

Last month the Norwegian State Pollution Control Agency published the results of studies it had carried out on polyfluorinated organic compounds at four fire training facilities in Norway. Dr Roger Klein explains the potential environmental implications as regards the use of fluorinated foam concentrates.



# Contaminated firewater – protecting the environment



*Dr Roger Klein, trained as a medical doctor and as a physical chemist at the University of Cambridge. He has 35 years of experience advising and working with the Fire Service both in the UK and internationally.*

Contaminated firewater run-off remains a serious problem, especially at major incidents involving hazardous or polluting materials. There are legal consequences in allowing run-off to pollute controlled waters at an incident. Fortunately for the Fire Service there may be a statutory defence (such as in the UK under Section 89(1)(b) of the Water Resources Act 1991) to the offense of causing or knowingly permitting a polluting substance to enter controlled waters under emergency conditions defined as a risk to human life or health but not to property. There is no defence for pollution caused during fire service training. Occupiers of premises, however, may find themselves held to account legally if it can be proved that their actions or lack of action, ie negligence, led to a situation which resulted in the release of contaminated run-off to controlled waters. This would be true, for example, if the bunding of a storage area was of insufficient volume to hold both stored material and any firefighting foam used, or had been poorly maintained so that bund integrity was compromised.

Firefighting operations almost always represent a balance between extinguishing fire, saving human life or property, or otherwise resolving the incident for example in the case of a hazardous materials spill, and the impact of these operations on the environment. Two different aspects of operational procedures need to be assessed both strategically and tactically for the risk these pose of damaging the environment. First, what effects, potential or immediate, do normal fire fighting procedures and extinguishing agents have on the environment; and secondly, at incidents involving hazardous materials (hazmat), what

procedures can be used to mitigate damage caused by release of toxic materials either directly or as part of fire-water run-off.

Halons are probably the best example of extinguishing agents with a serious and unacceptable environmental impact. Work which resulted in the 1995 Nobel Prize in Chemistry for Crutzen, Molina and Rowland, led to the banning of certain halons through the 1987 Montreal Protocol. Recent data indicate that atmospheric ozone depletion stopped by 1994 (2002, World Meteorological Organization, Global Ozone Research and Monitoring Project Report No. 47, WMO, Geneva, 2003), showing that concerted international effort can remedy or even reverse environmental damage, leading Kofi Annan to call it “perhaps the single most successful international agreement to date”.

Replacement of halons highlights a problem which is highly topical in the current discussion of fluorosurfactant-containing fire fighting foams (which include AFFF, FFFP and FP and AR foams) versus fluorine-free alternatives. Whereas there are still legitimate concerns about the efficiency of halon substitutes, similar critical concerns about fluorine-free foams expressed by manufacturers of traditional fluorosurfactant foams now seem unfounded and based on hearsay and commercial self-interest. Currently there are available on the market Class B foam concentrates that are completely fluorosurfactant-free, have the relevant approvals such as EN 1568 and ICAO, satisfy the petrochemical industry standard LASTFIRE for both freshwater and seawater, and can be used efficiently on both non-polar and polar fuels (AR-type foams). Indeed under certain rigorously and independently controlled test circumstances one of these fluorine-free products has even been found to outperform traditional fluorosurfactant-containing products!

An argument often put forward in the industry as well as by some regulators against fluorine-free Class B foam concentrates and indeed Class A foams or additives (also known as wetting agents), is that these are more acutely toxic to the aquatic environment than fluorosurfactant-containing AFFF foams because they use hydrocarbon surfactants. All foams contain surfactants which are detergents that cause lowering of the surface tension of water from its normal value of 72 dynes/cm to between 20 and 30 dynes/cm. This lowering of the surface tension of water is

inimical to most organisms. Acute toxicity is, by definition, short term and most ecosystems recover rapidly, except under arid or desert conditions. But what is important to remember is that the acute toxicity of different foams must be compared at their final working concentration as finished foam not as the concentrate. When this is done there is often little to choose between the various formulations.

What are the environmental issues involved in using fluorosurfactant firefighting foams operationally? All fluorosurfactants produce highly stable, environmentally persistent fluorinated degradation products, which can be toxic and bio-

accumulative to varying degrees. The combination of persistence, bio-accumulative potential and toxicity is known as the substance's PBT profile.

In the case of the legacy PFOS-based products the end-product of breakdown is PFOS itself. PFOS has been found to be dispersed worldwide in a large variety of animal species including man, as well as in animals whose habitats are far removed from any obvious source of contamination such as the polar regions. PFOS is known to be toxic, affecting hormonal metabolism and reproduction in test species, and is bio-accumulative showing bio-magnification in the food chain.



*The Norwegian reports shows – amongst other things – that the fluorotelomer sulphionate 6:2 FtS is bioaccumulated by earthworms to a similar extent as PFOS and PFOA.*



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*The bottom line, believes Dr Klein, is that all fluorosurfactants, whether PFOS-based or fluorotelomer-based, produce very persistent long-lived fluorinated degradation products which are widely dispersed throughout the environment.*

Jennifer Field's group at Oregon State University in a series of papers (Environmental Science & Technology 1999, 33, 2800 2000, 34, 2000; 2004, 38, 1828) has demonstrated that high levels of PFOS as well as the degradation product from fluorotelomer foams, the fluorotelomer sulphonate 6:2 FTs or H-PFOS, accumulate at very high concentrations in groundwater at former US military firefighting foam-training facilities and persist a decade or more after the sites were last used. In some instances groundwater still foamed! These data point up the extreme persistence of fluorochemicals like PFOS and 6:2 FTs with half-lives of the order of at least decades.

Although its extremely persistent nature is clear and accepted, there is currently little information in the peer-reviewed scientific literature regarding the toxicity or bio-accumulative potential of the 6:2 fluorotelomer sulphonate. Reports from the fluorotelomer industry at meetings have suggested that toxicity and bio-accumulation in limited test species are much less than for PFOS or PFOA.

#### Norwegian State Pollution Control Agency

This was the situation until 3rd February 2009 when the Norwegian State Pollution Control Agency (SFT) published an extremely important report (TA 2444/2009) which showed (i) that the fluorotelomer sulphonate 6:2 FTs is bioaccumulated by earthworms to a similar extent as PFOS and PFOA, (ii) that the predicted no-effect concentrations (PNEC) values for PFOS, PFOA and 6:2 FTs were similar within a factor of two, (iii) that local soil concentrations at sites that had used firefighting foams exceeded the PNEC, meaning that soil organisms were at risk, and (iv) shore-line sea snails had high levels of 6:2 FTs (see box opposite).

The Norwegian report completely changes the basis of the argument about the PBT profile for the fluorotelomer sulphonate 6:2 FTs. We have now to consider that 6:2 FTs, the degradation

product of fluorotelomer firefighting foams, is persistent, bioaccumulative and toxic in certain species such as the earthworm, rather than just persistent, with these parameters in the same ballpark as for PFOS and PFOA.

Why are earthworms important? Earthworms can be considered close to the bottom of the food-chain. Earthworm predators include many birds, fish, moles, shrews, hedgehogs, foxes, toads, snakes, beetles, leeches and slugs. Higher predator levels including man then eat birds and fish. As one passes up the food-chain each species will show differing bioaccumulative and toxicity profiles. This results in bio-magnification. For example, if the earthworm has a bioaccumulation factor (BAF) of N1, is eaten by a bird with a BAF of N2, which in turn is eaten by an animal with a BAF of N3, then the overall bio-magnification factor is simply (N1 x N2 x N3).

There are certain incidents at which foam must be used to protect human life or health even if this potentially puts the environment at risk. A decision has to be taken based on a comparative assessment of risk combined with a cost-benefit analysis given all the circumstances. This decision, which at the time has to be an operational one, must

be grounded on scientific data and strategic guidelines which have established politically and socially acceptable limitations and constraints to human risk and environmental impact. In European Member States local implementations of the EU Groundwater Directive forbid the discharge of organohalogens (this includes fluorosurfactants and their degradation products) to groundwater.

A foam concentrate with the correct specifications for the job in hand should be used. The current trend towards using a fluorosurfactant foam originally formulated for Class B hydrocarbon fires at a lower induction rate as a "one stop" solution for Class A carbonaceous fires, should be strongly discouraged. Class B fluorosurfactant foams do not penetrate carbonaceous fuels nearly as efficiently as properly formulated Class A products, so calling into question their "fitness for purpose" with all its legal implications. Moreover, because most Class B foams contain fluorosurfactant and most Class A fires, for example, wildland or bush fires, require highly dispersive application of foam directly onto vegetation and soil with no possibility of containing run-off, there is a very serious risk of contaminating surface and groundwater with highly persistent fluorinated degradation products. This is environmentally highly irresponsible, given that normal Class A concentrates do not contain fluorochemicals. The arguments given for a "one stop" philosophy range from procurement issues to a form of institutional laziness "...we can't expect firefighters to distinguish between different types of foam concentrate on the incident ground...". Why not? That is what training is for!

If a fluorosurfactant foam must be used then containment and subsequent treatment of fire-water run-off can be used to limit both the environmental impact and legal exposure. For incidents requiring Class B foam at which containment is impossible, for example, motorway incidents, aircraft crashes, petrol station fires, fires involving shipping or harbour facilities, one should consider

alternative solutions in addition to using a fluorine-free product; such as water mist or fog, compressed air foam systems (CAFS), hydrophilic gels, or free-radical chain breaking powders.

### The bottom line

The bottom line is that all fluorosurfactants, whether PFOS-based or fluorotelomer-based, produce very persistent long-lived fluorinated degradation products which are widely dispersed throughout the environment including isolated regions such as the Arctic not in obvious contact with these materials.

Moreover, based on the Norwegian report, these degradation products may be similarly bioaccumulative and toxic in certain species low down in the food-chain, for example, earthworms. Recent studies have identified such products throughout continental Europe in air samples, in rivers, lakes, soil and groundwater, in potatoes and in human breast milk, raising the toxicological spectre of maternal-foetal transmission. Stored human serum samples from before WWII when perfluorinated chemicals were not manufactured, were always negative for organic fluorine compounds which do not occur naturally. This is no longer true even for the general population not occupationally exposed to these chemicals.

Unfortunately because these fluorinated materials are so environmentally persistent, that continued release into soil and groundwater, whether direct or indirect, will result in increasing concentrations as time passes resulting ultimately in the predicted no-effect concentration (PNEC) being exceeded thus putting organisms at risk. This will occur whether or not the fluorinated material is toxic or relatively non-toxic. The time taken even for relatively non-toxic compounds will also depend on the mass flow into groundwater. It is only a matter of time!

## Summary: Norwegian State Pollution Control Agency Report

### Screening of Polyfluorinated Organic Compounds at Four Fire Training Facilities in Norway (to download visit [www.sft.no/publikasjoner/2444/ta2444.pdf](http://www.sft.no/publikasjoner/2444/ta2444.pdf)):

- High levels of polyfluorinated degradation products from both legacy 3M PFOS-based fire fighting foams (perfluorooctane sulphonic acid, PFOS) and also from more recent fluorotelomer foams (fluorotelomer sulphonate, 6:2 FTS), as well as perfluorooctane carboxylic acid (PFOA), have been found in soil, sediments and groundwater in the vicinity of the training sites, as expected based on previous work;
- Exposure of earthworms to soils from the four fire training grounds resulted in average bioaccumulation factors (BAFs) with ranges (n=12) in parentheses for 6:2 FTS, PFOS and PFOA of 2.4 (0.76-6.7), 2.6 (0.49-6.4) and 5.9 (0.31-14.0), respectively, confirming previous findings. Thus 6:2 FTS derived from fluorotelomer foams bioaccumulates in the earthworm to a similar extent to PFOS and PFOA. Field BAF values, as opposed to in vitro laboratory values, for 6:2 FTS tended to be somewhat higher;
- The predicted no-effect concentrations (PNEC) for earthworms exposed to PFOS, PFOA and 6:2 FTS in soil were estimated as 100, 160 and 210 microgram per kilogram ( $\mu\text{g}/\text{kg}$ ) dry weight, respectively, compared to a PFOS value of 77  $\mu\text{g}/\text{kg}$  derived from 3M data in 2003 – thus the PNEC for 6:2 FTS differs approx by only two-fold at most from those for PFOS and PFOA;
- Based on these PNEC values for 6:2 FTS, PFOS and PFOA in soil, soil organisms living within 100 metres of the training sites investigated, may be at risk;
- Sea snails (Patellidae) collected from stones along the seashore within the tidal zone in the vicinity of an effluent stream at one of the sites showed elevated concentrations of 6:2 FTS;
- 6:2 FTS, together with most perfluorosulphonates (PFOS and homologues) and perfluorocarboxylic acids such as PFOA, are mobile in soil and leach to groundwater, with leaching and hence bio-availability being highest in light sandy soils which are low in silt, clay and organic content and lowest when there is a high silt/clay content.

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