Minimising the Risk
The use of fire fighting foam is different to that of almost any other material. Enormous quantities comparable with the flow of small rivers may be used in chaotic situations at unpredictable times and places during emergencies. Foam run-off from emergencies may gush into surface waters at levels much higher than those normally expected by water authorities.

The level of foam usage may be reduced by careful selection of foam concentrate and foam-making equipment. For example, modern foams like Petroseal give faster extinguishment times with correspondingly lower usage levels. Likewise, the use of modern fixed foam systems that operate at lower foam application rates than manual fire fighting methods result in less foam being used to achieve extinguishment.

The choice of foam concentrate is important too. AFF was developed over thirty years ago, long before environmental issues assumed the importance they have today. While environmental shortcomings were tolerated back in the 1960s, they are no longer acceptable. Modern foams like Alcoseal, Petroseal, and FP70 Plus offer the best possible environmental features without compromising fire performance.

Toxicity to Aquatic Organisms
Foam is designed to be used with large quantities of water and so may end up in the water or aquatic environment. Aquatic toxicity tests are usually conducted on a variety of organisms that represent key links in the food chain. These include algae (primary producers), protozoa (single-cell primary and secondary consumers), crustacea (multi-cell consumers), and fish (multi-cell consumers with a central nervous system).

The result of an aquatic toxicity test is usually quoted as an LC_{50} value. This is the lethal concentration in water of foam that would kill 50% of a test batch of animals (eg. fish) within a given period of time. Occasionally, the more demanding LC_{10} or LC_{0} (No Observable Effect Concentration, NOEC) are recorded. The EC_{50} is the effective concentration in water of foam that would produce a particular response in 50% of a test batch of animals (eg. immobilisation of the water flea, Daphnia) or a 50% reduction in a particular response (eg. inhibition of growth of algae). The higher the LC_{50} or EC_{50}, the less poisonous the foam. This is because a foam that needs to be present at a high concentration to cause mortalities is by definition less toxic than one that exerts the same effect at a low concentration.

Toxicity values refer to foam concentrate. This is diluted by between 94 to 99 times to produce foam solution of concentration 1 to 6%. These concentrations are of the same order of magnitude which appear to be toxic to test species. Thus the dilution factor of the receiving water is important in determining whether the final concentration in the environment will reach toxic levels. In actual emergency incidents foam has been reported to have been washed into small water courses and recorded at concentrations in excess of 10,000 mg l^{-1} (or 1% or 10 gl^{-1}). At this concentration, foams produce “rafts” that are capable of causing fish-kills.

While all foams have been found to be of low toxicity compared to other classes of chemicals, there is enormous variation among the different foam categories. The most toxic foams are Syndets, followed by AFF. Protein-based foams are much less toxic. They have been found on average to be less toxic to every organism by factors ranging from 9 for fish to 40 for crustacea. Of all the protein-based foams, FFFP is the least toxic.

Biodegradability
The biodegradability of a foam is a measure of how readily it is broken down by micro-organisms (mostly bacteria) in the environment. The micro-organisms digest foam and in the process extract oxygen that is dissolved in the surrounding water.

Biodegradability is determined by carrying out two different tests and comparing the results. The first test measures the Chemical Oxygen Demand (COD). This is the total
amount of oxygen required to degrade a known quantity of foam. The lower the COD the better, so less oxygen is removed from the environment. The second test measures the Biochemical Oxygen Demand (BOD). This is the amount of oxygen consumed by aquatic micro-organisms in a specified number of days (usually 5) when metabolising the foam. Biodegradability is the BOD expressed as a percentage of the COD.

Foams with a BOD$_5$:COD ratio greater than 50% are generally considered to be rapidly biodegraded. In most environmental hazard assessments high biodegradability is considered desirable as it indicates low persistence. However, foams generally have high BOD values and their rapid biodegradation can deplete dissolved oxygen levels in water bodies which, in turn, may lead to asphyxiation of aquatic organisms. Slower biodegradability may therefore be desirable in certain circumstances.

Synthetic foams such as AFFF are generally less biodegradable than other foams. All foams tested in one independent study demonstrated acceptable biodegradability with the exception of three synthetic foams.

Effects on Wastewater Treatment Plants
In addition to the impact on the natural environment, if waste water containing foam is discharged directly to sewers there is a potential for adverse effects on waste water treatment plants.

In April 1991, fire water run-off containing AR-AFFF from an internal floating roof tank fire in the USA disrupted a refinery's waste water treatment plant. The toxicity of foam types to microbial organisms used in biological treatment works varies enormously. In one test, FFFP gave an LC$_{10}$ of 7,500 mg l$^{-1}$ compared to a value of only 0.6 mg l$^{-1}$ for a Syndet foam, making FFFP a remarkable 12,500 times less toxic!

More recently, AFFF and AR-AFFF have been blamed for carrying toxic hydrocarbons through oil separators into the water environment. Oil separators (interceptors) are increasingly being used in industrial waste water treatment systems to reduce the environmental risk posed by fire water run-off contaminated with toxic hydrocarbon fuels such as oil and gasoline. As contaminated water passes through a series of chambers, lightweight immiscible hydrocarbon fuels separate out by floating to the surface. The fuels are periodically drawn off into road tankers for disposal, and the remaining uncontaminated water is discharged safely into a watercourse or sewer with the consent of the appropriate authority.

This normal operation of oil separators is disrupted by the presence of detergent from AFFF and AR-AFFF. Detergent (oleophilic) prevents the oil and water from separating fully by forming an emulsion comprising small droplets of oil suspended in the water. So when seemingly innocent purified water is discharged from oil separators, harmful oil may insidiously find its way into rivers, streams, and reservoirs.

The devastating effects of massive oil spillages on wildlife and plant populations are wellknown. But even small quantities of oil from oil separators can cause serious long-lasting pollution. For example, one gallon of oil is all it takes to cover a one acre lake!

Oil accounts for 25% of all pollution incidents recorded by the UK Environment Agency. It warns that “the emulsion can kill fish either directly by poisoning, or else indirectly by drastically lowering the oxygen level in the water. Oil floating on the water can also prevent oxygen transferring from the air into the water body”. Similarly, the UK Institution of Water and Environmental Management (IWEM) points out that “foam containing detergent can mix with the fuel itself and carry it into the water environment, giving rise to much higher oxygen demands in the water”.

The disruption of oil separators is likely to encourage a further decline in the use of synthetic detergent-based AFFF and AR-AFFF. The UK National Environmental Technology Centre, which has carried out extensive research into the damaging effects of detergent on the operation of oil separators, explains that “the only solution for fire fighters is to avoid the use of foams that contain detergent”. The use of modern detergent-free foams eliminates the risk of polluting the water environment by emulsifying the contents of oil separators, while at the same time raising the level of fire protection.

Harmful Ingredients
Hydrocarbon Surfactant (“Detergent”)
The foaming agent is the most important ingredient in foam because it produces the bubbles. In protein-based foams the foaming agent is hydrolysed protein. This occurs naturally in the environment as a result of the breakdown of animal and plant proteins. It exhibits exceptionally low toxicity, and as a result it is commonly used in human foodstuffs. Protein-based foams may even enhance the growth rate of legumes.

In sharp contrast, the foaming agent in synthetic foams such as AFFF and AR-AFFF is hydrocarbon surfactant, more commonly known as synthetic detergent. It is the most acutely toxic of the main foam constituents, with LC$_{50}$ values less than 20 mg l$^{-1}$ for algae, molluscs, crustaceans, insects, and fish. It does not occur in Nature, it is a non-renewable resources, and it is not used in human foodstuffs.
Glycol Ether
Glycol ether is found in most AFFF and AR-AFFF foams. It is classified as a "hazardous substance" and is currently under review by the US Environmental Protection Agency (EPA).

Environmental regulators have paid increased attention to glycol ethers in recent years. Low molecular weight glycol ethers have been associated with adverse reproductive and developmental effects in humans.

In addition to human health concerns, glycol ether is also toxic to aquatic organisms with LC₅₀ values of around 1,500 mg l⁻¹. This compares with a value of over 10,000 mg l⁻¹ for hexylene glycol used in protein-based foams. Up to four times as much glycol ether may be used in synthetics, giving an advantage of 40 between a poorly formulated synthetic and a good quality FFFP.

The glycol ether used in most AFFF and AR-AFFF products is Diethylene Glycol Butyl Ether (DGBE), CAS number 112-34-5. It has many chemical synonyms. For example, 2-(2-butoxyethoxy) ethanol; ethanol, 2-(butoxyethoxy)-; 1-n-butoxy-3-oxabutan-5-ol. The quantity present varies from one brand to another, but it is usually in the range 10 to 40%. The precise quantity may be obtained from the manufacturer's Material Safety Datasheet (MSDS).

Some foam manufacturers have replaced DGBE with various propylene oxide-based glycol ethers. However, this "second best" approach provides little if any real environmental improvement and may lead to reduced fire fighting performance.

Petroseal and Alcoscald do not contain, and never have contained, any harmful glycol ether.

APE
Another group of substances found in many synthetic detergent-based AFFF and AR-AFFF foams, but not the latest protein-based foams, are Alkylphenol Ethoxylates (APE).

APE allegedly causes reproductive changes in fish by mimicking the female sex hormone oestrogen. Also it does not biodegrade easily and so high concentrations may be reached in drinking water. These two factors combined have led to APE being implicated in falling sperm counts among the Western male population.

APE is currently a major topic of discussion in the USA, and research is underway to ascertain the full impact of these substances. In Europe the issue is being addressed by the Oslo and Paris Commissions (PARCOM). Clearly foams that do not contain APE are sounder investments for the future than ones that do.

Further Reading
• A Review of Fire Fighting Foams to Identify Priorities for EQS Development, WRC plc.
• The Classification of foam compounds in relation to their water pollution category, E. Ising, German Army.
• New Scientist, 52, 13 March 1993.
• New Scientist, 26 August 1995.
• Toxic Substances Bulletin, 29, January 1996.