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Title: **The Environmental Impact of Fire Fighting Foams – Operational and Legal Implications**

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The Environmental Impact of Fire Fighting Foams – Operational and Legal Implications

by

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As a result of the 3M Company's decision in 2000 to discontinue the manufacture of PFOS-based fluorosurfactants including AFFF for firefighting on environmental grounds, there is now a heightened awareness worldwide of the potential impact on the environment of fluorosurfactants and their degradation products. Both PFOS-based and fluorotelomer-based surfactants breakdown to give a range of highly stable polyfluorinated molecules which have been reported at high concentrations in groundwater at former fire fighting foam training sites [1-3]. Perfluorinated sulphonates and carboxylic acids are widely dispersed throughout the environment and the animal kingdom, especially in remote sites such as the polar regions implying far-reaching atmospheric or oceanic transport.

Fire fighting foams, whether or not they contain fluorinated materials, have acute toxicity towards the aquatic environment as detergents. They also deplete oxygen levels, required for biological degradation. Finished fluorosurfactant foams are generally rather non-toxic; however, it is their polyfluorinated degradation products that are of environmental concern because of unfavourable persistence, bio-accumulation and toxicity (PBT). Bio-accumulation and toxicity depend critically on the chain length and structure of the degradation product. Extreme persistence, however, is a general property shared by all perfluorinated degradation products whether derived from PFOS- or fluorotelomer-based foams. Indeed perfluorocarbon derivatives are some of the most environmentally persistent known – CF_4 is estimated as having an atmospheric lifetime of between 10,000 and 20,000 years, and there is no known degradative pathway for trifluoroacetic acid, CF_3COOH, in the aqueous environment.

It is the highly persistent nature of pefluorinated materials that represents the biggest environmental challenge for the Fire Service in terms of dispersion resulting from the operational use of foam and the legal implications that follow.

Perfluorooctanyl sulphonate (PFOS) based fluorosurfactants (3M LightWater™ and ATC™ types) yield PFOS as the major degradation product under environmental conditions. PFOS is widely dispersed throughout the animal kingdom, bio-accumulates and is toxic. The lithium salt of PFOS is used as an insecticide against wasps and hornets. It is chemically extremely stable, able to withstand hot sulphuric or nitric acids, and extremely persistent. High concentrations of PFOS have been reported in groundwater at old military fire training sites, with foaming still seen more than 15 years after the site was last used [1,2]. The equivalent degradation product for fluorotelomer foams is the 6:2 fluorotelomer sulphonate (6:2FtS), also known as H-PFOS (1,1',2,2',tetrahydroperfluorooctane sulphonate). 6:2FtS is much less bio-accumulative and toxic than PFOS but is also extremely persistent and has been reported at exceptionally high concentrations in groundwater at old foam training sites a decade or more after they were last used [3]. Other degradation products, in addition to sulphonates, observed at sites used for training with fluorosurfactant foams include perfluorocarboxylic acids of various carbon chain lengths. The distribution of molecular species each containing a different number of carbon atoms and/or pattern of branching is characteristic of the particular fluorosurfactant and its method of manufacture.

Subsequent to 3M's decision, PFOS foams are no longer manufactured in Europe or the United States and their use for fire fighting is being phased out under regulatory control, with current stocks either being high temperature incinerated or used operationally under controlled conditions. Almost all film-forming foam formulations now available are based on fluorotelomer rather than PFOS chemistry.

Although the use of foam concentrates for fire fighting only represents about 5% of the total world market for fluorotelomers, with fabric and paper treatments, paints and varnishes, industrial anti-foaming and anti-misting products accounting for the bulk used, fire fighting represents the most *dispersive* application for fluorosurfactant products with considerable potential for contaminating the environment. Thus the overall *risk* posed to the environment by the *hazard* (the finished foam or even spilled concentrate) is out of all proportion to the relative tonnage of fluorosurfactant used. Fire fighting operations in which it is impossible to contain foam-contaminated fire-water run-off – e.g., at motorway incidents, aircraft crashes, at small or very old industrial premises, wildland fires, or on waterways or at sea – may result in serious environmental damage. The Allied Colloids fire in 1992 near Bradford UK resulted in tens of millions of litres of foam and chemically contaminated run-off being discharged into the local river system (the Aire and Calder), since not to have done so would have destroyed the local foul water treatment plant. The immediate effect was to render the river system biologically dead for some 50 km downstream.

The majority of large incidents requiring AFFF-type foams containing fluorosurfactants, in terms of the quantity of foam concentrate used, take place at petrochemical and chemical process sites. Relatively little AFFF is used by municipal fire departments by comparison. Dispersion is not (should not be) a problem at most large industrial complexes as these should have adequate bunding and containment facilities together with a foul water sewage system that can be isolated. In addition many have professional level fire departments on site, especially in mainland European countries, together with hazardous material and environmental response organisations – for example, the TUIS scheme.

The 1979 European Council Directive (80/68/EEC 17 December 1979) – the European Groundwater Directive - forbids the discharge of organohalogens or degradation products that are organohalogens to groundwater [List 1]. List 1 materials can only be derogated to List 2 by the competent national authority - the Environment Agency in the UK or the Umweltbundesamt in Germany, for example – if the regulators are satisfied that there are no persistence, bio-accumulation or toxicity problems (the PBT profile). The provisions of the European Groundwater Directive become subsumed into national legislation, e.g., the Groundwater Regulations 1998 SI 2746 in the UK, under the principle of subsidiarity.

The extreme chemical stability of fluorosurfactants and their degradation products is both a boon and a bane. Their use for fire fighting foam depends on both their excellent stability and efficiency as surface active (wetting) agents. Although very expensive on a weight basis compared to hydrocarbon or silicon-based surfactants, their effectiveness at low concentrations results in a favourable cost per unit volume of finished foam. Fluorosurfactants and their degradation products are, however, very environmentally persistent. This alone is a significant problem – even if levels of bio-accumulation and toxicity are low – since any material discharged to the aquatic environment, especially groundwater, will remain, resulting in increasing concentrations over subsequent decades. Ultimately one can predict that levels in groundwater, i.e., drinking water supplies, will exceed established no-effect levels for human and animal toxicity in coming generations. It is clearly a matter of environmental prudence and responsibility not to contaminate groundwater supplies, some of which are centuries old, with any highly persistent man-made material of unproven long-term bio-toxicity.

One must distinguish between hazard and risk. Hazards have a potential to cause harm, in this case to the environment. Assessment of the risk estimates the likelihood that harm or damage will be caused. Persistence itself represents no clear hazard but rather modifies the much clearer hazards of bio-accumulation and toxicity. The overall risk of causing environmental damage can be thought of as a combination of persistence (P), bio-accumulation (B) and toxicity (T), quantitatively expressed as follows:

$$\text{Environmental Risk (ER)} \quad = \quad P \times B \times T \qquad \text{……….} \ (1)$$

Clearly highly toxic materials which bio-accumulate will have an undesirable impact, even if of low persistence, i.e., in spite of being rapidly degraded. Few people would argue with this statement. On the other hand, contaminants with relatively low bio-accumulative potential and/or low toxicity but which are very persistent and do not degrade easily (thought to be the case, for example, with the degradation products of fluorotelomer fluororsurfactant foams), also represent a substantial risk since these materials will accumulate over time in groundwater or soil, and will continue to do so if their discharge is not controlled. The increasing environmental concentration or burden may end up ultimately exceeding no-effect toxicity levels. This is especially serious if the compartment in question – groundwater or a river sytem – provides drinking water for the general population. Thus the extreme persistence seen with perfluorinated materials, even if these materials are weakly bio-accumulated or have low toxicity, effectively *integrates or summates* the otherwise relatively low B and T components of the risk equation (1) over time. Increasing local concentrations also make it more likely long-term that widespread dispersion will occur. Based on this logic the precautionary principle dictates that discharge of highly persistent materials such as fluorosurfactants and their degradation products should be avoided if at all possible, especially when their long term effects are unknown.

Equation (1) needs to be modified to take account of the degree of dispersion (D) for the hazard associated with a particular application, as shown in equation (2):

$$\text{Environmental Risk } (ER_{disp}) \quad = \quad P \times B \times T \times D \quad \text{……..} \ (2)$$

Incidents involving the operational use of fire fighting foam frequently result in dispersion of very large quantities of finished foam and contaminated run-off water. This matters near water courses and lakes, in drinking water catchment areas, or with wildland fires in hydrologically sensitive areas. Thus the environmental risk associated with the use of fluorosurfactant foams by the fire service is dominated by the persistence (P) and dispersion (D) components.

A practice that should be most strongly deprecated on environmental grounds is to use a diluted AFFF Class B fluorosurfactant-containing concentrate as a substitute for a proper non-fluorosurfactant Class A additive on wildland or structural fires. A number of fire brigades have been misled into believing that this is acceptable. Not only is this practice environmentally highly irresponsible but also ignores the fundamental technical difference between Class A and Class B foam formulations. A fluorosurfactant-containing Class B AFFF is simply nowhere near as efficient as a correctly formulated Class A product in penetrating carbonaceous fuels such as encountered in wildland or structural fires.

There are both legal and ethical implications to the use by fire departments of fire fighting foams both operationally and for training purposes, especially those containing perfluorinated materials. In the United Kingdom there is now a Protocol, originally a Memorandum of Understanding (MOU), between the Local Government Association (LGA) representing the local Fire Authorities and the Environment Agency, regulating the use of foam within the framework of pollution legislation. The Agency must be informed of all incidents, excepting car fires, involving the use of foam as well as all exercises other than in designated areas – i.e., with custom-built training grounds with contained drainage. In particular incidents near water courses or in areas with combined foul/surface drainage must be notified.

Training with real AFFF is becoming less common. Indeed in some German Federal States, as a result of increasing awareness of the occurrence of perfluorinated fluorosurfactant degradation products in rivers, surface and groundwater, as well as in human breast milk, training with AFFF has been banned. Moreover, there is mounting political pressure to stop municipal brigades using fluorosurfactant-containing foams at all.

One must distinguish between the pattern of foam use by municipal fire brigades and by works fire brigades particularly in the petrochemical and chemical process industries. Municipal fire brigades do not in general require AFFF that cannot be substituted by a fluorine-free or low fluorine Class B foam. These incidents are also often such that containment of run-off is all but impossible – for example, on motorways or at an aircraft crash site. The petrochemical industry, on the other hand, is able to ensure that any run-off at fixed installations is well contained thus greatly limiting the environmental risk. Current wisdom in the petrochemical industry suggests that there is still a need for fluorosurfactant foams at very large hydrocarbon or polar solvent tank fires, although there are some fluorine-free products now available with all the relevant approvals, including the industry standard LASTFIRE test, whose overall operational performance approaches very closely that of classical AFFF formulations.

1. Moody, C.A.; Field, J.A.; (1999) "Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity" *Env. Sci. Tech.* 33, 2800.
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