



PFASs and the TOP Assay

New methods to measure poly- and perfluoroalkyl substance (PFASs) in firefighting foam and the environment, by Ian Ross, Erika Houtz, Erica Kalve, Jeff McDonough, Jake Hurst and Jonathan AL Miles.

Class B firefighting foams that contain fluorosurfactants, also known as poly- and perfluoroalkyl substances (PFASs), have been available since 1964. The term PFASs refers to a class of approximately 3,000 individual compounds that include both long and short carbon-chain compounds known, for example, as C8, C6, C4; many PFASs present in fire-fighting foams have been largely undetectable until introduction of a new analytical tool, the Total Oxidisable Precursor (TOP) Assay.

The TOP Assay analytical tool can assist organisations in their commercial and operational planning when considering the long-term environmental management and potential liabilities from PFASs, highlighted by emerging environmental regulations.

PFASs have historically been (and continue to be) used extensively to suppress liquid hydrocarbon and polar solvent fuel-based fires during fire training and emergency response, to protect fuel storage facilities with above-ground storage tanks, in sprinkler systems in some warehouses, aircraft hangars and for use in fire suppression systems in shipping.

The foams that contain PFASs include aqueous film forming foam (AFFF), film forming fluoroprotein foam (FFFP), and fluoroprotein foam (FP). Alcohol-resistant versions of these foams are also available.

Over the past decade, an increasing number of PFASs have become chemicals of emerging concern to environmental regulators. Their presence in the environment at relatively high concentrations is frequently linked to the use of Class B fire-fighting foams containing PFASs. These foams were used historically without awareness of the potential environmental and human health impacts of the PFASs they contain. In the last few years, however, there has been increasing concerns as some PFASs are being discovered in drinking water supplies.

In 2016, the US Environmental Protection Agency adopted a long-term health advisory level of 70 nanograms per litre (ng/L), or parts per trillion (ppt), for the sum of PFOS and PFOA detected in drinking water. These extremely low

standards are similar to concentrations considered acceptable in drinking water in other countries and individual US states. In New Jersey, an enforceable maximum concentration limit for PFOA of 14 ng/L in drinking water has been recommended with the state considering a recommended MCL of 13 ng/L for PFOS.

Considering other industrial applications of PFASs, use of these foams for fire training and in emergency response are among the most environmentally dispersive of all activities. These foams have often been applied repeatedly or in large quantities to the ground surface in many locations, creating potential legacy contamination issues.

C8-compounds, such as PFOS (perfluorooctane sulphonic acid) and PFOA (perfluorooctanoic acid), have been the initial focus of environmental regulations in many countries; however, many environmental regulators internationally are now focusing on some of the other chain length PFASs. The C6 compound, PFHxS (perfluorohexane sulphonic acid) is now regulated in Australia, Germany, Texas and New Zealand. There are environmental regulations considering the C6 compound, perfluorohexanoic acid (PFHxA), in Germany, Texas, Denmark, Switzerland, Italy, Canada, and Sweden; and the C6 compound 6:2 fluorotelomer sulphonate in Germany, Australia, Denmark, Switzerland, and Sweden.

It is clear that regulations considering many PFASs beyond PFOS and PFOA are evolving quickly. In some jurisdictions, the use of PFAS-containing Class B foams has already been restricted significantly, with a recent ban on PFAS-based foams announced in South Australia in February and similar restrictions progressing in the state of Washington in the US, where State Senate Bill 6413 was passed in February this year.

Owners and operators of high-hazard facilities that require the use of PFAS-containing Class B foam products may need to consider the environmental liabilities associated with the continued or historical use of these foams. Additionally, training and use of some PFAS-containing Class B foams may still be an ongoing activity at high-hazard sites.

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Testing PFASs in foams

Current PFAS testing methods are geared towards relatively few compounds, primarily perfluoroalkyl acids (PFAAs), such as PFOS, PFOA, PFHxS and PFHxA, which are the main focus of current regulations.

However, Class B fire-fighting foams contain many other types of polyfluorinated compounds that vary by manufacturer. These are often proprietary foam formulations, meaning their exact chemical content is not public knowledge due to its commercial value. Therefore, most of the chemical identifications and structures of polyfluorinated compounds in these foams are not definitively known.

The proprietary polyfluorinated compounds are generally termed as precursors to PFAAs because they ultimately biotransform in the environment and in higher organisms to become persistent PFAAs. Several hundred proprietary precursors have been identified either as components of Class B foams or as their environmental breakdown products in soil and water. The concentration of the majority of these precursors cannot be determined, in samples of soil, groundwater or firefighting foams using conventional analytical methods (ie techniques that currently measure PFAAs), so they remain hidden.

From an environmental risk assessment perspective, knowing the exact chemical structure of these precursors is important as it allows testing to determine toxicity, whether they bioaccumulate or biotransform, and how mobile they are in an aquifer.

Regulatory values that restrict chemicals to prevent human health effects are typically based on animal studies. These animal studies define a concentration below which there are no adverse health effects observed and then an extrapolation of that information informs a safe exposure value for humans. The largely unknown properties of these variable precursors add a general uncertainty when attempting to assess risks they potentially pose to the environment and human health. Therefore, more work is needed to understand the environmental risks posed by the many precursors. However,

it is known that the toxicity of some polyfluorinated fluorotelomer precursor compounds has been observed to be greater than that of the PFAAs they eventually form.

In the face of this uncertainty, the Australian Government Department of the Environment and Energy has recently published a PFAS National Environmental Management Plan which highlights that the precautionary principle should be applied to managing uncertainties considering PFASs. The precautionary principle states that when there are threats of serious or irreversible environmental damage a lack of full scientific certainty should not be used as a reason for postponing measures to prevent environmental degradation. How the precautionary principle will be applied to the uncertainties pertaining to precursors is yet to be defined.

TOP Assay

One powerful new tool to measure the concentration of total PFASs (both known PFAAs and proprietary precursor PFASs) is an indirect measurement technique known as the TOP Assay, which was developed at the University of California, Berkeley. TOP Assay is designed to chemically convert all precursors in a sample into PFAAs.

This method uses oxidative conditions that remove the proprietary part of the molecule, but leave the perfluoroalkyl group intact. This results in the generation of PFAAs which are used as a measure of the presence of the hidden precursors. By measuring PFAAs in the sample before and after chemical conversion, the concentration of precursors can be indirectly measured. In this way, the TOP Assay provides a conservative estimate of the concentration of total PFASs versus the limitations of the standard analyses.

Since publication of the TOP Assay in the academic literature in 2012, TOP Assay has been made commercially available at laboratories in the UK, Europe, North America, and Australia.

In 2016, the State of Queensland, Australia, became the first jurisdiction to codify the use of TOP Assay in the certification of firefighting foams. TOP Assay has gone from a research method to a well-established analytical method with a high reliability. Arcadis is currently assisting the State of Queensland with guidance on detailed interpretation of the TOP Assay output data and data quality objectives to ensure consistent use across multiple commercial laboratories and consistent application across jurisdictions.

As awareness of these hidden precursors is growing, approaching this issue using tools that provide insight into the total potential mass of PFASs at a site, seems likely to become more important over time for managing long-term latent liabilities. It is clear that environmental regulations are progressing to consider the full extent of PFASs and not just PFOS and PFOA. Commercial decision-making on managing risks and liabilities associated with historical and ongoing use of Class B fire-fighting foams containing PFASs may need to consider future-proofing their long-term management plans in light of the reality that all PFASs are being viewed by regulators as potentially causing permanent environmental damage.

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