dispose of it in the appropriate manner.
- In many cases AFFF waste-water is disposed of onto soil or grassed areas to evaporate, or it is released into stormwater drains.
- AFFF waste-water is sometimes disposed of into unlined evaporative ponds, possibly allowing AFFF pollutants (PFOS/PFOA) to infiltrate into soil and groundwater. These ponds have been known to overflow onto surrounding areas after heavy rain.
- About half of the bases with fire fighting crews spray the foam onto grassed areas. These grassed areas have been known to re-foam after heavy rain.

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Findings (cont.):

- Training foams do not realistically portray AFFF's properties; they can not be used in a real emergency fire fighting situation as they allow fuel to re-ignite; they can still disrupt sewage system operation; and can not be used to test systems on fire fighting vehicles because they may compromise the operational readiness of the fire fighting crew.
- If AFFF system is activated on a ship or submarine while at sea, the waste-water is usually discharged straight into the ocean.

Recommendation:

- A more comprehensive study be considered to identify and assess environmental and health issues relating to AFFF use and management at each site where AFFF is used.

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5. Defence AFFF use and management concerns

Based on the above (section 4), the management and use of AFFF across Defence facilities generally falls below the management practices undertaken by other Australian and international organisations (Table 5.1, section 3). In many cases across Defence the AFFF waste-water is being released into the environment (onto grass, soil, unlined ponds, or into stormwater drains), with the potential of AFFF pollutants such as PFOS/PFOA contaminating soil and groundwater on Defence bases as well as contaminating surrounding farm land and surface waters. AFFF has been released into the environment usually during AFFF system testing (hangers, ships, fuel farms, crash crew vehicle testing), flushing of fire fighting vehicles and during fire fighting training.

Table 5.1. General Australian Defence AFFF waste management practices as compared to UK Defence, US Defense, and Air Services Australia. AFFF management practices are not uniform across Australian Defence facilities (as indicated by each dot point).

	Collection	Oil Separation	Storage	Disposal
Defence	- Some not collected -Some sealed area without bunding -Some sealed area with bunding	- Some do not use - Most use but issues with separation process - Few use, no apparent issues	- Some do not store - Few have limited storage in oil separator - Few store in pond - Few store in tank	- Some soil or grass - Some into stormwater drain - Few into unlined pond for evaporation - Few lined pond for evaporation - Some sewage system - Some waste contractor
UK Defence	- Sealed area	- Use oil separator but have had issues with AFFF emulsifying with fuel	- Sealed collection tanks	- Incinerated by waste contractor, and where possible any separated fuel is recycled
US Defense	- Sealed area built to handle maximum flows	- Use oil separator that is sized to hold maximum anticipated spill	- Sealed underground or aboveground tank - Impermeable pond designed to hold greatest 24 hour rainfall event in 5 years	- Offsite or onsite sewage treatment - Waste contractor - Evaporation pond (approx. 40m in diameter and 8cm deep) in a hot, dry, windy climate with little rain
Air Services Australia	- Cement lined bunded area	- Use oil separator but have had issues with AFFF emulsifying with fuel	- Open ponds, but have had issues with fauna using the ponds	- Sewage treatment system with trade waste licence - Stormwater drains if water pretreated to meet Airport Environment Protection Regulations (1997)

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The discharge of AFFF into soil and surface waters on a Defence fire testing area was assessed by URS (2002) and received high to extremely high risk rating (based on the qualitative risk assessment methodology of Australian Standard AS/NZ 4360:1999 "Risk Management"). This risk ranking indicates that the release of AFFF solution and waste-water into the environment requires the attention of senior management and that immediate action is required (URS 2002). Only sampling and analysis of soil and water samples collected from potentially affected Defence land and neighbouring properties will determine if past and current Defence AFFF practices have caused contamination problems.

Although the management of AFFF waste across Defence falls below the best practice of other organisations, in some cases the disposal of AFFF across Defence meet the treatment and disposal regulations set out in the unrevised version of the Manual of Fire Protection Engineering (MFPE, Chapter 15, Annex A, Appendix 3).

This manual stated that:

- AFFF and its components are not considered to be dangerous substances, nor are they harmful to the aquatic environment after proper treatment;
- fluorocarbons are not significant environmental pollutants;
- The toxicity of AFFF can be reduced significantly by bacteria; and
- land treatment is an effective and inexpensive method of stabilising AFFF waste-water (Defence 2000).

Given the findings of this study and current literature, the above statements in the MFPE are currently being revised and aligned with AFFF best practice of other organisations (section 3). The findings in this report are being considered as a part of the MFPE review process.

With the current AFFF product used by Defence no longer being produced, Defence will have to source an alternative product. Although the replacement foam may not have the PFOS/PFOA issues that the current AFFF foam has, it is likely that the replacement foam will have some of the environmental issues discussed in section 3, (e.g. able deplete oxygen from aquatic systems), and therefore appropriate drainage, containment, and disposal of foam waste-water may still require consideration. Selecting a foam with the lowest environmental impact without compromising the standards/fire fighting capability could prove to be difficult due to the lack

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of complete and comparable information. Ideally manufacturers should demonstrate all environmental risks associated with their foam products and the constituents found in these foam products. The replacement foam product needs to meet Defence standards (e.g. DEF(AUST)). While conducting the investigation associated with this report it was discovered that Defence Material Organisation (DMO) are developing new DEF (AUST) standards for AFFF because the current AFFF product used by Defence will no longer be available after December 2003. The findings and recommendations of this report are currently being considered by DMO and may be incorporated into this new DEF(AUST) standard.

Within Defence the responsibility for fire fighting, and fire fighting equipment, materials and standards are widely dispersed, and no organisation has responsibility for the overall coordination of all related activities. According to one report (AMPST1A & STANCOORD 2003), unless a committee is formed (e.g. Defence Fire Fighting and Equipment Committee) to help solve these management issues, the AFFF replacement is heading for crisis management towards the end of 2003.

Currently the best practice for the management and disposal of AFFF containing PFOS/PFOA is yet to be resolved. NICNAS are hoping to provide some management and disposal option in the near future (pers. com. Dr Jane Weder, NICNAS). In the meantime, a recent NICNAS alert released on 30th April 2003 recommends that the AFFF currently used by Defence be restricted to essential use only, and should not be used for fire training purposes (NICNAS 2003). Also NICNAS recommends that up to date information on the safe use and handling of AFFF be supplied to all users.

Findings:

- The management and use of AFFF across Defence facilities falls below the management practices undertaken by other Australian and international organisations.
- In many cases across Defence the AFFF waste-water is being released into the environment, with the potential of AFFF pollutants contaminating soil, surface waters and groundwater on Defence land and neighbouring properties.

(cont. next page)

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Findings (cont.):

- Defence Materiel Organisation (DMO) are currently producing new DEF(AUST) standards in anticipation of a replacement AFFF product. AFFF waste-water handling in Defence is also currently being reviewed for the next amendment of the Manual for Fire Protection Engineering (MFPE). The findings in this report are being considered as a part of the MFPE review process.
- No organisation in Defence has the sole responsibility for the overall coordination of all fire related activities. Unless a committee is formed (e.g. Defence Fire Fighting and Equipment Committee) to help solve these management issues, the AFFF replacement is heading for crisis management towards the end of 2003.
- Best practice for the management and disposal of AFFF containing PFOS/PFOA is yet to be resolved.
- NICNAS released an alert on 30th April 2003 recommending that PFOS/PFOA products such as AFFF be restricted to essential use only, and that AFFF foam should not be used for fire training/testing purposes.

Recommendations:

- Defence should revise its AFFF practices (use/handling/disposal) and aim to meet the best practice of AFFF management methods used by other national and international organisations.
- A detailed investigation into the drainage, containment, and disposal of foam waste-water is required.
- Form a committee (e.g. DFFEC) to help solve fire management issues.
- If environmental and health risks are to be minimised, the AFFF replacement product should not contain PFOS/PFOA. Until a suitable product has been identified some interim measures may need to be undertaken to minimise the release of AFFF that contains PFOS/PFOA to the environment. Where no adequate containment of AFFF is available, AFFF use should be restricted.
- Ensure that Defence is kept up to date with new findings and disposal methods and recommendations (e.g. keep in regular contact with NICNAS).

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6. Conclusion

The information contained in this report indicates that in order for Defence to meet its environmental vision and objectives and minimise environmental risks, Defence will need to revise its AFFF practices and update its infrastructure to adequately manage AFFF waste-water. This includes selecting a suitable product to replace 3M's AFFF product that does not contain PFOS/PFOA, yet does not compromise fire fighting capability aimed at saving life and property. Until a suitable product has been identified, some interim measures may need to be undertaken to minimise the release of AFFF to the environment, such as restricting AFFF use for essential purposes only (within operational requirements).

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Appendix 1: PFOS identity and properties

Chemical name	Perfluorooctane Sulfonate (PFOS)
Molecular formula	C ₈ F ₁₇ SO ₃
Synonyms	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro
	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-1-octanesulfonic acid
	1-Octanesulfonic acid, heptadecafluoro-
	1-Perfluorooctanesulfonic acid
	Heptadecafluoro-1-octanesulfonic acid
	Perfluoro-n-octanesulfonic acid
	Perfluorooctanesulfonic acid
	Perfluorooctylsulfonic acid
Melting point	>40 °C
Boiling point	not calculable
Vapor pressure	3.31x10 ⁻⁴ Pa at 20°C (3.27x10 ⁻⁹ atm)
Air/water partition coefficient in pure water	0 (<2x10 ⁻⁶)
Solubility	pure water - 570mg/L, freshwater - 370mg/L, unfiltered seawater - 12.4 mg/L, filtered seawater - 25mg/L

Source: OECD, 2002

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Appendix 2: AFFF disposal regulations

Commonwealth Legislation

- Airports Act 1996 (Commonwealth)
- Airports (Environment Protection) 1997
- Environment Protection and Biodiversity Conservation Act 1999
- National Environment Protection (Implementation) Act 1988

Australian Standards/Codes/Strategies/Policies etc.

- AS/NZS 4494: 1998 Discharge of Commercial and Industrial Liquid Waste to Sewer – General Performance Requirements
- ANZECC National Strategy for the Management of Scheduled Waste
- ANZECC PCB Management Plan
- ANZECC/ARMCANZ 2000, Australian Water Quality Guidelines
- Draft Waste Avoidance and Resource Recovery Strategy 2002
- Environmental Purchasing Policy (Commonwealth Government)
- Guidance Note for the Storage of Chemicals (NOHSC: 3009 1990)
- National Code of Practice for the labelling of workplace hazardous substances (NOHSC:2012 1994)
- National Model Regulation (NOHSC:1005 1994) and National Code of Practice for the Control of Workplace Hazardous Substances (NOHSC: 2007 1994)
- National Standard (NOHSC:1014 1996) and Code of Practice for the Storage and Handling of Workplace Dangerous Goods (NOHSC:2017 2001)
- National Waste Minimisation and Recycling Strategy
- NHMRC National Guidelines for Waste Management in the Health Industry

Defence Documents

- Defence Environmental Policy Statement (2001)
- Defence Environmental Strategic Plan 2002-2005

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- Defence - The Air Force Environmental Management Handbook (1996)
- FACMAN 2: Management of Fire Protection Engineering, Chapter 20 Annex B
- ADFP 475, Minimum standards of practice for the storage and handling of petroleum oils and products
- DI(AF) AAP 3504.01: Hazardous Goods Management Manual
- DI(AF) PERS 56-6 The Management of Hazardous Wastes and Hazardous Discharges - Environmental Health Aspects
- DEF(AUST) 5603 – Foam, Liquid, Fire Extinguishing; Aqueous Film Forming Foam (AFFF) 6 percent Concentrate Specification
- DEF(AUST) 5639 – Foam, Liquid, Fire Extinguishing; Aqueous Film Forming Foam (AFFF) 3 percent Concentrate Specification

Victoria

- Country Fire Authority Act 1958
- Dangerous Goods (Storage and Handling) Regulations 1989
- Dangerous Goods Act 1985
- Metropolitan Fire Brigades Act 1958
- Environmental Protection (Prescribed Wastes) Regulations 1998
- Environmental Protection Act 1970
- Health Act 1958

New South Wales

- Environmentally Hazardous Chemical Act 1985
- Protection of the Environment, Operations Act NSW 1997
- Water Management Act, NSW 2000
- EPA Environmental Guidelines: Bunding and Spill Management Guidelines(Technical Appendix Bu to the Authorised Officers Manual)
- EPA Environmental Guidelines: Assessment, Classification and Management of Liquid and Non-liquid Waste 1999

Queensland

- Dangerous Goods and Safety Management Regulation 2001

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- Environmental Protection Act 1994
- Environment Protection Regulation 1998
- Fire and Rescue Authority Act 1990
- Health Act 1937
- Health Regulation 1996
- Nature Conservation Act 1992
- Nature Conservation Regulation 1994
- Queensland Environment (Water) Protection Policy 1997
- Rural Lands Protection Act 1985
- Sewage and Water Supply Act 1949
- Waste: Environment Protection (Waste Management) Regulation 2000

South Australia

- Country Fires Act 1988
- Dangerous Goods Regulations 1978
- Dangerous Substance Regulations 1998
- Dangerous Substances Act 1978
- Environment Protection (General) Regulations 1994
- Environment Protection Act 1993
- Environment Protection (Waste Management) Policy 1994
- Local Government Act 1934
- Public and Environment Health Act 1987
- Sewage Act , SA 1929
- Sewage Regulations 1996

Northern Territory

- Public Health Act 1997
- Waste Management and Pollution Control Act 2002
- Dangerous Goods Act 1996
- Fire and Emergency Act 2001

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Western Australia

- Environmental Protection Act 1986
- Metropolitan Water Supply and Sewage and Drainage Act 1909
- Dangerous Goods Regulation 1992
- Explosives and Dangerous Goods Act 1961
- Environmental Protection (Controlled Waste) Regulations 2001
- Health Act 1911
- Environmental Protection (Liquid Waste) Regulations 1996
- Environmental Protection (Diesel and Petrol) Regulations 1999

Australian Capital Territory

- Dangerous Goods Act 1984
- Dangerous Goods Regulations 1978
- Environmental Protection Act 1997
- Environmental Protection Regulations 1997
- Nature Conservation Act 1980
- Water and Sewage Act 2000 ActewAGL Trade Waste Policy
- Water Pollution Act 1984

Tasmania

- Environmental Management and Pollution Control Act 1994
- Dangerous Goods Act 1988
- Sewers and Drain Act 1954
- Fire Services Act 1979

University of South Australia



PROJECT REPORT:

Environmental Fate of New Fire Suppressing Products (Ansulite AFFF & 3M RF) compared to Light Water: A verification of Manufacturer's claims

Prepared for

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4 April, 2006

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List of Acronyms

AFFF: Aqueous Film Forming Foam
CERAR: Centre for Environmental Risk Assessment and Remediation
¹³C NMR: ¹³C Nuclear Magnetic Resonance
DAD: Diode Array Detection
DoD: Department of Defence
ESI: Electron Spray Ionisation
FNMR: Fluorine Nuclear Magnetic Resonance
GC-ECD: Gas Chromatography – Electron Capture Detector
GC-MS: Gas Chromatography-Mass Spectrometry
HPLC-MS: High Performance Liquid Chromatography-Mass spectrometry
(HPLC) MS-MS: Tandem Mass spectrometry
LC: Liquid chromatography
MSA: Mass Spectral Analyses
MS-MS: Tandem Mass spectrometry
OECD: Organisation for Economic Cooperation and Development
POSF: Perfluorooctane sulfonyl fluoride
PFOS: Perfluorinated octane sulfonate
PFOA: Perfluorooctanoic acid
PPFD: Photosynthetic Photon Flux Density
SIM: Selective Ion Monitoring
TTC: 2,3,5-Triphenyltetrazolium Chloride
TPF: Triphenyl Formazan

Glossary

AFFF 3 and 6% concentrates: AFFF 3 and 6% concentrates relates to the AFFF product for 3 and 6% proportioning i.e. 3 and 6% concentrates to be mixed with 97 and 94% water, respectively.

Aliphatic moiety: a continuous (uninterrupted) carbon chain

Aliquot: small portion

Anionic: Compound with negative charge

Amphotoic: Molecule with polar group on one end and non-polar group on the other end

Bioaccumulation: refers to net accumulation over time of the persistent compounds (such as heavy metals or persistent organic compounds) within an organism originating from biotic or abiotic sources.

Detergent: Detergents are molecules that have a hydrophobic (fat loving) tail and a hydrophilic (water loving) head. When detergents are mixed with dirt (or oils) the hydrophobic tail of the detergent binds to the dirt rendering it water soluble.

Emulsion: Emulsion is a mixture of two liquids that are not miscible in one another. When they mixed small particles can be seen under microscope. Oil in water can be an example.

Growth inhibition: Reduction in growth caused by a (chemical) treatment

Neubaur haemocytometer: a device used for counting blood cells. This device is used for counting unicellular organisms such as algae and bacteria.

Surfactant: Many surfactants are linear detergents and lower the surface tension of a liquid (soap is a good example). Surfactants can be fluorinated or non-fluorinated.

Trophic level: Trophic level is the organism's place in the food chain. Thus, green plants including algae (producers) can be distinguished from herbivores (consumers) and carnivores (secondary consumers).

EXECUTIVE SUMMARY

Aqueous film forming foam (AFFF) is an effective and efficient fire suppressing agent used against hydrocarbon fuel fires. Generally, the foam concentrates are supplied as 3% or 6% products to be diluted with 97% and 94% water respectively. The key ingredients of AFFF are mixtures of hydrocarbon and fluorocarbon surfactants, which act as major surface-active components. Of these, perfluorooctane sulfonate (PFOS) is of major environmental concern because of its known persistence, potential to bioaccumulate, while perfluorooctanoic acid (PFOA) has recently come under scrutiny because of its similarity to PFOS. Hence, AFFF products containing PFOS (3M brand) have recently been phased out and PFOA is under international investigation. Ansulite AFFF has been on the market for sometime however claims not to contain PFOS. In addition, a new fire-suppressing product 3M 'RF' has been manufactured by 3M as an alternative to their PFOS-based AFFF. Knowledge about the environmental fate of these products is very important in selecting the right agent, as well as for determining the management required for its use and the best disposal and/or remediation methods. Currently, there is little scientific data regarding the environmental fate and behaviour of AFFF and RF products, and in particular their toxic effects on terrestrial and aquatic environments and on their biodegradability.

The Department of Defence (DoD) is currently in the process of using purchased new fire suppression foams (Ansulite AFFF and 3M RF). Considering the use of these new products and their potential to enter the environment it is important to ensure that the product selected by DoD has well-understood environmental risks that can be effectively managed.

The Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia, was commissioned by the DoD to investigate the potential environmental impacts of Ansulite AFFF and 3M RF products. This report summarises the investigations carried out on the project. Although the focus of this proposal is limited to the fire suppression foams, Ansulite AFFF and 3M RF3, we included 3M AFFF Light Water™ (a PFOS-based product) for comparison.

This investigation evaluated the environmental toxicity and biodegradability/persistency and bioaccumulation of 'Ansulite' AFFF and 3M 'RF' products and compared these to 3M 'Light-Water' (AFFF containing PFOS), verification of supplied manufacturing information and to determine environmental safe levels of the product for disposal. The suite of toxicity tests used in this study included (a) fresh water (*Selenastrum* sp.), and marine (*Dunaliella* sp.) algal growth inhibition assays; (b) water flea (*Daphnia* sp.) survival assay; (c) earthworm survival assay; (d) plant root growth (*Lettuce* sp.); (e) soil algal density and diversity; (f) soil enzyme activity (dehydrogenase); and (g) potential nitrification.

Method development: High performance liquid chromatography- mass spectrometry (HPLC-MS) analytical methods based on finger printing of selected ions that are unique to a product for all the 3 AFFF products (Ansulite, Light-Water and RF) were developed. Also an analytical method based HPLC-MS was developed for PFOS and PFOA.

The salient findings of these studies are:

Chemical characterisation: Determination of fluorine (F) by ion-selective electrode revealed the presence of F in Ansulite (0.21 and 0.41% F in the 6% and 3% dilutions respectively) and Light-Water (1.02 and 2.1% F in 6 and 3% dilutions, respectively) but not in RF products. Furthermore, the presence of F in these products was confirmed, as an independent analytical method, by fluorine- nuclear magnetic resonance (F-NMR). F data indicated that components within Ansulite AFFF contain four distinct groups of F atoms. The molecules within Ansulite AFFF are segmented by spacer groups that are possible sites of hydrolysis (sites of cleavage) in soil and water matrices. PFOS was detected only in 3M Light-Water AFFF but not in Ansulite AFFF or 3M RF products.

These results are consistent with the manufacturer's specifications that Ansulite AFFF does not contain PFOS. No F of any type was detected in 3M RF as revealed by ion-selective electrode and F-NMR data. Therefore 3M RF does not contain any perfluorinated compound which is in accordance with the manufacturer's specification.

Toxicological characterisation: Toxicity assays play an important role in environmental risk assessment of chemicals and are included in the regulatory framework. Exposure (48 hours to 4 weeks depending on the assay) of all the recommended test organisms (freshwater and marine algae; water flea, earthworm and higher plant) representing various trophic levels to Ansulite AFFF (6% and 3% concentrates), 3M RF (6% and 3% concentrates) and 3M AFFF Light-Water (6% concentrate) revealed that the 3M RF product was the most toxic, followed by 3M AFFF Light-Water and then by Ansulite AFFF. Thus, the toxicity ranking was: 3M RF > 3M AFFF Light-Water > Ansulite AFFF. Considering the fact that manufacturing of 3M Light-Water has been phased out, its 6% concentrate was only included in the toxicity testing for comparison. The results of soil microbial activities, as measured by dehydrogenase and nitrification enzyme activities, confirmed results obtained from the bioassay experiments noted above.

Persistence: It is likely that the receiving environments (soils, water, sediments) for fire suppression foams will differ in their physicochemical properties and hence three different soils (neutral, acidic and alkaline), freshwater, marine water and sediments were used in the persistence studies. The results (over 4 weeks) of persistence studies of fire suppression foam in natural soils, sediment and water indicated that Ansulite AFFF and 3M RF are labile and degrade to 90% and 70%, respectively within one week. Both substances persist in sterilised soils and sediments. This suggests that microbial action is a major pathway for degradation of these compounds. Neither PFOS nor PFOA was detected in soils spiked with Ansulite AFFF and 3M RF products. This data contrasts with those of 3M AFFF Light-Water which was persistent in all studied matrices (soils, sediments and water). The disappearance of Ansulite AFFF and 3M RF products (as revealed by HPLC-MS) was mirrored by a disappearance of the toxicity after 4-weeks, as indicated by an algal growth inhibition assay using aqueous extracts of soil. Among the three fire suppression foams, Ansulite AFFF is the least persistent followed by 3M RF, with 3M Light Water being the most persistent.

Environmental risk: Environmental risk is dependent on the receiving environment, the presence of susceptible biota and the toxicant loading. Aquatic systems are usually

more susceptible to damage than terrestrial systems. The results of our studies suggest that Ansulite AFFF is the least toxic and least persistent of all three tested products. No bioaccumulation (of the parent material) was observed in algal and earthworm studies. For example, a loading of greater than 1% (by weight % in soil) Ansulite AFFF is likely to damage biota on spillage. However, these negative impacts are less evident after 6 weeks in soil, although they may be more prevalent in an aquatic environment (depending on dilution). It is highly unlikely that Ansulite AFFF will form PFOS or PFOA (C8 aliphatic fluorinated compounds) from (fluorinated) C4 aliphatic moieties. Indeed, to synthesise PFOS and PFOA from the breakdown products of Ansulite AFFF would require a specific assembly process in the environment using (a diluted source of) small perfluorinated molecules. However, the long-term ecological implications of this product, including its potential to form perfluorinated daughter products other than PFOS/PFOA, need to be investigated.

The studies of three fire suppression foam products were conducted over a short term. Ansulite AFFF is less toxic and less persistent, under the laboratory test conditions, compared to the other two products. A summary of the toxicity, persistence, bioaccumulation and suggested safe disposal levels for all the three AFFF products are given in Appendix B (Tables B1 and B2). These results have not been compared to any established environmental criteria, thus even though RF was evaluated as the most toxic, it means only most toxic when compared to the other 2 products. It should be noted that there are no toxicity guidelines available that are directly relevant to Ansulite AFFF and 3 M RF products. However, based on the overall toxicity data the suggested safe disposal levels for Ansulite AFFF and 3M Light water AFFF are 0.01% dilution in aquatic environment and 0.5% dilution in soil environment, respectively. Where as the suggested safe disposal level for 3M RF AFFF in water and soil environments are <0.007% and 0.5%, respectively.

In summary:

- PFOS was detected in 3M Light Water;
- Of the 2 new fire suppression foams, F is present in Ansulite AFFF but not in 3M RF products, in accordance with manufacturer's specifications;
- PFOS and PFOA were not dedected in Ansulite AFFF and 3M RF products;
- It is highly unlikely that PFOS/PFOA will be formed from Ansulite AFFF;

- Ansulite is the least toxic of all the 3 fire suppression foams;
- Ansulite AFFF is the least persistent of the 3 fire suppression foams.

RECOMMENDATIONS

Based on the short term laboratory studies of toxicity, persistence (4-weeks) and bioaccumulation (of the parent compounds) Ansulite AFFF appears to be the safer product, with the caveat that there should be some further investigation into its potential to form fluorinated persistent end-products. Long-term studies (both laboratory and field) are recommended into Ansulite AFFF chemical characterisation and the fate of any fluorinated end-products of Ansulite that may be created in the environment before it is possible to issue a definitive recommendation on the toxicity and persistence of daughter products. It is recommended that analysis of soil and water samples in spillage and receiving environments where these products have previously been used by DoD is undertaken in order to estimate the likely concentrations and persistence of these products in receiving environments. It is proposed that appropriate (suitable) management strategies and treatment technologies be developed in association with AFFF product usage.

Given the demonstrated toxicity of Ansulite AFFF at 0.5%, one possible management strategy is to contain the outflow of the foam until the foam degrades to safe levels under a suitable treatment or disposal regime, as appropriate.

Environmental Fate of New Fire Suppression Products (Ansulite AFFF & 3M RF) compared to Light Water: A verification of Manufacturer's claims

1 Introduction

1.1 Background

Aqueous film forming foam (AFFF) is an effective and efficient fire suppressing agent used against hydrocarbon fuel fires. AFFF was first developed at a Naval Research Laboratory (USA) in the 1960s. Since then AFFF has been widely used in both military and civilian applications worldwide. Generally, the foam concentrates are supplied as 3% or 6% products to be mixed with 97% and 94% water respectively. Although mostly made of water, the key ingredient of the fire fighting foam solution is a mixture of several chemicals comprising hydrocarbon and fluorocarbon surfactants, which act as major surface-active components. Of these perfluorooctane sulfonate (PFOS) is of major environmental concern due to its toxicity, bioaccumulation and extreme persistence. Animal studies have demonstrated negative effects on liver, pancreas and testes including an increase in risk of liver cancer (OECD, 2002; EPA, 2002; Kudo and Kawashima, 2003). Bioaccumulation of PFOS has been noted in plasma and tissues of a variety of wildlife across the globe (Giesy and Kannan, 2001). Perfluorooctanoic acid (PFOA), formed during electrochemical fluorination synthesis procedure for PFOS, has recently also come under scrutiny because of its similarity to PFOS. As a result, 3M Corporation, the US-based manufacturing company for 3M AFFF, voluntarily phased out manufacture of perfluorooctane sulfonyl fluoride (POSF) derived fluorochemicals for use in its AFFF. These include Light-Water™, a widely used AFFF product containing PFOS. While the manufacturing of PFOS has phased out, PFOA is currently under international investigation. However, areas contaminated with both these compounds are likely to exist in Australian Defence sites due to past use of AFFF products. A potential therefore exists for the release of these agents into the environment. There has been increasing awareness (Giesy and Kannan, 2001; OECD, 2002; EPA, 2002; Kudo and

Kawashima, 2003) among the public about the environmental impact of such chemicals.

Knowledge of the environmental fate of these fire suppression foam compounds is very important in selecting the right product, as well as for determining the most effective disposal and/or remediation methods. There is currently a paucity of scientific information about the environmental fate and behaviour of fire suppression foam products, in particular their toxic effects on terrestrial and aquatic (including marine) biota, and their biodegradability and stability.

The Department of Defence (DoD) is currently in the process of using fire suppression foams (Ansulite AFFF and 3M RF) and is currently investigating a number of manufacturing claims in addition to whether the Ansulite AFFF product excludes PFOS or PFOA constituents. Investigations also include whether Ansulite AFFF constituents transform into PFOA and that 3M RF excludes perfluorinated compounds (PFOS/PFOA). Considering the future use of these new products and their potential to enter the environment it is important to ensure that the product selected by the DoD has known environmental risks and that these risks can be properly managed. This project has focussed on assessing and comparing the environmental impacts of the supplied products viz., Ansulite AFFF and 3M RF, and on developing analytical methods suitable for these chemicals.

The Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia was commissioned by the Department of Defence to investigate the environmental impacts of two fire suppressing products, Ansulite AFFF and 3M RF, supplied by the DoD.

This report presents the findings of CERAR's investigation into the persistence (biodegradation), bioaccumulation, environmental toxicity and verification of manufacturer's claims, of the DoD supplied fire suppression foam products. The main objectives of this project are given below.

1.2 Objectives

The main objectives of this investigation are to generate Australia-specific knowledge of the environmental impacts of the two supplied products, Ansulite AFFF and 3M RF (in both concentrated and dilute form) on aquatic and terrestrial environments and to verify the manufacturer's supplied data. These environments were considered because fire suppression foam products may be used in Australia in close proximity to water bodies. The specific objectives included:

- To determine the toxicity of Ansulite AFFF and 3M RF on aquatic (freshwater) organisms such as alga and daphnia;
- To determine the toxicity of Ansulite AFFF and 3M RF on marine organisms (such as marine alga);
- To determine the toxicity of Ansulite AFFF and 3M RF on soil biota and their key activities in soil;
- To determine the biodegradability and persistence of Ansulite AFFF and 3M RF in soil and water (both freshwater and marine) systems;
- To determine the potential for bioaccumulation in aquatic organisms;
- To determine environmentally safe levels of the supplied products, AFFF and RF3, in a receiving environment; and
- To verify manufacturer's claims.

1.3 Scope of the work

The focus of this proposal was limited to the supplied new fire suppression foams viz., Ansulite AFFF and 3M RF. 3M AFFF Light-WaterTM (PFOS based product) was included for comparative purposes. The work included:

- Chemical characterisation of the three fire suppression foam products (Ansulite AFFF, 3M AFFF Light-WaterTM and 3M RF);
- Analysis of the fluoride content of fire suppression foam products by using a fluoride electrode and Fluorine-NMR;
- Analytical method development for PFOS and PFOA using HPLC-MS;

- Analytical method development for all the three fire suppression foam products using HPLC-MS;
- Chemical characterisation using HPLC/MS-MS, GC-MS, GC-ECD and ^{13}C -NMR;
- Toxicological assessment of the three fire suppression foam products, including both 3% and 6% concentrates (except 3M AFFF Light-Water 3%), by using:
 - (a) Freshwater algal growth inhibition assays;
 - (b) Marine algal growth inhibition assays;
 - (c) Lettuce root elongation assays;
 - (d) Water-flea survival assays;
 - (e) Earthworm survival assays;
 - (f) Soil enzyme activities (dehydrogenase, potential nitrification) ; and
 - (g) Soil algal density and diversity studies.
- Measurements of the potential for bioaccumulation of fire suppression foam products in algae and earthworms; and
- Determination of persistence of the three fire suppression foam products in soils (slightly acidic, neutral and alkaline), sediments (freshwater and marine) and water (fresh and marine).

2 Materials and Methods

2.1 Fire suppression foam products

The three fire suppression foam products, 3% and 6% (Ansulite AFFF, 3M AFFF Light-WaterTM and 3M RF) were supplied by the DoD. The chemical compositions of these products are given in Table 1. All other chemicals (analytical standards of PFOS, PFOA, hexafluoroglutarate, diethyleneglycol monobutylether, sodium fluoride, sodium metal, agar and nutrient media) used in this investigation were purchased from Sigma-Aldrich Ltd. unless otherwise stated.

2.2 Soils, sediments and water

Three soils (moderately acidic, neutral and alkaline), two sediments (freshwater and marine) and two waters (freshwater and marine) were used in this study. Particulars of these matrices are given in Table 2.

2.3 Analytical Methods

2.3.1 Chemical characterisation – Fluoride analysis by fluoride electrode

Fire suppression foam products (1.0 ml of each) were added to ignition tubes (Fortuna^R) and the liquids were dried on a heating block at 140 °C. Diethyl ether-washed sodium metal (ca. 200 mg as excess) was then added to each cooled ignition tube, which was then heated over a bunsen flame until the sodium became molten. The red-hot ignition tube was then quickly immersed in cold Milli-Q water (15 ml, 25 °C) and the pH of the resultant solution was adjusted to between pH 4 and pH 6 with glacial acetic acid (ca. 250 µl). A standard dilution series of sodium fluoride (from 0 ppm to 100 ppm) was prepared in Milli-Q water and pentadecafluorooctanoic acid ammonium salt was used as a recovery standard at 7.9 mg and 11 mg. A fluoride-specific probe (I.C.I. instruments, ICI 611) was then used to measure the milli-volt response of standard solutions, recovery standards and samples. Fluoride concentrations were then calculated from the standard curve. The standard curve was linear over the concentration range 0 to 100 mg/L sodium fluoride. Greater than 90% of the fluorine was recovered from the pentadecafluorooctanoic acid ammonium salt recovery standard.

2.3.2 Chemical characterisation – Fluoride analysis by Fluorine nuclear magnetic resonance (FNMR)

Fire suppression foam products (Ansolite AFFF and 3M RF, both 3% concentrates) were acidified to pH 1.8 with phosphoric acid and then extracted into diethyl ether (3 x 200 ml). The combined ethereal extracts were dried at 60 °C (water bath) in a fume cupboard and subjected to FNMR.

2.3.3 Chemical characterisation – Carbohydrate analysis

A total carbohydrate analysis (phenol-sulphuric acid) was performed in a qualitative assessment of the fire suppression foam concentrates. Briefly, phenol (500 μ l, 5%) and fire suppression foam concentrate (500 μ l). The test tube was allowed to cool, after the exothermic reaction, for 5 minutes and the contents were mixed. Positive controls (100 mg, glucose) and Milli-Q water 'blanks' were also analysed.

2.4 Fire suppression foam persistence studies

The environmental persistence of most chemicals is primarily governed by the microbial activity in the receiving environment. Hence, the role of microorganisms in the stability of fire suppression foam products was studied in sterilized and non-sterilized soils and water (freshwater and marine) microcosms. Fire suppression foam concentrates and their products were extracted from soil and water samples at different time intervals. These were then analysed using either gas chromatography-mass spectrometry (GC-MS) or Liquid chromatography- mass spectrometry (LC-MS).

2.4.1 Preliminary soil - study

A preliminary persistence study was conducted in a neutral soil (Table 2) with the three fire suppression foam products (6% concentrates). Fire suppression foam concentrate (50 μ l) was added to a purge and trap vial (40 ml volume) containing 10 g soil (10 % moisture). The vial was sealed and the contents were thoroughly mixed by inversion to a paste consistency. Test vessels and controls (containing no fire suppression foam) were then placed in the dark at constant temperature (25 °C). Each vessel was opened periodically (every 2 days) and then re-sealed to prevent the development of anaerobic conditions in the soil. The experiment was terminated after 4 weeks incubation. Freshly spiked soils were then prepared in the same manner as above and extracts of the soils were analysed by high performance liquid

chromatography-mass spectrometry (HPLC-MS) and gas chromatography-mass spectrometry (GC-MS).

2.4.2 Soils and sediments

Following the preliminary experiment, the persistence of the three fire suppression foam products (3% concentrates of Ansulite AFFF, 3M AFFF Light-Water and 3M RF) was studied by using 3 soils differing in their physico-chemical properties (moderately acidic, neutral and alkaline; Table 2) and two sediments (freshwater and marine). The experiment was conducted in duplicate and each product was spiked at a final concentration of 1% (volume by weight of soil) in the receiving matrix (soil or sediment) (300 g soil placed in 1 L glass jars). The soils and sediments were maintained at 70% water holding capacity by adding appropriate amounts of distilled water. Sterilised (autoclaved) soils and sediments were spiked with fire suppression foam products and served as abiotic controls. The unspiked soil and sediment served as blank controls. All the treatments and controls were incubated at room temperature (20 ± 1 °C) for 4-weeks. At designated intervals (weekly), a 10 g soil or sediment sample was withdrawn from each jar and the chemical extracted and analysed by HPLC-MS and GC-MS.

2.4.3 Persistence study – water

In order to study the persistence of fire suppression foam products in fresh and marine waters, water was spiked with fire suppression foam concentrates (3%) at a final concentration of 0.01% (vol/vol). Samples were then incubated at room temperature. Unspiked water served as blank while sterile water spiked with fire suppression foam served as abiotic controls. Duplicate water samples were withdrawn at weekly intervals (for 4-weeks) for extraction and analysis of fire suppression foam contents.

2.5 Extraction of surfactants from fire-fighting foams

2.5.1 Background and rationale

Perfluorooctane sulphonate (PFOS) is a principal (detergent) component in 3M AFFF 'Light-WaterTM', a fire-fighting foam, and its structure is shown below.

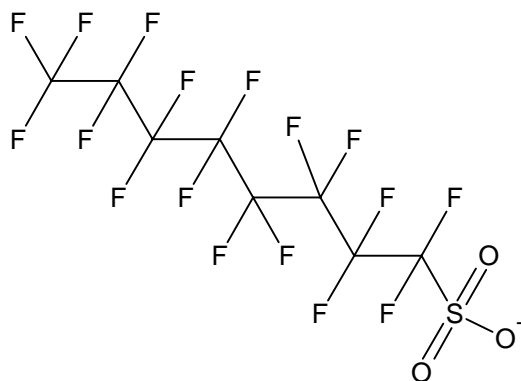


Figure A. Perfluorooctane sulphonate (PFOS) at pH 7

PFOS is a linear and perfluorinated hydrocarbon. At neutral pH the molecule is negatively charged and in acid solutions it is neutral and hydrophobic as shown in Figure B. Hydrophobic compounds adsorb to hydrophobic surfaces such as commercially available C18 SepPak^R cartridges. The hydrophobic portions of PFOS and PFOA are fat soluble and the polar head group (sulfonyl) is water soluble, thereby conferring detergent-like activity on PFOS and PFOA.

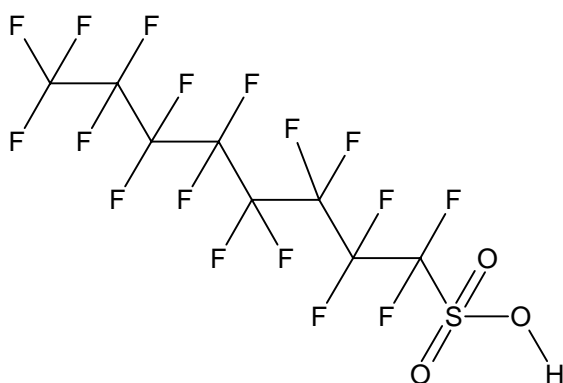


Figure B. Perfluorooctane sulphonate (PFOS) in acid solution

It is possible to concentrate these hydrophobic molecules by passing a solution of them through a commercially available hydrophobic cartridge (Sep Pak^R C18). The sorbed hydrophobic chemicals can then be eluted from the Sep Pak^R C18 cartridge, as a concentrated solution, by using a small volume of methanol. It was reasoned that 'Ansulite AFFF' and '3M RF' would contain chemicals with similar physicochemical properties to those found in '3M AFFF Light-Water'. A common extraction method was therefore developed based on the principles discussed above.

2.5.2 Extraction of anionic detergents from soil matrices

A solvent mixture (1:1 vol./vol., ethyl acetate:methanol containing 7% orthophosphoric acid; 23 ml) was added to soil (10 g) in a glass vessel fitted with a screw-capped Teflon-coated lid. The mixture was shaken for 2 hours in an end-over-end shaker and centrifuged (500 g, 20 min.). An aliquot (15 ml) of the supernatant was filtered (0.22 µm Teflon filter) and diluted six times with Milli-Q water (80 ml). The acid (pH 2.4) extract was then passed through an activated SepPak^R C18 cartridge on a Vac Elut manifold apparatus. The sorbed analytes were washed by passing 4 ml of 10% acetic acid through the cartridge. Analytes were eluted from the cartridge by using methanol (2 ml). Samples were then analysed by high performance liquid chromatography with mass spectral detection (HPLC-MS).

2.5.3 Extraction of anionic detergents from water matrices

Ethyl acetate, methanol and orthophosphoric acid were added to a filtered water sample (100 ml) in the same proportions as were described above (in section 2.5.2). The acid (pH 2.4) solution was then passed through an activated SepPak^R C18 cartridge and the sorbed analytes were washed by passing 4 ml of 10% acetic acid through the cartridge. Analytes were eluted from the cartridge by using methanol (2.5 ml). Samples were then analysed by high performance liquid chromatography with mass spectral detection (HPLC-MS).

2.5.4 Extraction of anionic detergents from algal pellets

A solvent mixture (1:1 vol/vol., ethyl acetate:methanol containing 7% orthophosphoric acid; 23 ml) was added to algal pellets in a glass vessel fitted with a screw capped Teflon coated lid. The mixture was sonicated and centrifuged (500 g, 20 min.). An aliquot (15 ml) of the supernatant was filtered (0.22 µm Teflon filter) and diluted six times with Milli-Q water (80 ml). The acid (pH 2.4) extract was then passed through an activated Sep Pak^R C 18 cartridge on a Vac Elut manifold apparatus. The sorbed analytes were then 'washed' by passing 4 ml of 10% acetic acid through the cartridge. Analytes were eluted from the cartridge by using methanol (2 ml). Samples were analysed by high performance liquid chromatography with mass spectral detection (HPLC-MS).

2.5.5 Extraction of anionic detergents from earthworm tissues

Frozen (liquid nitrogen) worm tissues (ca. 2 g) were pulverized using a mortar and pestle. A solvent mixture (1:1 vol./vol., ethyl acetate:methanol containing 7% orthophosphoric acid; 23 ml) was then added to the powdered worm tissue in a glass vessel fitted with a screw capped Teflon coated lid. The mixture was shaken in an end-over-end shaker for 2 hours and centrifuged (20 min. 500 g). An aliquot (15 ml) of the supernatant was filtered (0.22 µm Teflon filter) and diluted six times with Milli-Q water (80 ml). The acid (pH 2.4) extract was then passed through an activated SepPak^R C18 cartridge on a Vac Elut manifold apparatus. The sorbed analytes were washed by passing 4 ml of 10% acetic acid through the cartridge. Analytes were eluted from the cartridge by using methanol (2 ml). Methanol extracts were centrifuged (6000 g, 10 min.), to remove proteinaceous material, and then analysed by HPLC-MS.

2.6 Liquid chromatography (LC) - Electrospray Ionization Mass Spectrometry for the separation and detection of fluorinated surfactants

Separation and mass spectral detection of the chemical components in AFFF products was achieved with an Agilent 1100 series LC/MSD (Agilent Technologies, USA). A diode array detection (DAD) system was connected in-line with an electron spray ionisation (ESI) interface. LC separation of surfactants (key ingredients of AFFF) was carried out with a Zorbax C₈ column (C₈, 5 µm, 150×4.6 mm, Agilent Technologies, USA). A linear gradient was used for the separation of anionic and amphoteric surfactants on the C₈ column. The program started with 10% “A” [(10% MeOH, 5 mM NH₄Ac, 0.1% HAc (v/v))] at 3 min and the concentration was changed linearly to “B” [(90% MeOH, 5 mM NH₄Ac, 0.1% HAc (v/v))] within 12 min. The composition then remained constant for 15 minutes as “B”. The overall flow-rate was adjusted to 0.8 ml min⁻¹, 10 µl of standard solutions or extracts were injected onto the column.

A Mass spectrometer controlled by a working station (ChemStation) was used for detection. The following conditions were used for ESI: vaporizer temperature, 350 °C; capillary temperature, 180 °C. Capillary voltage was operated at 3 kV. Gas pressure was operated at 35 Pa and the dry gas flow was 12 l/min. Full scan from 50-600 m/z was used for the detection of analytes (Schroder, 2003).

2.6.1 High Performance Liquid Chromatography with Mass Spectral Detection (HPLC-MS) and Tandem Mass Spectrometry (MS-MS)

Two modes were used. In the first, diluted samples of the three AFFF products (Ansolite, Light-Water and RF) were monitored for their characteristic negative ion mass fragmentation patterns. Positive ion spectra proved complex (signal-to-noise ratio was not optimal for data interpretation and further investigation) and were not further investigated. The initial ions targeted were those identified as significant from the preliminary LC-MS work. Both continuous flow and flow injection techniques were employed. The flow injection conditions were as follows: Column: 25 cm (column length), 4.6 mm (column width), 5 µm C-18; Mobile phase: Gradient of 10%

5 mM ammonium acetate in methanol to 90%; 5 mM ammonium acetate in methanol; run time: 30 min at 0.4 ml/min. MS-MS was conducted under standard run conditions in accordance with normal operating procedures for the instrument.

2.6.2 Data processing of fire fighting foams: High Performance Liquid Chromatography with Mass Spectral Detection

Data (1200 MB) comprising mass spectral (MS) and diode array (DAD) outputs were collected on ChemStation^R software. ‘Selective ions’ were extracted manually from the raw MS data [scan mode from 50 to 600 atomic mass units (a.m.u)] and then transferred into Excel^R. The selective ions were *unique* to each fire fighting foam formulation and each ion chromatographed at a *unique* retention time. Retention times of ions that differed (in the 35-minute HPLC run) by more than 4 seconds from those in the quality controls were rejected. These stringent parameters permitted the collection of MS data that was specific for each technical grade fire fighting foam. Quantitation (Mass of unknown calculated relative to the mass of a standard by using the same ions) was achieved by comparing the cumulative areas associated with selective ions, of each technical grade, to data obtained by standard additions. The ‘scan mode’ MS analyses (described above) of fire fighting foams has now permitted the development of an automated ‘selective ion monitoring’ (SIM) HPLC-MS technique.

2.7 Toxicological Assays

Toxicity assays play an important role in environmental risk assessment of chemicals and are included in the regulatory framework. Bioavailability plays a major role in risk assessment of chemicals as total concentrations of chemicals alone are not sufficient to establish risk. The bioavailable fraction of chemicals gives a more realistic indication of the risk posed to biota. A chemical has to be bioavailable to an organism in order to cause an effect. Contaminants rarely occur as single compounds but often occur as mixtures in contaminated environments. Fire suppression foam is made up of a mixture of chemicals with surfactants being the main ingredients. Chemical analysis alone of these mixtures provides no indication of synergistic toxic effects that may affect organisms.

Toxicity is a direct measure of the bioavailability of chemicals and toxicological assays are therefore used in environmental risk assessment. Since no test species is consistently sensitive to all contaminants, a battery of toxicity assays comprising different organisms is required for toxicological assessment of chemicals (Megharaj et al., 2000). Toxicity testing of discharges into the aquatic system has become an integral part of the regulatory framework in the USA for protection of water bodies (Dorne, 1996). Data from these studies assists in risk characterisation and decision making about possible remediation measures. The toxicity of fire suppression foam concentrates (Ansulite and RF) at the concentrations recommended for end use (concentrates of 3% and 6%) was tested on soil and aquatic organisms. Considering the fact that the manufacturing of Light-Water (PFOS based product) has been phased out, we included its 6% concentrate in toxicity testing for comparison. However, toxicity testing of Light-Water was not the focus of this study.

Information about the toxicity of fire suppression foam products to aquatic and terrestrial organisms is necessary in order to make sound decisions about the management of these foam products. The following toxicity assays, which are routinely used for risk assessment of chemicals/effluents, were used in this case:

- (a) freshwater algal growth inhibition assays;
- (b) marine algal growth inhibition assays;
- (c) root elongation assays;
- (d) water-flea survival assays;
- (e) earthworm survival assays;
- (f) algal density and diversity in soils;
- (g) dehydrogenase activity in soils; and
- (h) potential nitrification in soils.

2.7.1 Freshwater algal growth inhibition assay

A freshwater algal growth inhibition assay was conducted using a freshwater green alga *Raphidocelis subcapitata* (formerly known as *Selenastrum capricornutum*). *R. subcapitata* growth inhibition, an assay sensitive to a variety of chemicals, is widely used for toxicity assessment of contaminated sediments and waters (Greene et al.,

1988; Joner et al., 2004). The algal growth inhibition assay (acute toxicity) was performed by exposing the axenic culture of the alga to fire suppression foam dilutions prepared in the algal growth medium following the standard methods. Axenic culture of *Raphidocelis subcapitata* was maintained in OECD-recommended growth medium (OECD, 1984), under continuous illumination at 25 °C in an orbital shaker set at 100 rpm.

Portions of sterile growth medium containing various (0 – 0.5%: v/v) concentrations of fire suppression foam product placed in sterile culture flasks were inoculated with exponentially-growing cultures of *R. subcapitata*. Controls containing only growth medium and alga were included in the test. The test vessels were incubated in a temperature-controlled (25°C) orbital shaker set at 100 rpm under continuous illumination [200 µE/m²/sec PPFD (Photosynthetic Photon Flux Density)] provided by cool white fluorescent lamps. At the end of 120 hours, the growth of the alga in terms of cell count in a Neubaur haemocytometer was estimated using a phase-contrast microscope (Megharaj et al., 2000). Growth inhibition of the alga was used as the end point in this bioassay. All the assays were conducted in triplicate.

2.7.2 Marine algal growth inhibition assay

The marine algal growth inhibition assay was conducted using the marine green alga, *Dunaliella tertiolecta* following standard procedure. The alga was grown in F/2 marine algal culture medium (Guillard, 1975). Exponentially growing *D. tertiolecta* cells were exposed to a dilution series of fire suppression foam product prepared in growth medium and incubated under continuous light in a temperature-controlled illuminated incubator as described above (in section 2.7.1) for freshwater algal assay. The test was conducted in triplicate and untreated medium inoculated with alga served as the control. Growth inhibition was assessed in terms of cell numbers measured using a Neubaur haemocytometer. The test duration was 120 hours.

2.7.3 Root elongation assay

Seedling emergence and root elongation assays are recommended by USEPA for toxicity screening of hazardous waste sites (Greene et al., 1988). Root elongation is generally considered sensitive to toxicants and root elongation assays have been widely used in risk assessments (Linder et al., 1990; Wang, 1991). This root elongation test used lettuce seeds with 5 ml of water or dilutions of test solution prepared in sterile water placed in petri dishes. After 7 days, the root length was measured in mm. Tests were conducted in triplicate with 10 seeds per each replicate.

2.7.4 Water-flea survival assay

Water-flea acute toxicity testing was performed according to OECD guidelines for the testing of chemicals (OECD, 2000), with slight modifications. The test organisms were *Daphnia carinata*, a freshwater crustacean (invertebrate) of less than 24 hour old (neonates). These Daphnia were cultured in commercial mineral water (20% in Milli-Q water) with *R. subcapitata* as food source. The Daphnia survival test was conducted in 30 ml volume of water or dilutions of the test solution in water at a temperature of 21 ± 1 °C with a 16 hours light and 8 hours dark cycle and a light intensity of 1000 lux. The test was conducted in triplicate with 5 organisms per replicate.

2.7.5 Earthworm Survival assay

Earthworm survival assay was performed by using *Eisenia foetida* according to Norton (1996b). Earthworms (ten) were added to soils (spiked with different concentrations of fire suppression foam products, 0-12% vol/weight and unspiked soils served as controls) placed in 1 L wide mouthed glass jars. The mortality of the earthworms was recorded after 4 weeks. All assays were conducted in triplicate.

2.7.6 Algal density and diversity in soil

The effect of fire suppression foam products on algal populations in soil was assessed using neutral soil (Mawson Lakes soil, South Australia). The soils (20 g) were placed

in 50 ml culture tubes and spiked with various concentrations of fire suppression foam ranging from 0-12% (vol/weight). Soils were maintained at 70% water holding capacity. Unspiked soils served as controls. The treatments and controls were incubated at room temperature ($20 \pm 1^{\circ}\text{C}$) under diffuse light. At the end of incubation period (45 days after spiking) the duplicate soil samples were withdrawn for estimation of algae by most probable number (MPN) method and algae were identified to the genus level (Megharaj et al., 1986).

2.7.7 Dehydrogenase (DHA) Analysis

Dehydrogenase activity (DHA), is a measure of total microbial activity in soils and is considered useful in assessing the harmful effect of metals on microorganisms (Ohya et al., 1988; Obbard et al., 1994). Field-moist soil samples were used for DHA measurement using well-established methods based on the dehydrogenation reaction of 2,3,5-triphenyltetrazolium chloride (TTC) to triphenyl formazan (TPF) by microbial dehydrogenases (Casida et al., 1964).

Soils (5 g of neutral soil) placed in 50 ml culture tubes were spiked with fire suppression foam products at concentrations ranging from 0-12 % (vol/weight) and incubated at room temperature (21°C) in darkness. Unspiked soils served as controls. At designated time intervals (2 weeks and 6 weeks) treatments and controls were withdrawn for dehydrogenase activity measurements. DHA activity was determined in triplicate. Each sample (5 g) was treated with 0.05 g CaCO_3 and incubated in the dark with 3% (w/v) TTC (1 ml) at 37°C for 24 hours. After 24 hours incubation the produced TPF was extracted with methanol and the optical density of the supernatant measured at 485 nanometers (nm) wavelength. The extracted TPF was quantified from a calibration curve prepared from standard solutions of TPF in methanol. Total DHA activity was expressed as $\mu\text{g TPF g}^{-1}$ of dry sample.

2.7.8 Potential nitrification

Soil samples treated as above (2.6.7) were assessed for potential nitrification at 2 weeks and 6 weeks incubation after the initial treatment. At the end of the incubation period soils were amended with a solution of ammonium sulfate along

with sodium chlorate to inhibit further oxidation of nitrite to nitrate. The samples were shaken for 5 hours and extracted using a potassium chloride solution. The supernatant was then analysed for its nitrite content (Kandeler, 1996).

3. Results

3.1 Chemical characterisation

Fluorine analysis: Determination of fluorine by ion selective electrode revealed the presence of fluorine in Ansulite AFFF (0.21 and 0.41% F in 6 and 3% concentrates respectively) and 3M AFFF Light-Water (1.02 and 2.1% F in 6 and 3% concentrates, respectively) but not in 3M RF products (Table 3). FNMR results indicate that Ansulite AFFF concentrate contains fluorine while the 3M RF concentrate contains no fluorine. The integrated peak areas and the chemical shift data suggest that a perfluorinated linear (aliphatic) compound may be present within the Ansulite AFFF product. The FNMR results are consistent with the detection of fluoride using a Fluoride-specific electrode.

It is concluded that fluorine is present in Ansulite AFFF and Light Water and is absent in 3M RF. Additionally, there are different groups of fluorine atoms present within Ansulite AFFF that are distinct from Light Water. This means that fluorinated compounds within Ansulite AFFF are different to those of Light Water.

Mass Spectral Analyses (MSA): The acidified ethereal extracts obtained from the Ansulite AFFF and 3M RF products were also analysed by MS. The mass spectrum of Ansulite AFFF concentrate contains a series of ions that differ by 100 a.m.u. with m/z values of 432.2, 532.2, 632.2, 732.2, 832.2 and possibly 932.2, 1032.2. The ions may have been derived from the parent molecules by successive losses of C_2F_4 units that have an m/z value of 100 a.m.u.

It is concluded that fluorine within Ansulite AFFF is arranged as C_2F_4 units (100 a.m.u for each unit).

Carbohydrate analysis: The 3M RF product is likely to contain substantial amounts of carbohydrate while 3M AFFF Light-Water contains little carbohydrate. This was deduced after comparing the colour-development with the positive controls and the blanks. It is particularly noteworthy that the Ansulite AFFF product provided a *dark bronze* coloured solution rather than the 'black' carbohydrate-positive colour obtained by the positive controls and 3M RF product.

It is concluded that 3M RF would be more degradable than Light Water since carbohydrate can serve as a source of nutrient to the microorganisms.

Analytical method for fire suppression foam products: The HPLC-MS analytical method is based on the selected unique ions listed in Table 4. The chromatograms showing the total ion extraction with selected ions for all the three fire suppression foam products are shown in Appendix A. The selected ions provide a unique fingerprint for each fire suppression foam product. The selected ions unique to Ansulite AFFF were 238, 366, 380 and 472. The identity of PFOS in 3M AFFF Light-Water was verified by using PFOS standard (m/z 499). PFOS was not detected in either Ansulite AFFF or 3M RF products. Another selected ion in Light-Water was also identified as perfluoro hexane sulfonate (m/z 399). The selected ions detected in 3M RF were 325, 482 and 532. PFOA (m/z 413) was not detected in any of the three products.

It is concluded that the selective ions, that are distinct from those present in soil and water matrices, for each fire fighting foam product can be used for detection and quantitation of parent compounds.

Persistence study - Soils: The results indicate that more than 95% of the Ansulite AFFF was degraded within one week in all the tested soils (Figure 1). Based on these data it is also likely that the half life of Ansulite AFFF is less than one week in the studied matrices. These data contrast with those of the 3M AFFF Light-Water, which persisted under the same experimental conditions (Figure 2). The degradation of the 3M RF product more closely resembled that of Ansulite AFFF, with a loss of more than 50% within one week (Figure 3). There was no appreciable degradation in all the

fire suppression foam products from sterilised soils suggesting a microbial role in the degradation process.

Persistence study - Sediments: More than 85% of Ansulite AFFF was degraded within one week within freshwater sediment (Figure 4). These results contrast with those of Ansulite AFFF in marine sediment in which 30% was degraded within the same time period. Additionally, the Ansulite AFFF product did not show any appreciable degradation during the remaining study period. The data contrasts with that of 3M AFFF Light-Water which persisted under the same experimental conditions (Figure 5). The degradation of the 3M RF product more closely resembled that of Ansulite AFFF with a loss of more than a 50% within one week (Figure 6). However, the observed persistence of Ansulite AFFF over 3M RF in marine sediment was likely caused by the stimulation of the sparse microbial growth by carbohydrate present in the 3M RF product. There was no appreciable decrease in the fire suppression foam products within sterilised sediments.

Persistence study - Water: More than 95% of the Ansulite AFFF was found to have degraded within one week in freshwater (Figure 7). These results contrast with Ansulite AFFF in marine water where only 28% was degraded in the same time period. The Ansulite AFFF product showed complete degradation in freshwater during the remaining study period by 4-weeks. The data contrast with those of 3M AFFF Light-Water which persisted (85% remaining) under the same experimental conditions (Figure 8). The degradation of the 3M RF product was similar to that of Ansulite AFFF with more than an 80% loss within one week in freshwater and complete loss within two weeks (Figure 9). The degradation of 3M RF product in marine water was slower at week 1 with a subsequent decreases (to 20%) in the remaining experimental period. No degradation of Ansulite AFFF and 3M RF was observed in sterilized waters.

It is concluded that of the new fire fighting foams, Ansulite AFFF is less persistent than 3M RF in soil, sediment and water matrices. It is likely that freshwater contains more microbial activity than marine water since Ansulite AFFF and 3M RF degraded more readily in freshwater. The half-lives (time taken to degrade half of the original material) of Ansulite AFFF and 3M RF were less than one week. Light Water is the

most persistent of the 3 fire fighting foams in all tested matrices. The decrease in persistence of the fire fighting foams was caused by microbial activity.

Results of GC-ECD analyses suggested that electroactive compounds are present in Ansulite AFFF treated soils that were incubated for 30 days. Results of GC-MS analyses suggested that perfluorinated aliphatic compounds are present in the soils that contained Ansulite AFFF. These data suggest that some perfluorinated (degradation products) compounds, other than PFOS and PFOA, may have been formed during degradation of Ansulite AFFF.

3.2 Toxicological analysis

The environmental impact of potential toxicants is usually assessed through toxicity experiments in which selected test organisms are exposed to the test chemical. Toxicity tests included both aquatic (freshwater and marine algal growth inhibition, water flea survival) and terrestrial (higher plant root elongation, soil algal density and diversity, earthworm survival, soil enzyme activity). For aquatic toxicity testing the test dilutions of fire suppression foam products (commercial concentrates) used ranged from 0.0075%-0.5% vol/vol basis. Preliminary experiments for aquatic toxicity showed that a concentration of 0.5% was lethal in most cases. For terrestrial toxicity testing the final test concentration in the soils ranged between 0.5% - 12% vol/weight basis. For soil experiments 0.5% is close to a realistic application considering a 3% dilution is used on the soil and the dry soil can hold 20% moisture). However repeated applications can result in higher (>0.5%) concentrations. These concentrations are expected to cover normal usage regimes. The purpose of these experiments was to find the safe level at which there was no observable effect and also the acutely toxic concentration for the various test organisms.

Freshwater algal growth inhibition assay: Raphidocelis subcapitata, a freshwater unicellular green alga commonly used for toxicity testing of freshwaters, was used in this assay. The effect of various dilutions of fire suppression foam products both 3% and 6% concentrates on the growth of *R. subcapitata* are shown in figures 10 and 11. The 3M RF product was found to be the most toxic of the three products. Both Ansulite AFFF and 3M Light-Water AFFF were non-toxic to the alga at 0.0075%

dilution (both 3 and 6% concentrates of Ansulite AFFF and of 6% concentrate of Light Water-AFFF). The 3M RF6 product at the same dilution inhibited algal growth by nearly 85%. A progressive decrease in growth was observed with increasing concentrations of all the foam products. 3M Light-Water AFFF was more toxic than Ansulite AFFF and both were highly toxic to the alga at a 0.5% dilution of the 6% product concentrates, with 90% growth inhibition shown by Ansulite AFFF and 96% inhibition by 3M Light-Water AFFF. Both 3% concentrates of Ansulite and RF were found to be lethal to the alga at a dilution of 0.5% (Figure 11). It is concluded that 3M RF formulation is the most toxic, to fresh water alga, followed by Light Water and then Ansulite AFFF

Marine algal growth inhibition: Both 6% and 3% concentrates of the 3M RF product were lethal to the marine alga, *D. tertiolecta* at 0.015% dilution (Figures 12 and 13). The 3% concentrate of Ansulite was more toxic to the alga than the 6% concentrate. A 3% concentrate of Ansulite was toxic to the alga at 0.062% dilution but the 6% Ansulite AFFF was non toxic to alga at the same dilution. The 3% and 6% concentrates of Ansulite AFFF were lethal to the alga at 0.125% and 0.25% dilutions respectively. The observed results were similar to fresh water alga with Ansulite AFFF being the least toxic of the three fire fighting foams.

Root elongation assay: Milli-Q™ water (clean water) was used as a control for the seed germination and root elongation assays used to establish germination efficiency. Germination of lettuce seeds was >95 per cent in control. Root growth did not show appreciable inhibition from exposure to all 6% concentrates of the three fire suppression foam products up to 0.062% dilution. In fact Ansulite AFFF stimulated root growth at 0.015 and 0.031% dilutions (Figure 14). The toxicity ranking of the three products was, in order: Light-Water > RF > Ansulite.

Water flea survival assay: 3M RF exhibited higher toxicity to the water flea (*Daphnia carinata*) than did 3M Light-Water and Ansulite AFFF (Figures 15 and 16). Thus 3M RF 3% concentrate was lethal to the water flea even at 0.0075% dilution. Ansulite AFFF 3% concentrate was lethal to the water flea at 0.125% dilution in contrast to the 6% concentrate which was lethal at 0.25% dilution. In general Ansulite

AFFF was found to be the least toxic to *Daphnia*, followed by 3M Light-Water AFFF and 3M RF.

Effect on soil algae: The effect of varying levels (0-6%) of 3% fire suppression foam concentrates on viable count estimates of algal populations and their diversity in soil 45 days after treatment are presented in Tables 5 and 6. 3M Light-Water AFFF was highly toxic to the indigenous algal populations in soil resulting in complete loss of algae at even a 1% dilution. Ansulite AFFF was non-toxic to the algae at 0.5% dilution whereas a 1% dilution greatly reduced the algal populations. In contrast to aquatic toxicity studies, the RF product was found to be less toxic to the native algal populations in soil, with no toxicity observed up to 3% dilution. Thus the toxicity, from highest to lowest, followed the order: Light-Water > Ansulite > RF. The species composition of algae in the control and fire suppression foam-treated soils is presented in Table 6. There were a total of six genera of algae present in the control (unspiked) soil. Only one of the six algal genera was present in 3M Light-Water AFFF spiked soil while two of six were present in Ansulite AFFF spiked soil. 3M RF did not affect the species diversity up to 1% dilution, while at 3% only two genera out of 6 were present. This clearly suggests that the 3M RF product can decrease the species diversity at dilutions of 3% and above, even though there was no effect on the density of algal populations at 3% dilution.

Earthworm survival: All three fire suppression foam concentrates were non-toxic to earthworms at 0.5% loading (vol/weight) whereas a loading of 1% and greater resulted in 100% mortality with 3M RF treatment (Figures 17 and 18).

Dehydrogenase activity: Dehydrogenase activity, a measure of total microbial activity, was enhanced by the Ansulite product up to 3% loading at the end of 15 days and 45 days incubation periods (Figures 19 and 20). There was no significant difference in microbial activity between the control, Ansulite AFFF and 3M RF at a 0.5% loading in the 15 days incubation study. However, the microbial activity of 3M RF and 3M Light-Water AFFF treatments decreased equally within 1-12% loading in the same study. Interestingly, microbial activity increased with the 3M RF product at 1-3% loading in the 45 days incubation study. This suggests that the microorganisms are actively using the 3M RF degradation products as a nutrient source.

Potential nitrification: There was no appreciable inhibitory effect on potential nitrification in soil spiked with all 3 fire suppression foam products at the end of 15 days. However, higher loadings (>1%) decreased the nitrification process in soil (Figure 21). In a 45 days incubation period there was also no appreciable inhibitory effect on potential nitrification activity in soil (Figure 22). It is noteworthy that 3M Light-Water AFFF and 3M RF had a negative impact on nitrification activity beyond 1% loading, while absolutely no activity was detected at a 12% loading.

Bioaccumulation in earthworms and algae: Bioaccumulation refers to net accumulation over time of the persistent compounds (such as heavy metals or persistent organic compounds) within an organism originating from biotic or abiotic sources. Only 3M Light-Water AFFF bioaccumulated in earthworms and algae (Table 7). Bioconcentration factors were calculated on the basis of fire suppression foam content in test organisms relative to the surrounding matrix (soil or water). The bioconcentration factor for earthworms was 3.8. (In comparison, bioconcentration factors for algae were 315 for marine alga (*D. tertiolecta*) and 270 for freshwater alga (*R. subcapitata*) respectively.) The AFFF concentrate Ansulite did not bioaccumulate on the basis of the presence of *all selected ions*. However, one unique ion (m/z 472) was present in tissues of treated worms. While the parent compound did not bioaccumulate some compound(s) related to the parent compound *may* have accumulated in worm tissue. This may require further investigation with regards to the identity and fate of daughter products.

Test for residual toxicity in fire suppression foam pretreated soils after 45 days incubation: In order to confirm whether there was any residual toxicity remaining in soils that were pretreated with fire suppression foam products (Ansulite, 3M Light-Water and 3M RF) the soils (20 g) were extracted with 20 ml of OECD algal growth medium and the extracts were then subjected to an algal growth inhibition assay using by *R. subcapitata*. Freshly spiked soils and unspiked control soils were also extracted with algal growth medium and subjected to algal growth inhibition assay as described in section 2.7.1. The results of this assay are shown in Figure 23. No toxicity was observed in the soil extracts from Ansulite AFFF and 3M RF treated soils after 45 days of incubation, in contrast to freshly spiked soil extracts that were acutely toxic.

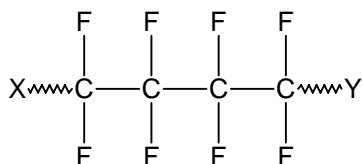
In fact algal growth was stimulated in the soil extract from 3M RF treated soil (after 45 days incubation). Extracts from soils spiked with 3M Light-Water AFFF were toxic to alga irrespective of incubation time, suggesting the persistence of toxic compounds in this product. These data suggest that the Ansulite AFFF and 3M RF products degraded to non toxic levels within 45 days as assessed by algal bioassay.

4 Discussion

Persistence studies of fire suppression foam in unsterilised soil, sediment and water indicated that Ansulite AFFF and 3M RF are labile and degraded to 10% and 30%, respectively, within one week. However, Ansulite AFFF and 3M RF persisted in sterilised soils and sediments. This suggests that microbial action is the main pathway for degradation of these compounds. However, the degradation of both Ansulite AFFF and 3M RF products was slow in marine water and sediments, compared with the freshwater environment. This can be ascribed to the presence of higher microbial activity in freshwater and sediment compared to marine water and sediment. In fact, marine sediment did not show any measurable organic carbon. The observed persistence of Ansulite AFFF over 3M RF in marine sediment was likely caused by the stimulation of the sparse microbial growth by carbohydrate present in the 3M RF product. Neither PFOS nor PFOA was detected in soils spiked with Ansulite AFFF and 3M RF products. This data contrasts with those of 3M Light-Water AFFF which was refractory in all studied matrices (soils, sediments and water). The disappearance of Ansulite AFFF and 3M RF products (as revealed by HPLC-MS) was mirrored by a disappearance of toxicity as revealed by an algal growth inhibition assay using aqueous extracts of soil (Figure 23). The persistent 3M Light-Water AFFF product served as a positive control, retaining its toxicity at 45 days.

The results of fluorine analysis revealed the presence of fluorine in Ansulite AFFF and 3M Light-Water AFFF but not in 3M RF. Therefore it is unlikely that 3M RF will form PFOS (fluorinated surfactants). However, Ansulite AFFF contains nearly 5 times less fluorine than 3M Light-Water AFFF and no PFOS. The results of tandem mass spectrometry (MS-MS) data suggests that Ansulite AFFF contains fluorine within an aliphatic structure with repeat units of C_2F_4 . This is consistent with a mass

difference of 100 a.m.u. between several ions within the mass spectrograms which is supported by FNMR data. The generalized structure is given below.



Where 'X' and 'Y' are unknown. X and Y represent unknown parts of the molecular structure. However, X *may* be equivalent to Y. The curved bond represents an unknown bonding between parts of molecular structure.

If there are 7 losses of C₂F₄ units from the parent molecule then the original structure may have contained 7 x C₂F₄ or C₁₄F₂₈.

There are some common structural features associated with chemicals in the 3M RF product. This is supported by the presence of a common (terminal) mass fragment of 97 (98) a.m.u. in mass spectrograms. These data are consistent with a polymeric structure within the 3M RF product. Nuclear Magnetic Resonance (¹³C NMR) confirmed the presence of diethyleneglycol butyl ether, previously detected by GC-MS, in Ansulite AFFF, 3M Light-Water AFFF and 3M RF. The GC-ECD analyses of the extracts obtained from doped soils (30 day incubated) suggested the presence of electroactive (F, Cl, Br, I) compounds when Ansulite is degraded. The substantial amount (c.a. 90%) of diethyleneglycol butyl ether in samples prevented the derivation of detailed structural information relating to other minor components in the fire fighting foams.

Exposure of the recommended test organisms (freshwater and marine algae; water flea, earthworm, higher plant) representing the various trophic levels to Ansulite AFFF (6% and 3% concentrates), 3M RF (6% and 3% concentrates) and 3M Light-Water AFFF (6% concentrate) revealed that the 3M RF product was the most toxic, followed by 3M Light-Water AFFF followed by Ansulite AFFF. Thus, toxicity followed the rank order: RF > Light-Water > Ansulite. The results of soil microbial

activities, as measured by dehydrogenase and nitrification activities, confirmed results obtained from the bioassay experiments noted above.

However after 45 days incubation 3M RF treated soils (at 0.5 and 1% loading) were not toxic to indigenous algal populations and had no effect on species composition. Ansulite AFFF (at 0.5% loading) did affect the species composition. 3M Light-Water AFFF at 0.5% resulted in complete elimination of algae.

Based on the overall toxicity data the suggested safe disposal levels for Ansulite AFFF and 3M Light water AFFF in are 0.01% dilution in aquatic environment and 0.5% dilution in soil environment, respectively. Where as the suggested safe disposal level for 3M RF AFFF in water and soil environments are <0.007% and 0.5%, respectively.

Environmental risk is dependent on the receiving environment and the loading. Aquatic systems are likely to be more susceptible to damage than terrestrial systems. Our study suggests that Ansulite AFFF is least toxic of all three tested products. For example a 1% or higher loading of Ansulite AFFF concentrate is likely to damage biota on spillage. The negative impacts will be less evident in soil after 6 weeks but are likely to be more prevalent in an aquatic environment (depending on dilution). It is unlikely that Ansulite AFFF will form PFOS or PFOA (C8 aliphatic compounds) from (fluorinated) C4 aliphatic moieties. However, the long-term ecological implications of this product including its potential to form perfluorinated daughter products other than PFOS/PFOA needs to be investigated. It is therefore, recommended that DoD consider long-term studies of the Ansulite AFFF product in addition to developing management strategies for the use and disposal of this product and potential treatment technologies.

5. Conclusions

A summary of the toxicity, persistence, bioaccumulation and suggested safe disposal levels for all the three AFFF products are given in Appendix B (Tables B1 and B2). The results of the present investigation suggests that Ansulite AFFF is the least toxic

and least persistent fire suppression foam product. However, its potential to form fluorinated byproducts (other than PFOS and PFOA) requires further investigation.

In summary:

- Of the 2 new fire suppression foams, F is present in Ansulite AFFF but not in 3M RF products, in accordance with manufacturer's specifications;
- PFOS and PFOA were not detected in Ansulite AFFF and 3M RF products;
- It is highly unlikely that PFOS/PFOA will be formed from Ansulite AFFF;
- Ansulite is the least toxic of all the 3 fire suppression foams; and
- Ansulite AFFF is the least persistent of the 3 fire suppression foams.

6. Management Strategies

Based on the short term laboratory studies of toxicity, persistence (4-weeks) and bioaccumulation (of the parent compounds) Ansulite AFFF appears to be the least toxic product, with the caveat that there should be some further investigation into its potential to form fluorinated persistent end products. Long-term studies (both laboratory and field) are recommended into Ansulite AFFF chemical characterisation and the fate of any fluorinated end-products of Ansulite that may be created in the environment before it is possible to issue a definitive recommendation on the toxicity and persistence of daughter products. It is recommended that analysis of soil and water samples in spillage and receiving environments where these products have previously been used by DoD is undertaken in order to estimate the likely concentrations and persistence of these products in receiving environments. It is proposed that appropriate (suitable) management strategies and treatment technologies be developed in association with AFFF product usage.

Given the demonstrated toxicity of Ansulite AFFF at 0.5%, one possible management strategy is to contain the outflow of the foam until the foam degrades to safe levels under a suitable treatment or disposal regime, as appropriate.

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Table 1. Chemical composition (%) of AFFF product concentrates

Chemical	Ansulite 3%	Ansulite 6%	Light-Water 3%	Light-Water 6%	RF 3%	RF 6%
Water	70-80	75-85	50-60	75-85	<80	<80
Diethyleneglycol monobutylether	14	7.9	30-40	10-20	5-10	5-10
Propylene glycol	2-3	1.2				
Amphotoric perfluoroalkyl surfactant	<2	<1				
Non-ionic perfluoroalkyl- thio-surfactant	<0.5	<0.5				
Synthetic alkylsulfate surfactants (primarily C8 and C10)	1-2	1-2				
Alkyl polyglycoside surfactant	1-2	1-2				
Magnesium sulfate heptahydrate	1-2	0.5-1.5				
Tolytriazole	0.03	0.02				
Fluoroalkyl surfactants			1-7	1-5		
Synthetic detergents			1-6	1-5		
Residual organic fluorochemicals			nd	nd		
Surfactants					<5	<5
Detergents					<5	<5
Emulsifiers					8-12	8-12

nd; not determined

Table 2. Selected properties of soils and waters

Location	Soil/water i.d	pH	EC (uS/m)	Organic carbon (%)	Sand	Silt	clay
Mawson Lakes	Neutral	6.87	63.3	1.9	47.0	37.4	15.5
Kersbrook	Acidic	6.2	29.5	3.6	46.5	36.75	16.5
Wakefield	Alkaline	8.5	163.1	2.1	77.8	12.8	9.4
Willowbrook	Freshwater sediment	7.7	445	1.5	87.5	9.0	3.5
Henley Beach	Marine sediment	8.9	2280	nd	99.0	0	1.0
Willowbrook	Freshwater	7.7	1553				
Henley Beach	Marine water	8.5	67320				

nd; not detected

Table 3. Fluoride analysis of AFFF products

AFFF product	Fluoride concentration (% weight/vol)
Ansulite 6%	0.21 ± 0.05
Ansulite 3%	0.41 ± 0.04
Light-Water 6%	1.02 ± 0.19
Light-Water 3%	2.10 ± 0.49
RF 3%	nd
RF 6%	nd

nd; not detected

Table 4. Selected ions unique to AFFF products

AFFF product	Ion (m/z)			
Ansulite	238	366	380	472
Light-Water	399	499		
RF	325	482	532	

Table 5. Effect of AFFF products (6% concentrates) on algal populations [Most Probable Number (MPN) x 10³ g⁻¹ dry soil] in soil

AFFF concentration (%)	soil MPN x 10 ³	95% confidence limits	
		Upper	Lower
Untreated	25.3	46.4	13.7
Ansolite			
0.5	21.5	39.6	11.7
1.0	4.2	6.9	<4.0*
3.0	0	0	0
Light-Water			
0.5	<4.2	<6.9	<4.0
1.0	0	0	0
3.0	0	0	0
RF			
0.5	21.5	39.6	11.7
1.0	25.3	46.4	13.7
3.0	21.5	39.6	11.7

*Calculation of the exact lower fiducial limit (at 95%) was not feasible as only <4 culture tubes were scored positive for algae out of 30 tubes.

Table 6. Qualitative occurrence of algae in AFFF treated (6% concentrates) and untreated soils

organism	control	Ansolite (%)			Light-Water (%)			RF (%)		
		0.5	1.0	3.0	0.5	1.0	3.0%	0.5	1.0	3.0
					%					
<i>Chlorella</i> sp.	+	-	-	-	-	-	-	++	+	-
<i>Chlorococcum</i> sp.	++	++	-	-	-	-	-	+	++	+
<i>Euglena</i> sp.	++	-	-	-	-	-	-	++	+	-
<i>Scenedesmus</i> sp.	++	-	-	-	-	-	-	+	+	-
<i>Stichococcus</i> sp.	++	-	-	-	-	-	-	+	+	-
Green unicell*	++	++	+	-	+	-	-	+	+	+

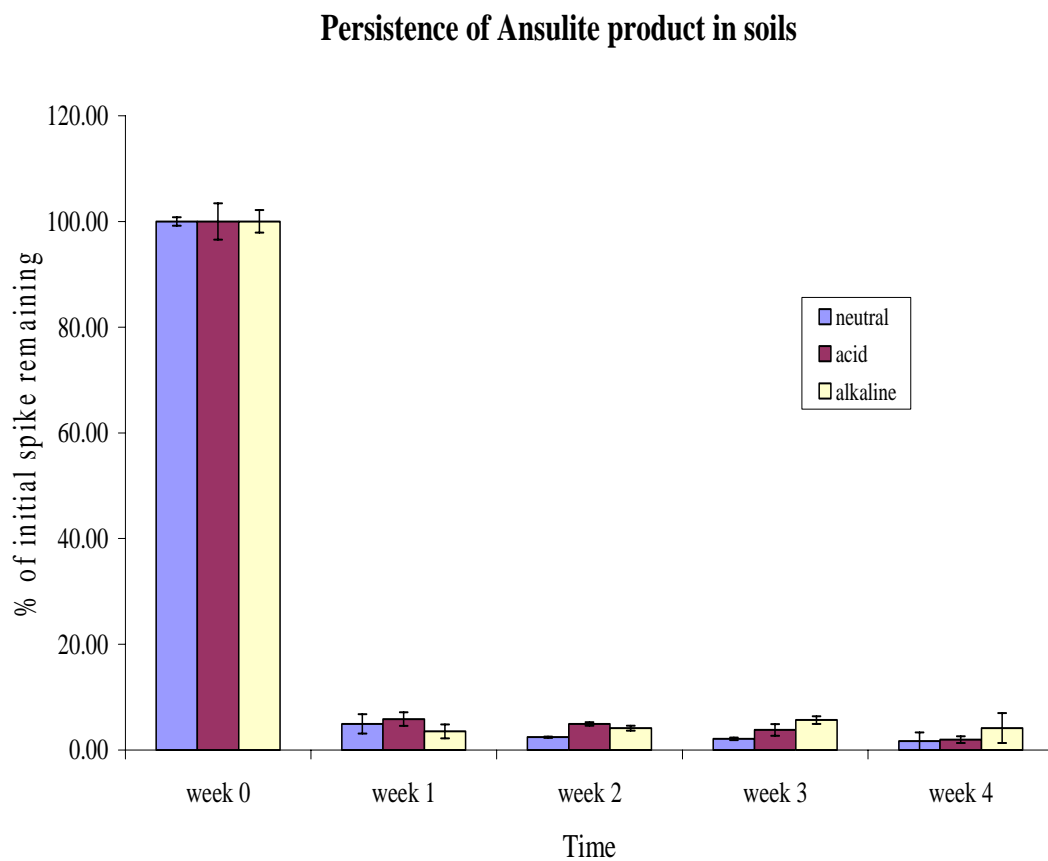
-, absent; +, common; ++, abundant

* unidentified green unicellular alga

Table 7. Bioaccumulation factor for fire-fighting foams in earthworms and algae

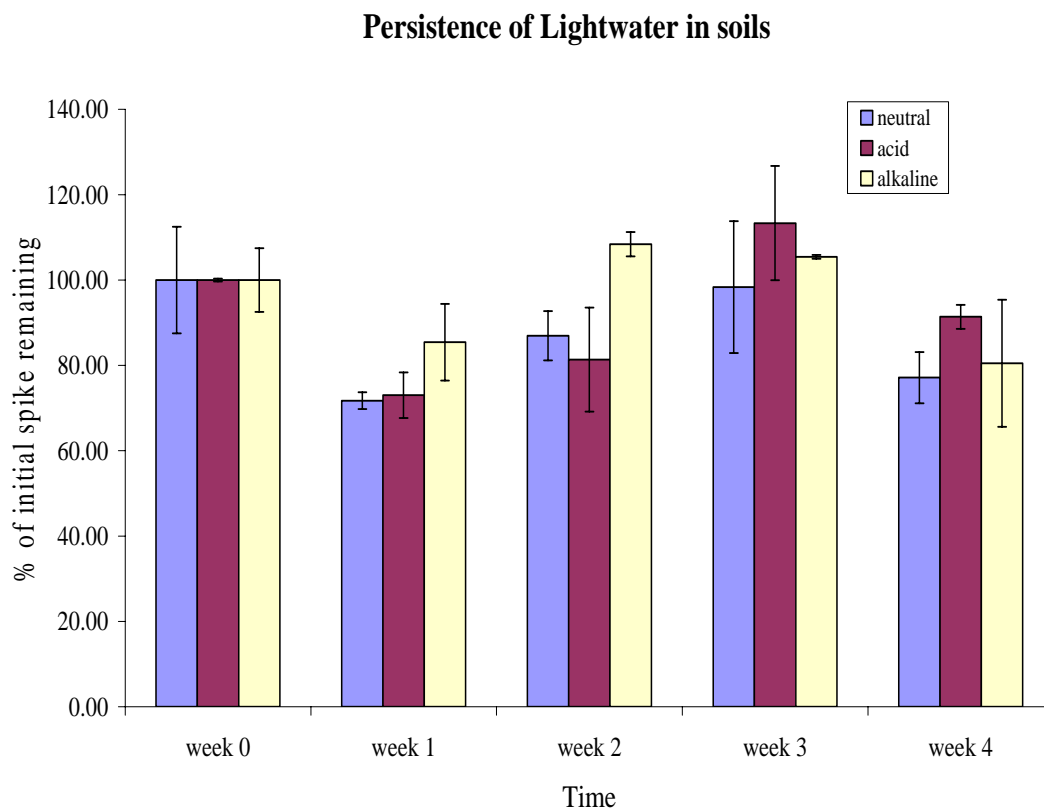
	Ansulite	Light-Water	RF
Earthworm			
<i>E. faetida</i>	0	3.8	0
Algae			
<i>R. subcapitata</i> (freshwater)	0	270	0
<i>D. tertiolecta</i> (marine)	0	315	0

Figure 1. Persistence of Ansulite product in soils



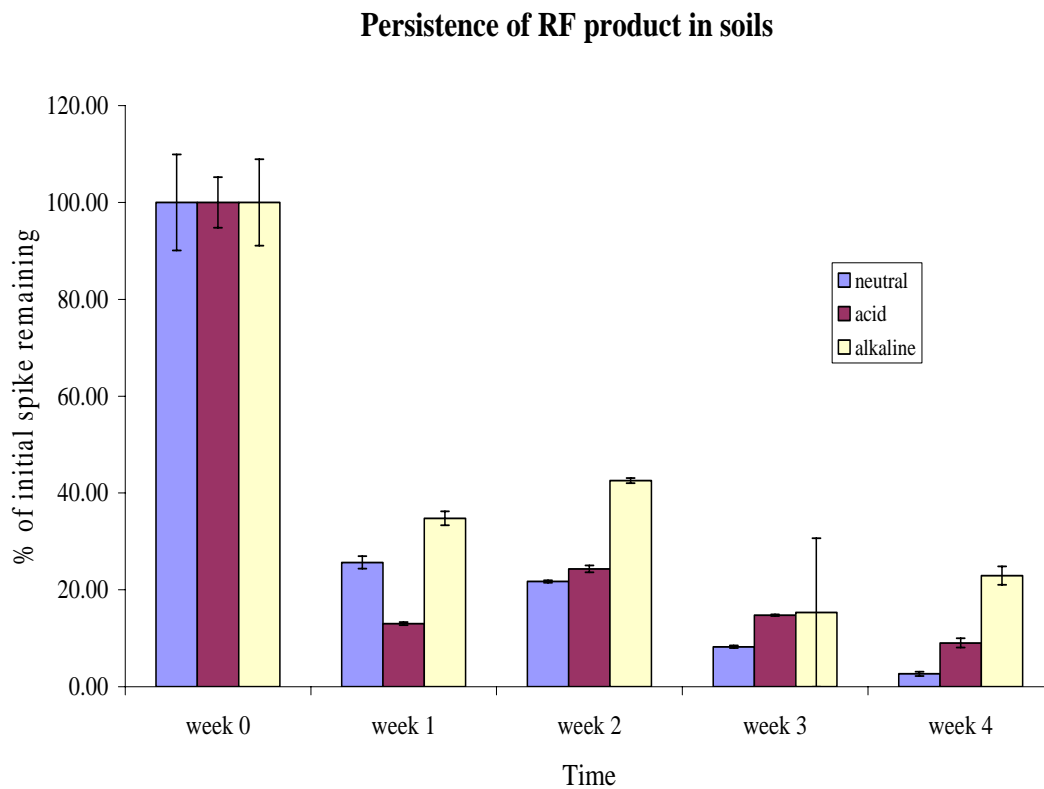
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 2. Persistence of Light-Water product in soils



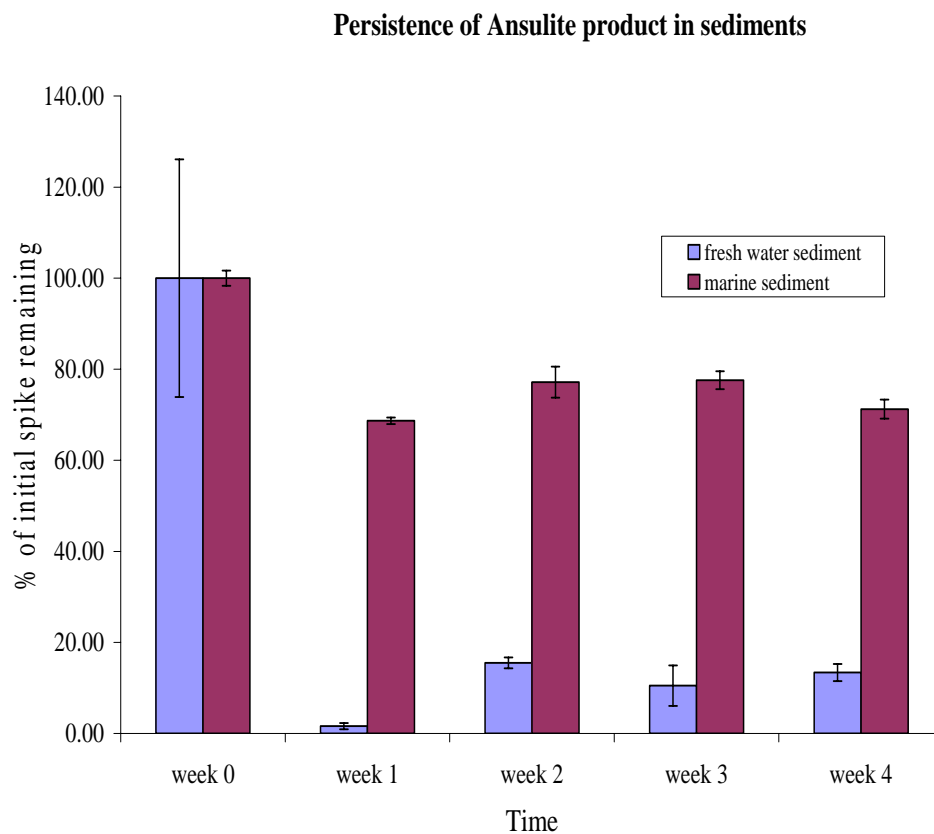
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 3. Persistence of RF product in soils



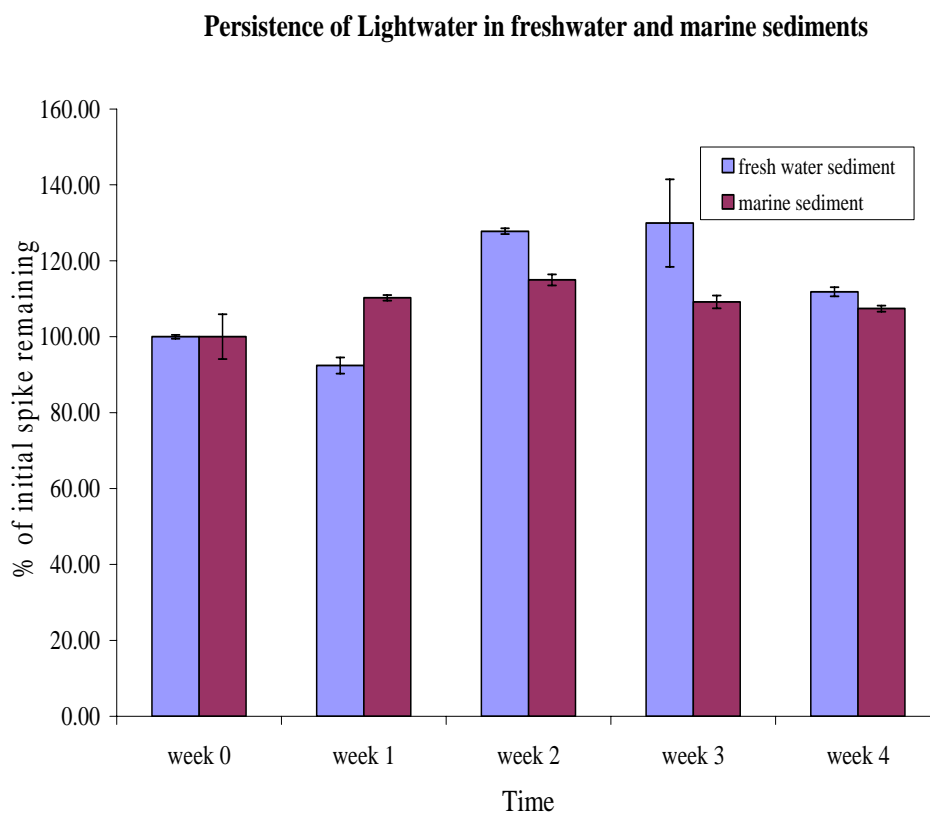
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 4. Persistence of Ansulite product in sediments



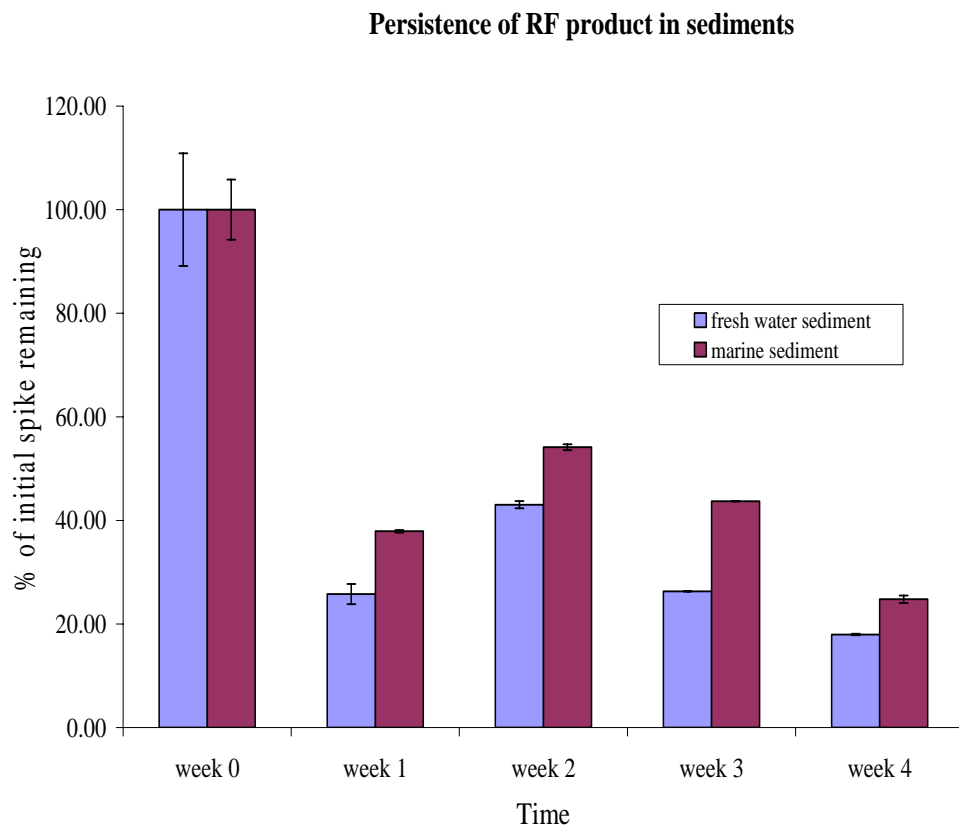
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 5. Persistence of Light-Water product in sediments



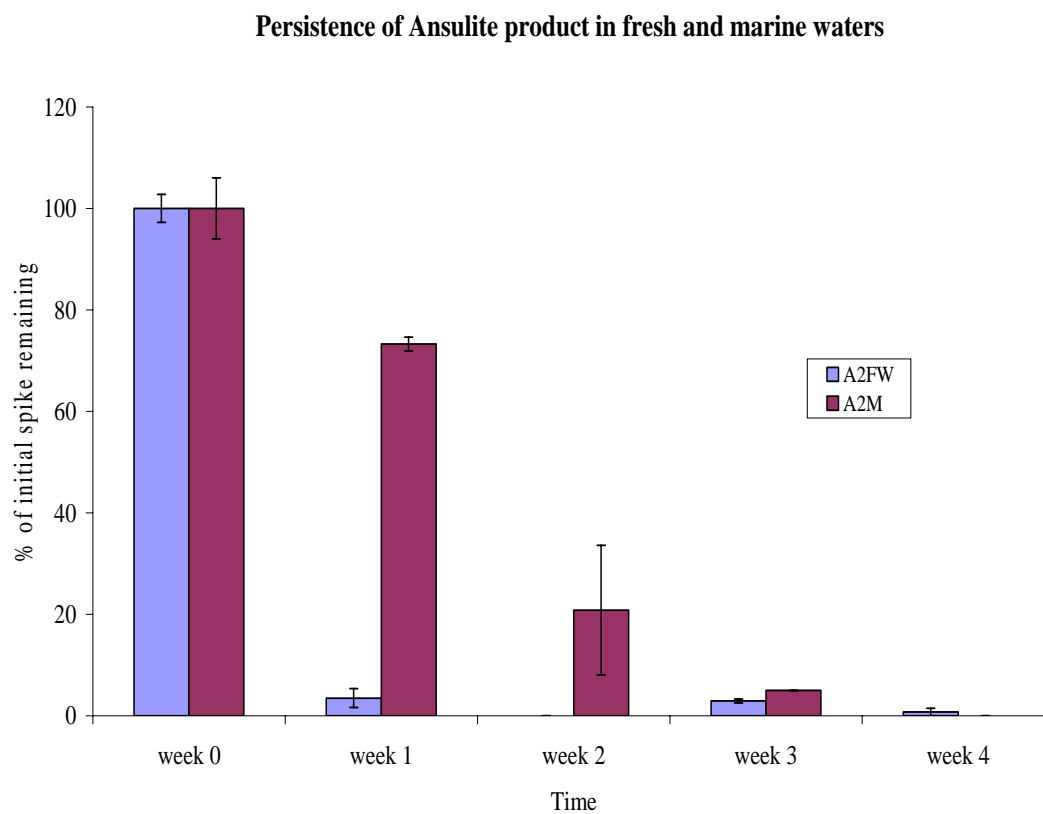
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 6. Persistence of RF product in sediments



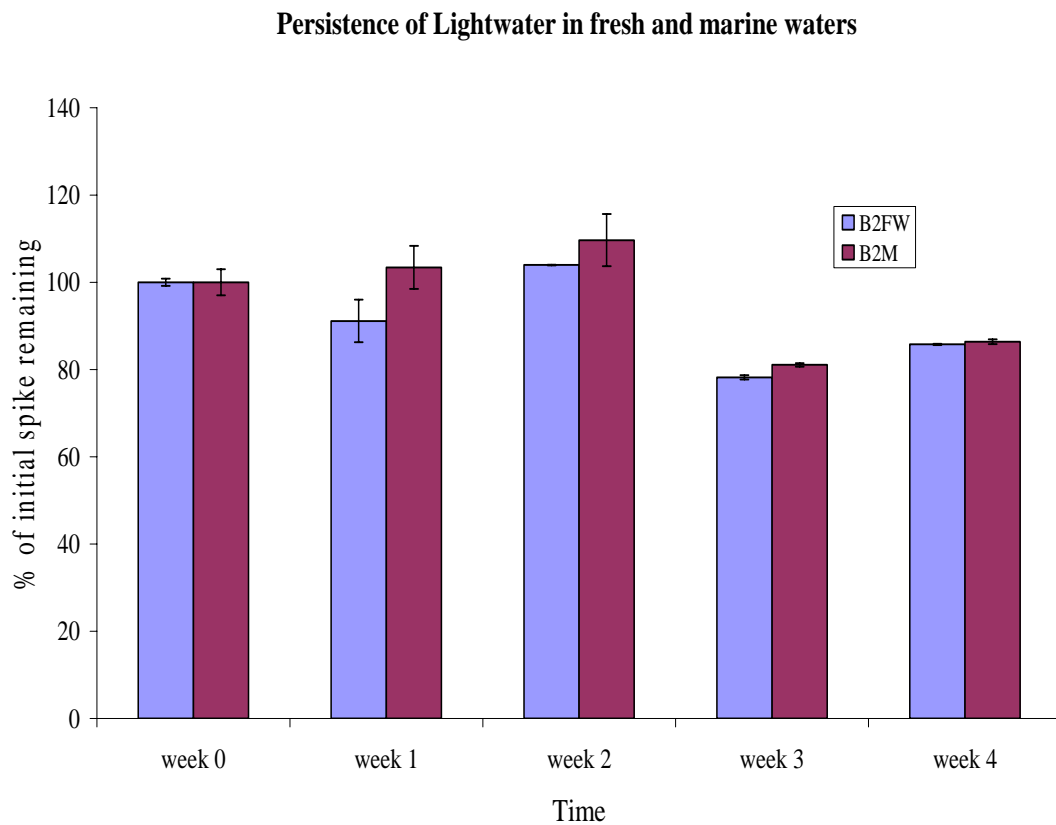
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 7. Persistence of Ansulite product in fresh and marine waters



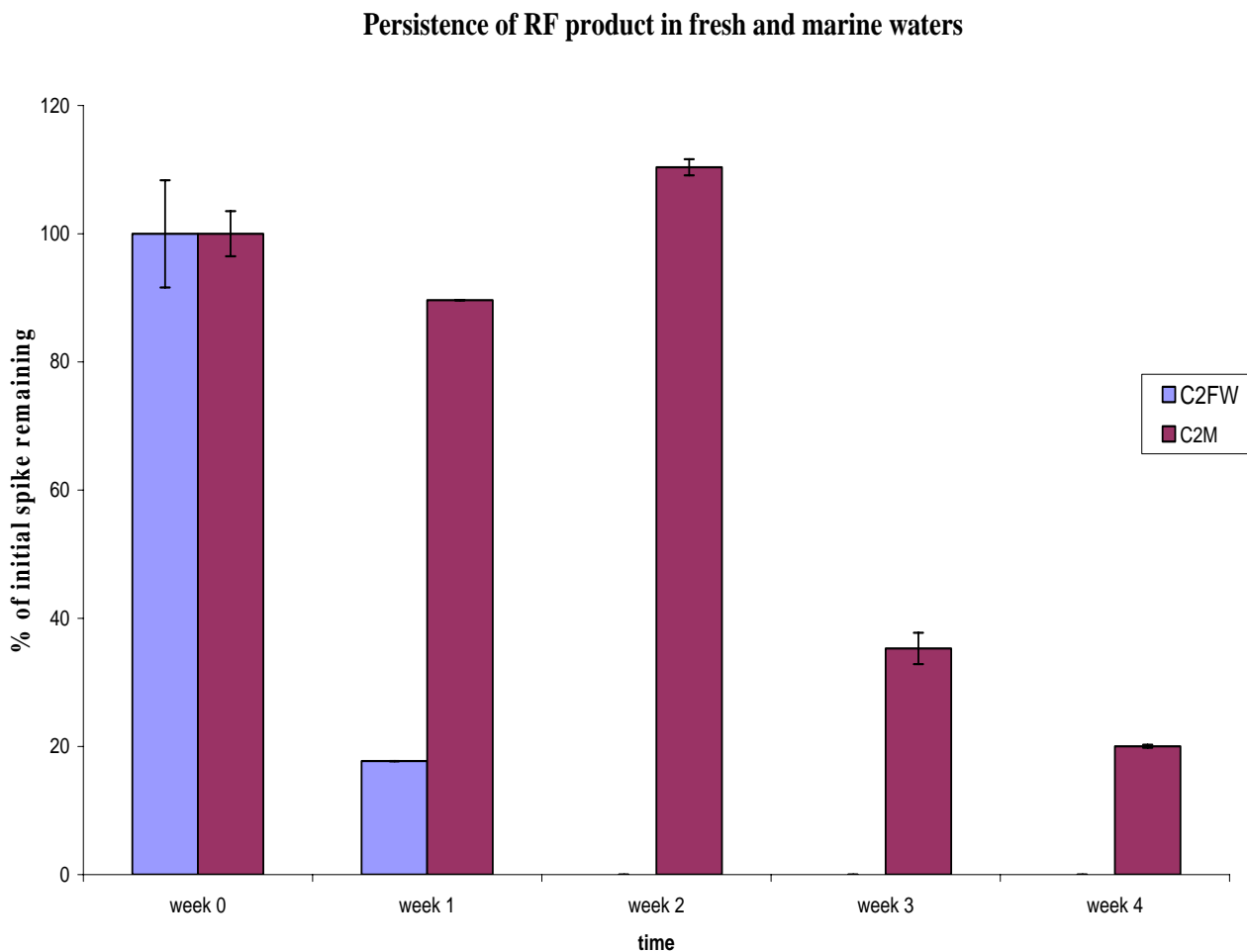
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 8. Persistence of Light-Water product in fresh and marine waters



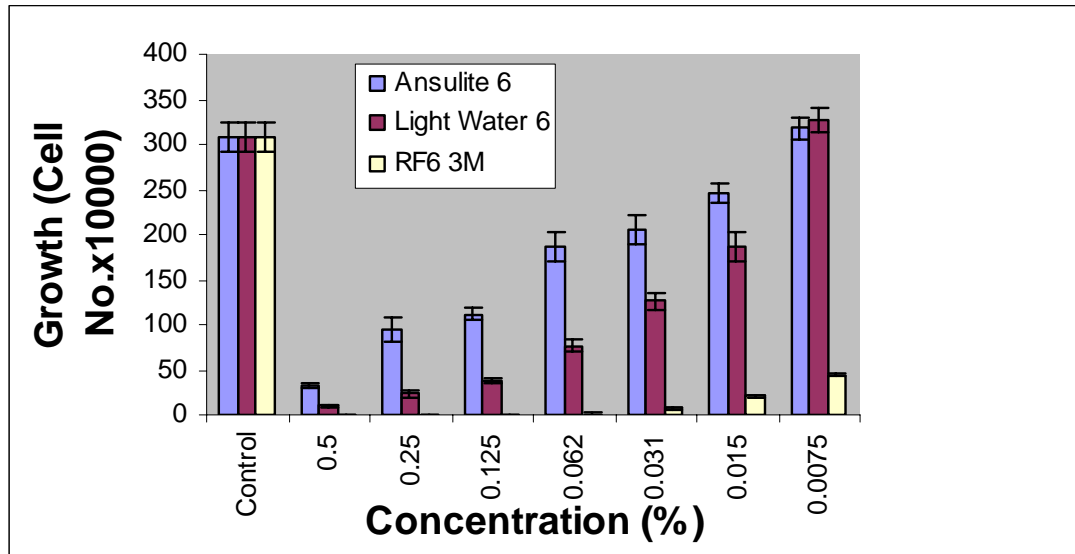
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 9. Persistence of RF product in fresh and marine waters



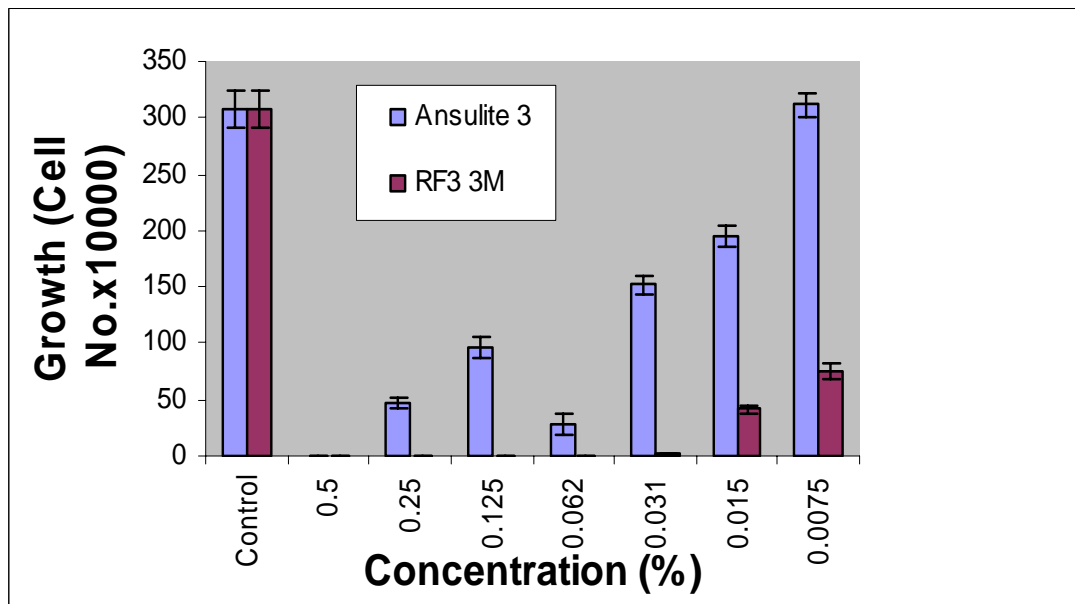
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 10. Effect of AFFF products (6% concentrates) on the growth of *R. subcapitata*



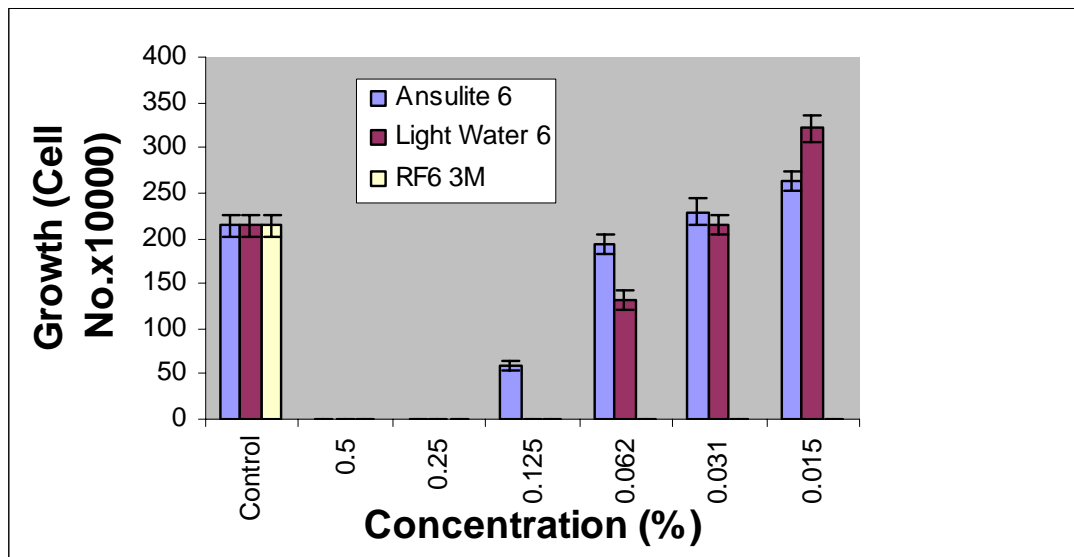
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 11. Effect of AFFF products (3% concentrates) on the growth of *R. subcapitata*



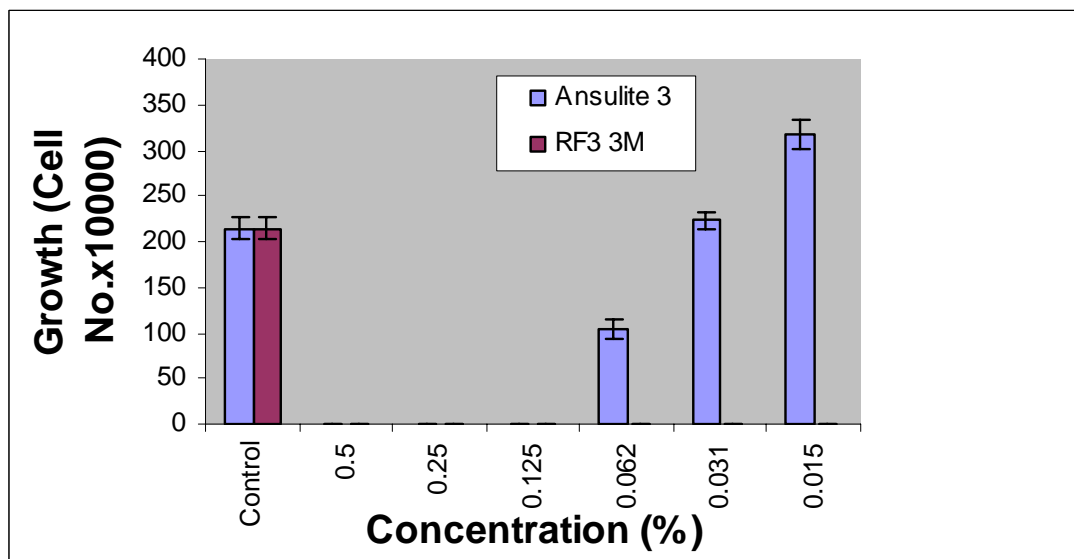
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 12. Effect of AFFF products (6% concentrates) on the growth of *D. tertiolecta*



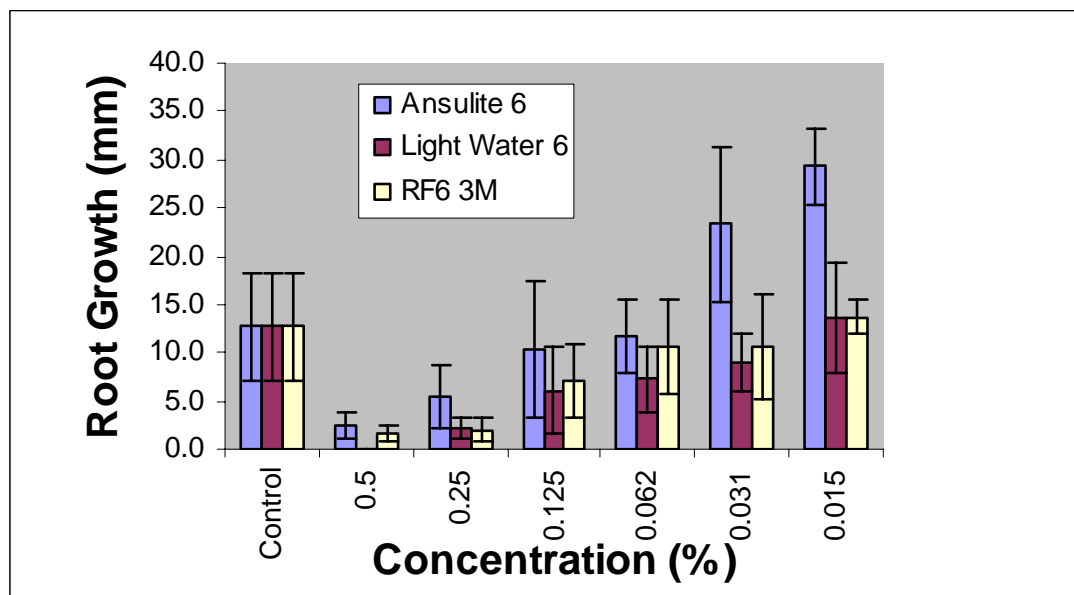
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 13. Effect of AFFF products (3% concentrates) on the growth of *D. tertiolecta*



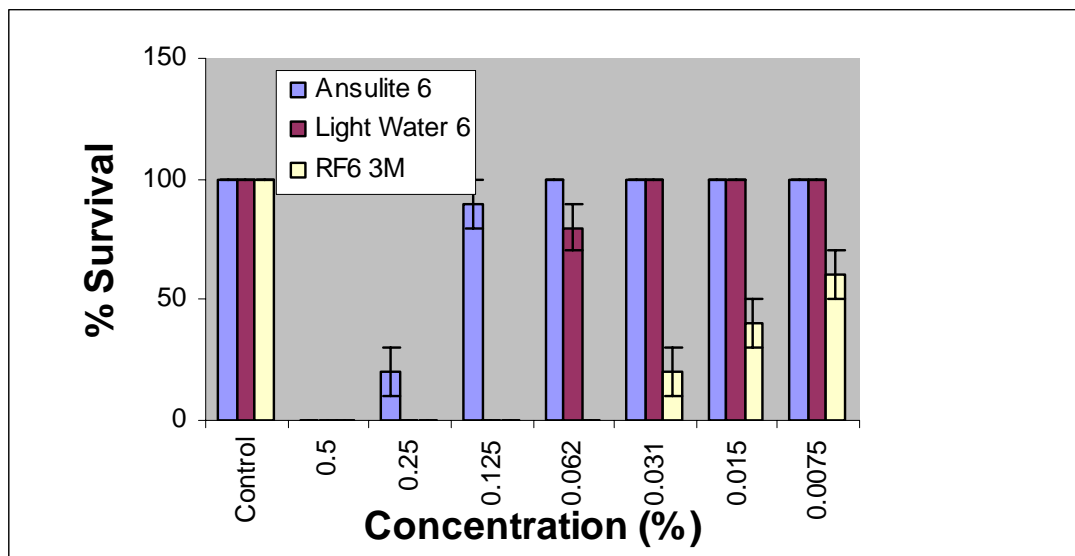
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 14. Effect of AFFF products (6% concentrates) on Lettuce root growth



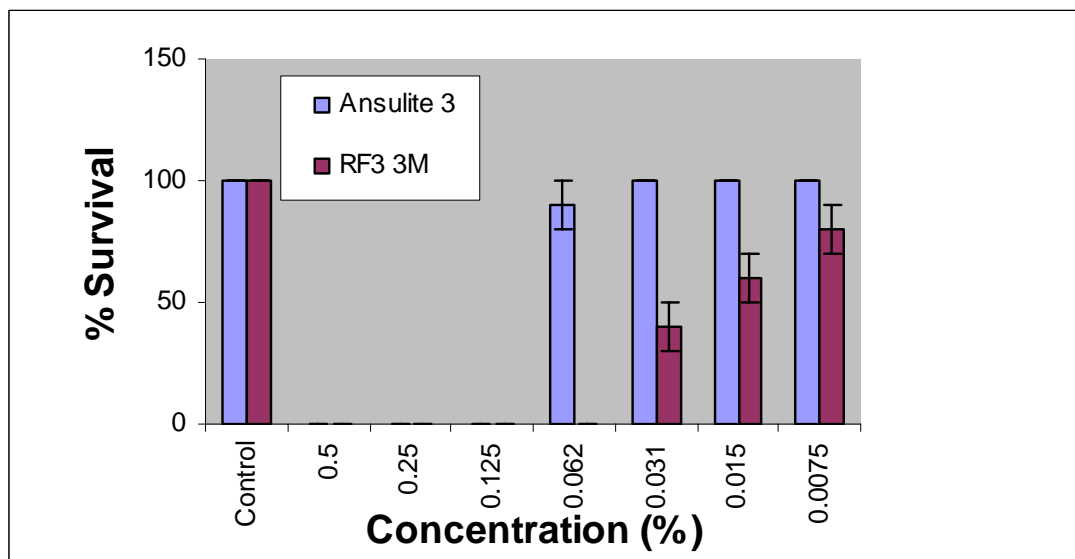
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 15. Effect of AFFF products (6% concentrates) on the survival of water-flea



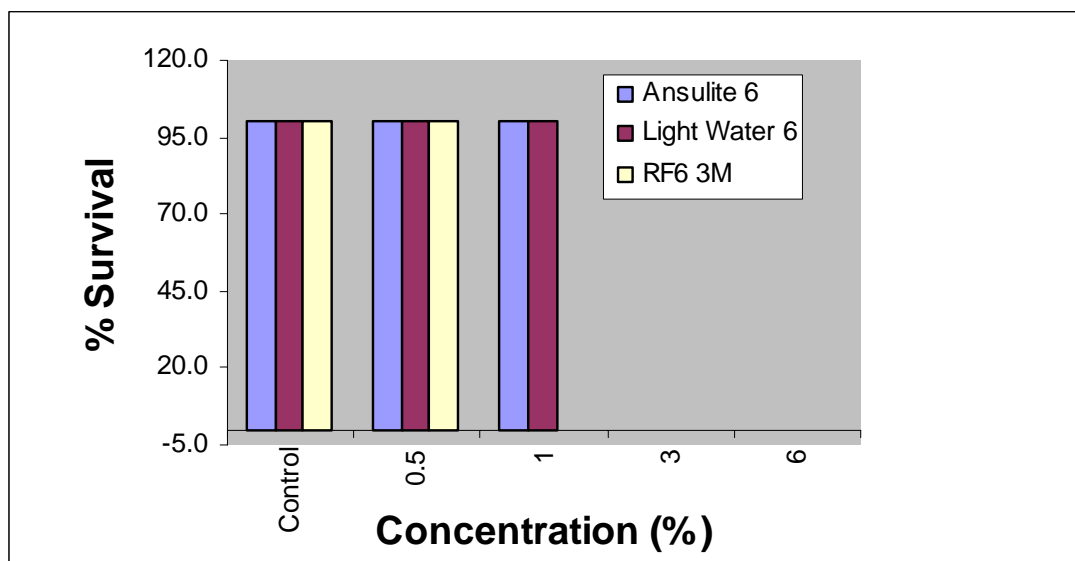
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 16. Effect of AFFF products (3% concentrates) on the survival of water-flea



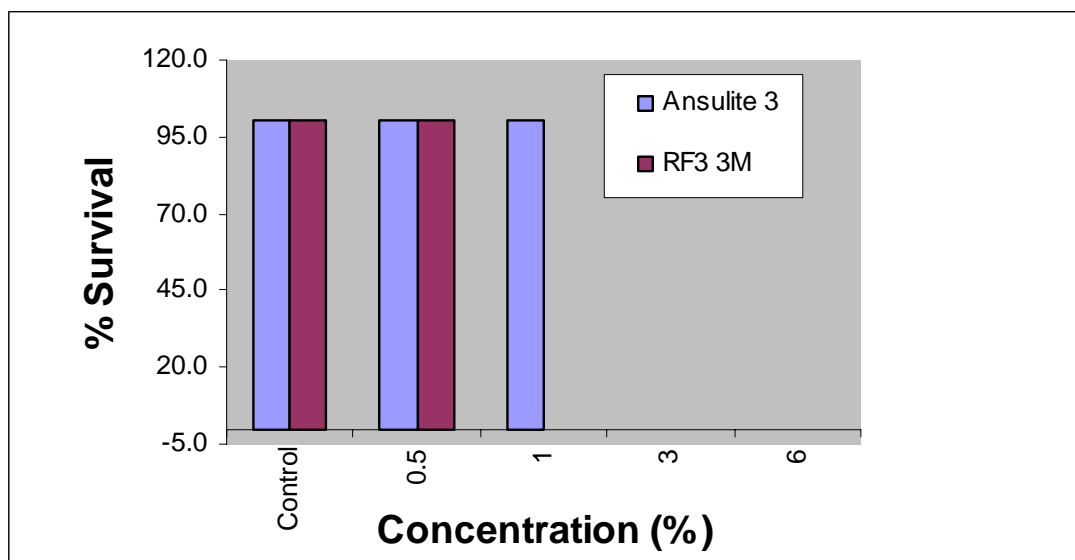
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 17. Effect of AFFF products (6% concentrates) on the survival of Earthworm



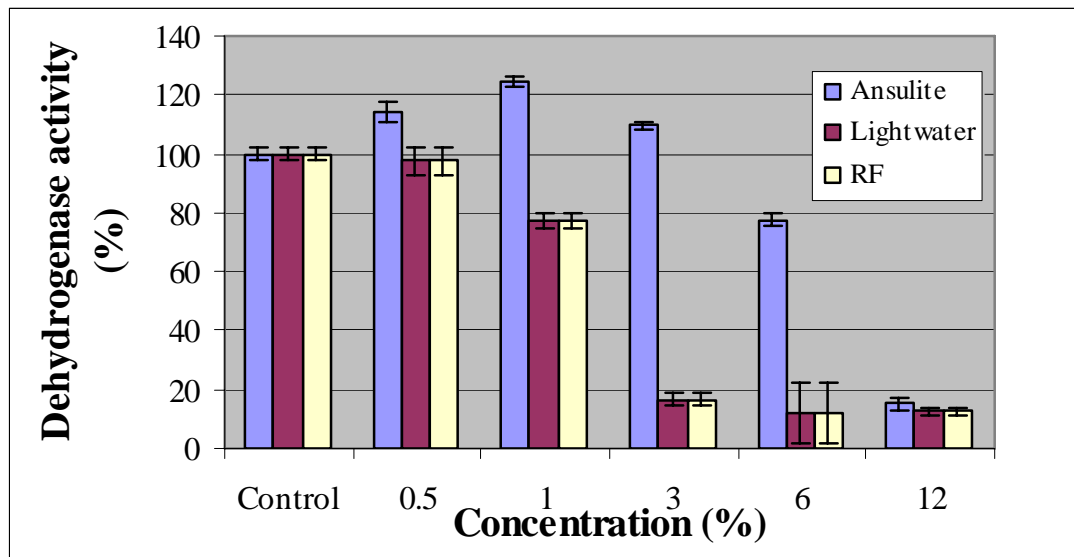
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 18. Effect of AFFF products (3% concentrates) on the survival of Earthworm



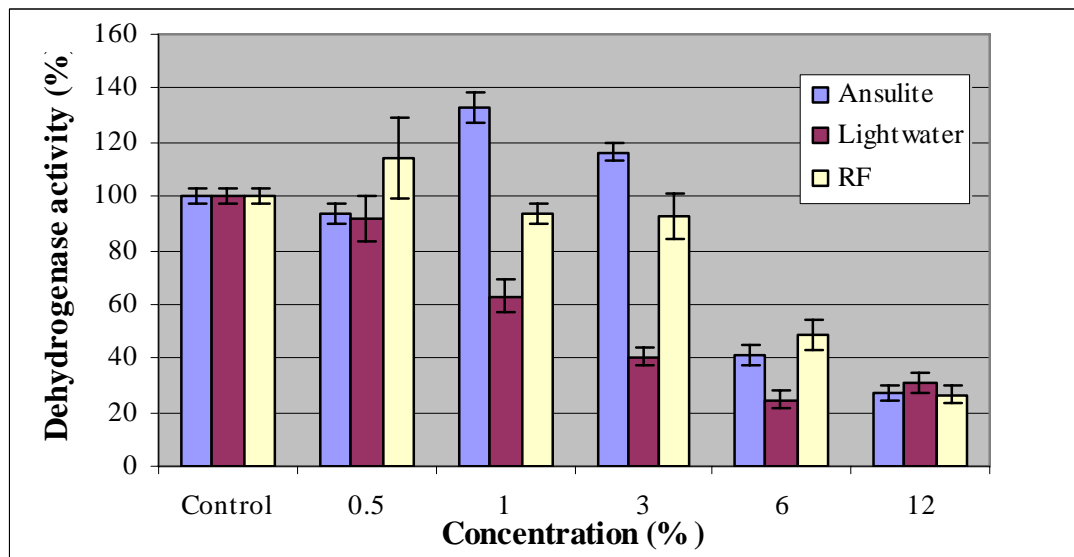
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 19. Effect of AFFF products (6% concentrates) on dehydrogenase activity at 15 days after spiking



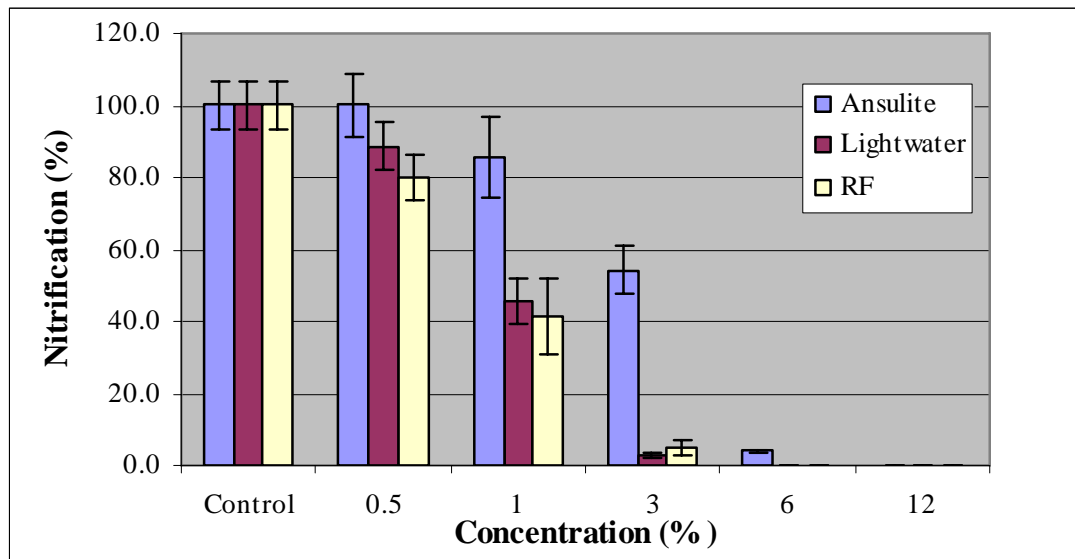
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 20. Effect of AFFF products (6% concentrates) on dehydrogenase activity at 45 days after spiking



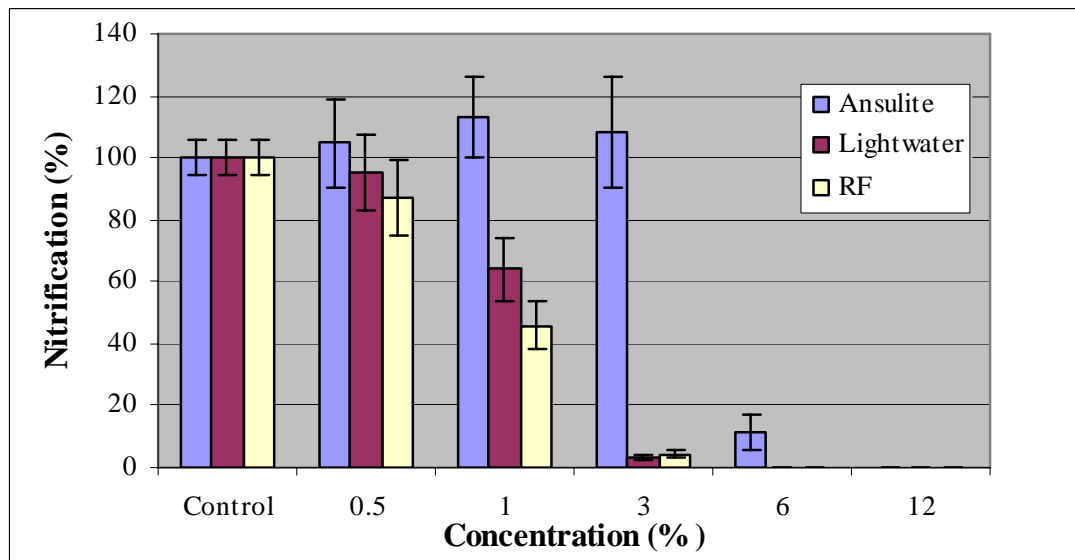
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 21. Effect of AFFF products (6% concentrates) on potential nitrification of soil at 15 days after spiking



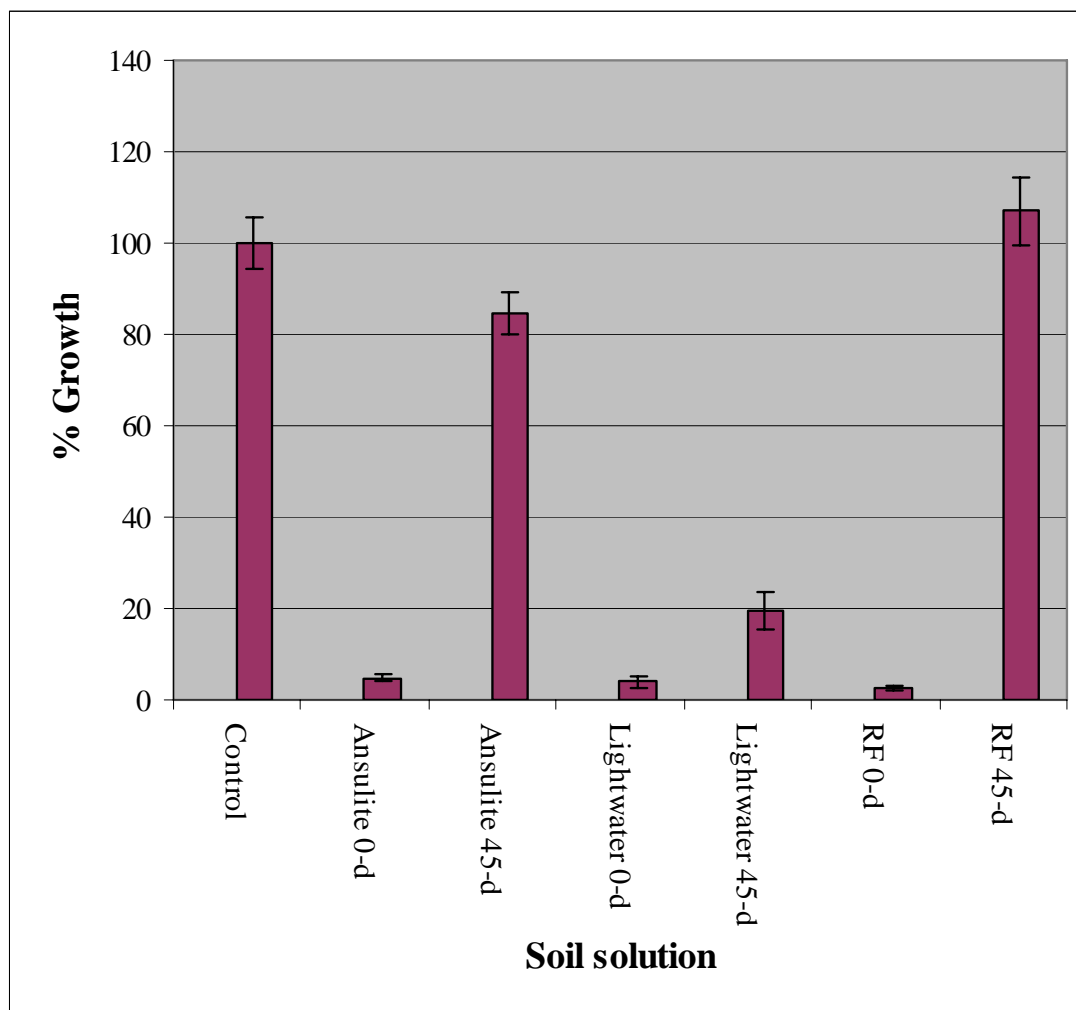
Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

Figure 22. Effect of AFFF products (6% concentrates) on potential nitrification of soil at 45 days after spiking



Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

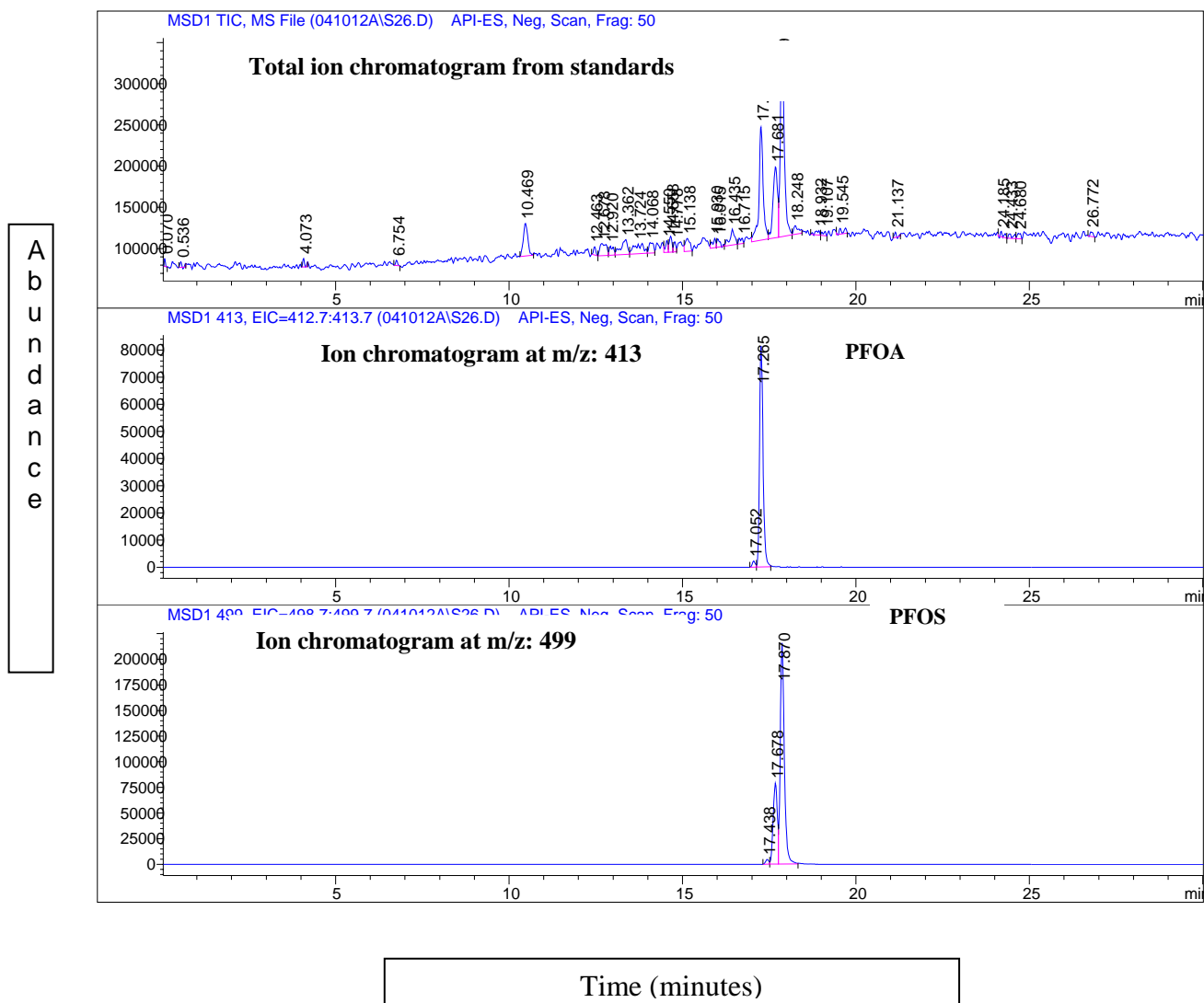
Figure 23. Residual toxicity in AFFF pretreated soils after 45 d incubation as revealed by algal bioassay



Note : The vertical bar on each column represents standard deviation of the mean (n = 3)

8. Appendix A

Figure A1. Liquid chromatography-mass spectrometry separation of a mixture containing PFOA and PFOS



FigureA2. Liquid chromatography-mass spectrometry chromatogram and mass fragmentation pattern from soil spiked with Light-Water

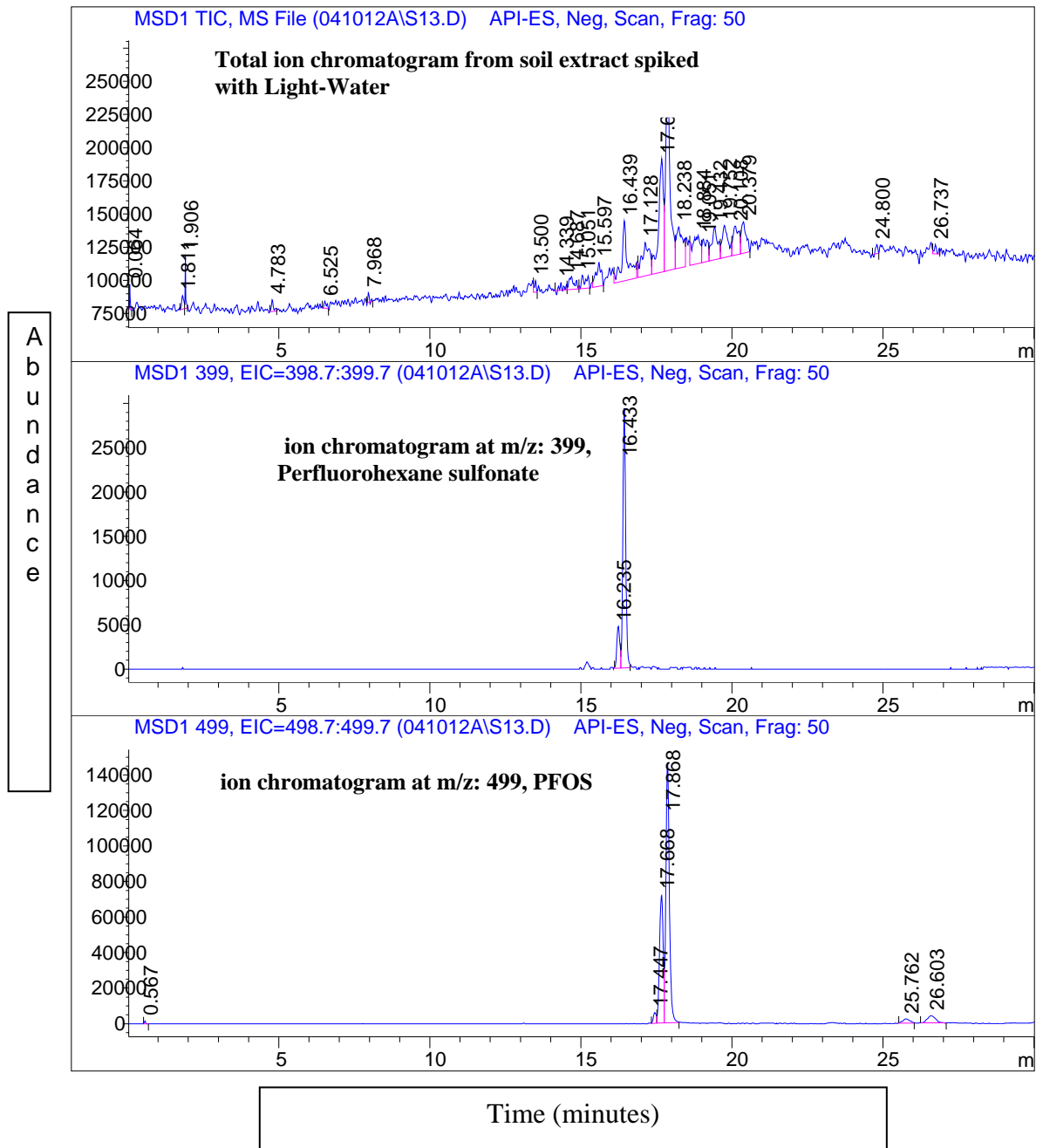


Figure A3. Liquid chromatography-mass spectrometry chromatogram showing the separation of Ansulite product (total ion chromatogram and selected ions)

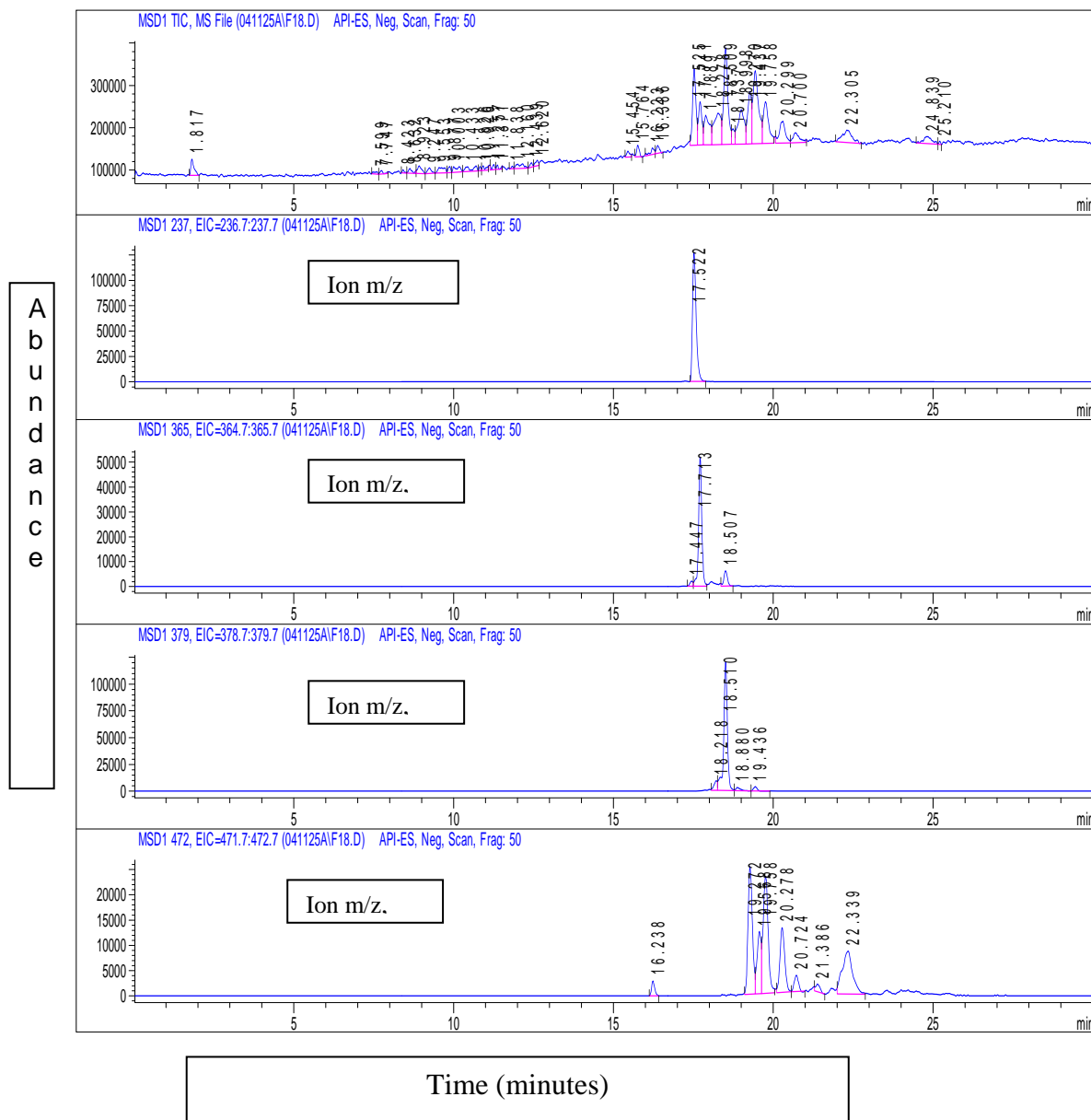


Figure A4. Liquid chromatography-mass spectrometry chromatogram showing the separation of RF product (total ion chromatogram and selected ions)

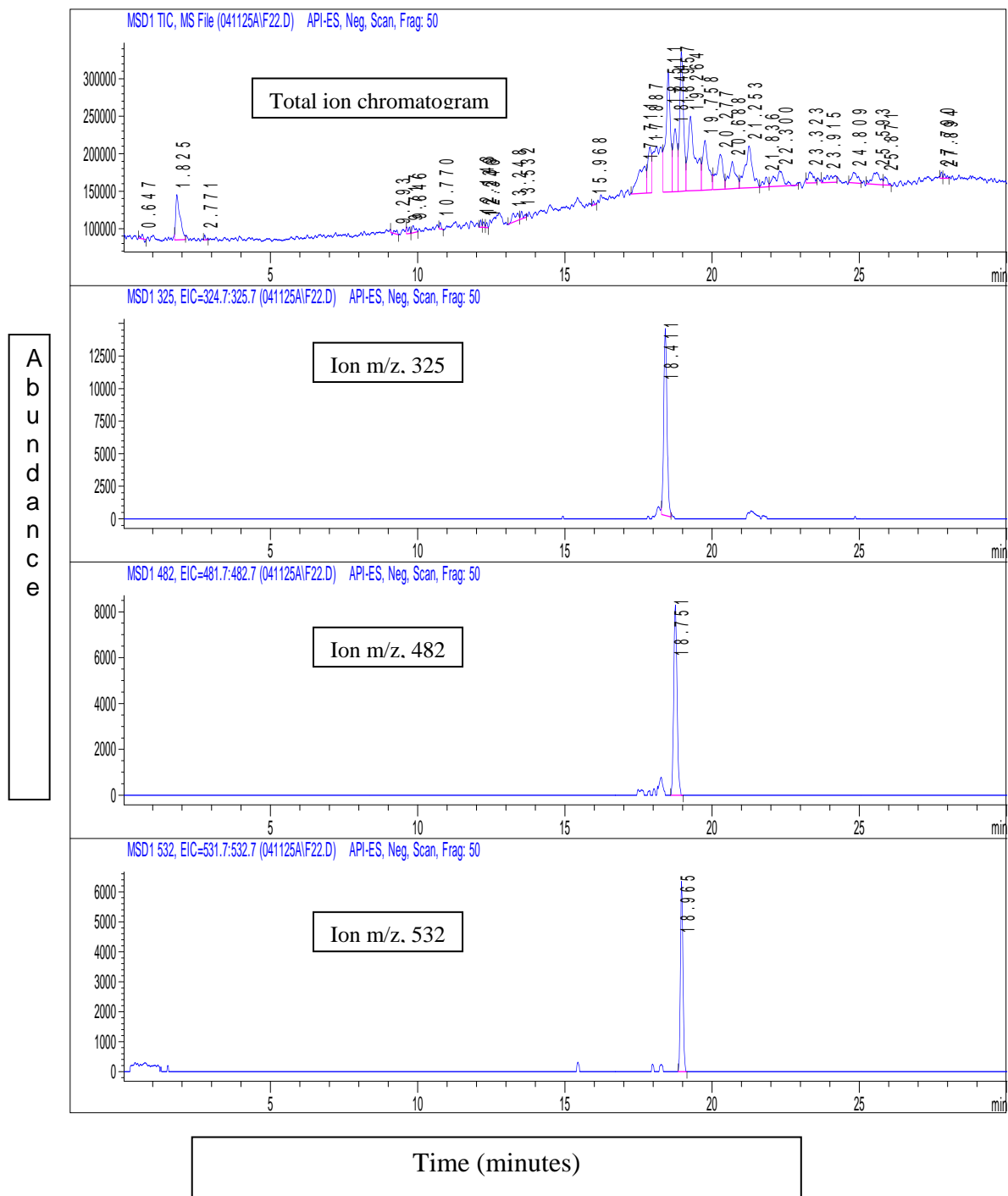


Table A1. Effect of AFFF products (6 and 3% concentrates) on the growth (cell number $\times 10^4 \text{ ml}^{-1}$) of *R. subcapitata*

	Ansulite 6		Ansulite 3		Light Water 6		RF6 3M		RF3 3M	
	Cell No.	SD	Cell No.	SD	Cell No.	SD	Cell No.	SD	Cell No.	SD
Control	308	16	308	16	308	16	308	16	308	16
0.5	32	3	0	0	10	2	0	0	0	0
0.25	95	14	46	5	23	5	0	0	0	0
0.125	112	8	96	10	38	3	0	0	0	0
0.062	187	16	28	9	77	7	1	1	0	0
0.031	205	16	152	8	126	10	7	1	1	1
0.015	246	11	195	10	186	17	20	3	32	3
0.0075	318	12	311	10	327	13	44	2	47	7

SD; standard deviation

Table A2. Effect of AFFF products (6 and 3% concentrates) on the growth (cell number $\times 10^4 \text{ ml}^{-1}$) of *D. tertiolecta*

	Ansulite 6		Light Water 6		RF6 3M		Ansulite 3		RF3 3M	
	Cell No.	SD	Cell No.	SD	Cell No.	SD	Cell No.	SD	Cell No.	SD
Control	214	12	214	12	214	12	214	12	214	12
0.5	0	0	0	0	0	0	0	0	0	0
0.25	0	0	0	0	0	0	0	0	0	0
0.125	59	7	0	0	0	0	0	0	0	0
0.062	193	11	131	10	0	0	105	11	0	0
0.031	229	15	215	11	0	0	223	9	0	0
0.015	263	11	321	15	0	0	317	17	0	0

SD; standard deviation

Table A3. Effect of AFFF products (6% concentrates) on Lettuce root growth

	Ansulite 6		Light Water 6		RF6 3M	
	Root ength (mm)	SD	Root ength (mm)	SD	Root ength (mm)	SD
Control	12.7	5.5	12.7	5.5	12.7	5.5
0.5	2.5	1.4	0.0	0.0	1.6	0.8
0.25	5.4	3.3	2.3	1.1	2.0	1.3
0.125	10.3	7.1	6.1	4.6	7.1	3.8
0.062	11.7	3.7	7.3	3.4	10.6	4.8
0.031	23.3	8.0	8.9	3.0	10.6	5.5
0.015	29.3	4.0	13.6	5.6	13.7	1.8

SD; standard deviation

Table A4. Effect of AFFF products (6 and 3% concentrates) on the survival of water-flea

	Ansulite 6		Ansulite 3		Light Water 6		RF6 3M		RF3 3M	
	survival	SD	survival	SD	survival	SD	survival	SD	survival	SD
Control	100	0	100	0	100	0	100	0	100	0
0.5	0	0	0	0	0	0	0	0	0	0
0.25	20	10	0	0	0	0	0	0	0	0
0.125	90	10	0	0	0	0	0	0	0	0
0.062	100	0	90	10	80	10	0	0	0	0
0.031	100	0	100	0	100	0	20	10	40	10
0.015	100	0	100	0	100	0	40	10	60	10
0.0075	100	0	100	0	100	0	60	10	80	10

SD; standard deviation

Table A5. Effect of AFFF products (6 and 3% concentrates) on the survival of Earthworm

	Ansulite 6	Ansulite 3	Light Water 6	RF6 3M	RF3 3M
Control	100.0	100.0	100.0	100.0	100.0
0.5	100	100	100	100	100
1	100	100	100	0	0
3	0	0	0	0	0
6	0	0	0	0	0

Table A6. Effect of AFFF products (6% concentrates) on dehydrogenase activity at 15 days after spiking

	%control Ansulite	%SD	%control Lightwater	%SD	%control RF	%SD
Control	100	2.2	100	2.2	100	2.2
0.5	114	3.1	98	4.8	98	4.8
1	124	2.0	77	2.4	77	2.4
3	110	1.6	17	2.4	17	2.4
6	78	2.4	12	10.4	12	10.4
12	15	2.4	13	1.6	13	1.6

SD; standard deviation

Table A7. Effect of AFFF products (6% concentrates) on dehydrogenase activity at 45 days after spiking

	%control Ansulite	%SD	%control Lightwater	%SD	%control RF	%SD
Control	100	2.7	100	2.7	100	2.7
0.5	93	3.5	92	8.1	114	15.2
1	133	5.7	63	6.2	93	3.5
3	116	3.5	41	3.5	93	8.3
6	41	3.7	25	3.1	49	5.4
12	27	2.7	31	3.7	26	3.5

SD; standard deviation

Table A8. Effect of AFFF products (6% concentrates) on potential nitrification of soil at 15 days after spiking

	%control Ansulite	%SD	%control Lightwater	%SD	%control RF	%SD
Control	100.0	6.5	100	6.5	100	6.5
0.5	100	8.9	89	6.5	80	6.5
1	86	11.3	46	6.5	41	10.8
3	54	6.5	3	0.7	5	2.0
6	4	0.5	0	0	0	0.0
12	0	0.0	0	0	0	0.0

SD; standard deviation

Table A9. Effect of AFFF products (6% concentrates) on potential nitrification of soil at 45 days after spiking

	%control Ansulite	%SD	%control Lightwater	%SD	%control RF	%SD
Control	100	5.7	100	5.7	100	5.7
0.5	105	14.2	95	12.4	87	12.4
1	113	13.0	64	9.8	46	7.5
3	108	17.7	3	1.0	4	1.5
6	11	5.7	0	0.0	0	0.0
12	0	0.0	0	0.0	0	0.0

SD; standard deviation

9. Appendix B

Table B1. Summary of AFFF toxicity tests

Test	Ansulite 6%		Ansulite 3%		3M RF 6%		3M RF 3%		3M Light Water 6%	
	Toxic threshold*	Lethal**	Toxic threshold*	Lethal**	Toxic threshold*	Lethal**	Toxic threshold*	Lethal**	Toxic threshold*	Lethal**
Fresh Water algal growth	0.015	>0.5	0.015	0.5	<0.0075	0.06	<0.0075	0.06	0.015	>0.5
Marine Water algal growth	0.062	0.25	0.062	0.125	<0.015	<0.015	<0.015	<0.015	0.062	0.125
Plant root growth	0.25	>0.5	nd	nd	0.125	>0.5	nd	nd	0.062	0.5
Water-flea survival	>0.125	0.5	>0.062	0.125	<0.0075	0.062	<0.0075	0.062	0.062	0.125
Earth worm survival	>1	3	>1	3	>0.5	1	>0.5	1	>1	3
Dehydrogenase activity-15 days	>3	>12	nd	nd	1	>12	nd	nd	1	>12
Dehydrogenase activity-45 days	>3	>12	nd	nd	>3	>12	nd	nd	>0.5	>12
Nitrification- 15 days	>0.5	>6	nd	nd	>0.5	>3	nd	nd	>0.5	>3
Nitrification- 45 days	>3	>6	nd	nd	>0.5	>3	nd	nd	>0.5	>3
Soil algal density	>0.5	>3	nd	nd	>1	>3	nd	nd	<0.5	1

*The % dilution of the AFFF product above which toxicity occurred.

**The % dilution of AFFF showing complete inhibition/death of the test organism/activity. Nd; not determined.

Table B2. Consolidated results of the experiments on all the three AFFF products

Constituents/Properties/Processes	Ansulite AFFF	3M RF AFFF	3M Light Water AFFF
Constituent: PFOS	Nil	Nil	Present
Presence of PFOS in soil and water after 4 weeks	Nil	Nil	Present
Constituent: PFOA	Nil	Nil	Nil
Presence of PFOA in soil and water after 4 weeks	Nil	Nil	Nil
Constituent: Fluorine (fluorinated compounds)	Present	Not detected	Present
Constituent: Carbohydrate test	Positive	Positivet	Negative
Constituent: Diethylene glycol butyl ether	Present	Present	Present
Overall toxicity	Less toxic	Highly toxic	Medium toxic
Bioaccumulation of parent chemicals	Nil	Nil	Present
Persistence/biodegradation: Soils	About 95% after week 1 to 98% after week 4	65-85% after week 1 to 87-97% after week 4	10 – 23 % after week 4
Persistence/biodegradation: Sediments-Fresh water	80 to 90% degradation in 4 weeks	75% to 82% in 4 weeks	No appreciable degradation in 4 weeks
Persistence/biodegradation: Sediments-Marie	About 30% during 4 weeks	60% to 75% during 4 weeks	No appreciable degradation in 4 weeks
Persistence/biodegradation: Fresh water	About 97% in week 1 to 99% in week 4	About 82% in week 1 to complete degradation in week 2	About 9% in week 1 to 14 % in week 4
Persistence/biodegradation: Marine water	About 27% in week 1 to complete degradation in week 4	10% in week 1 to 80% degradation in week 4	0-14% degradation in 4 weeks
Overall persistence in general	Least persistent	Less persstent	Highly persistent
Safe disposal level: soils	0.5% dilution	0.5% dilution	0.5% dilution
Safe disposal level: Water	0.01% dilution	<0.007% dilution	0.01% dilution

