



# UNDERSTANDING FATE AND TRANSPORT OF PFAS TO DEVELOP EFFECTIVE MANAGEMENT PLANS

## Introduction

Poly- and Perfluoroalkyl substances (PFAS) are used in a wide range of industrial applications and commercial products due to their unique oil and water repelling properties. As PFAS are extremely persistent and mobile in the environment they are being discovered in drinking water supplies above safe levels in many countries, with a drinking water supply well in Cambridgeshire recently described to have been impacted at four times the UK legal limit of 100 ng/L [1].

It's clear that the use of all PFAS will be subject to regulatory scrutiny to determine if alternatives are available or if specific uses are essential.

PFAS, termed fluorosurfactants are also major components of firefighting foams used to extinguish flammable liquid fires such as aqueous film forming foam (AFFF) and fluoroprotein foams. For this highly dispersive application, advancing regulations are curtailing their use, with alternative fluorine free firefighting (F3) foams demonstrating comparable extinguishment performance using large scale tests [2-4].

This article aims to describe the fate and transport of PFAS, discuss analytical tools and treatment options / uncertainties such that PFAS sources and plumes can be effectively managed.

## Regulatory Focus

Drinking water standards for PFAS continue to be set at exceptionally low levels in what may be perceived as a "race to the bottom". The concern being that as compliance levels are set so low, they are at comparable levels to those identified in multiple environmental matrices as "background" detections such as rainwater. The regulatory level for perfluorooctanoic acid (PFOA) in drinking water was recently set at 2 ng/L in Illinois [5] whilst in Denmark a 2 ng/L level has been set for the sum of PFOA, perfluorooctane sulphonic acid (PFOS), perfluorohexanesulphonic acid (PFHxS) and perfluorononanoic acid (PFNA) in drinking water [6].

In the US the EPA recently released a PFAS strategic roadmap [7] which, amongst many other actions requires the EPA to set enforceable drinking water limits for certain PFAS under the Safe Drinking Water Act in the winter of 2022 and by the spring of 2022, draft a proposed rule designating certain PFAS as hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Whilst in October 2021 the UK the drinking inspectorate instructed water companies to assess every raw drinking water abstraction for some 47 different PFAS [8] following announcement of new lower drinking water standards for PFOS and PFOA (at 100 ng/L) in January 2021 [9]. Meanwhile European regulations on PFAS in drinking water required that the sum of 20 individual PFAS are below a 100 ng/L limit value [10].

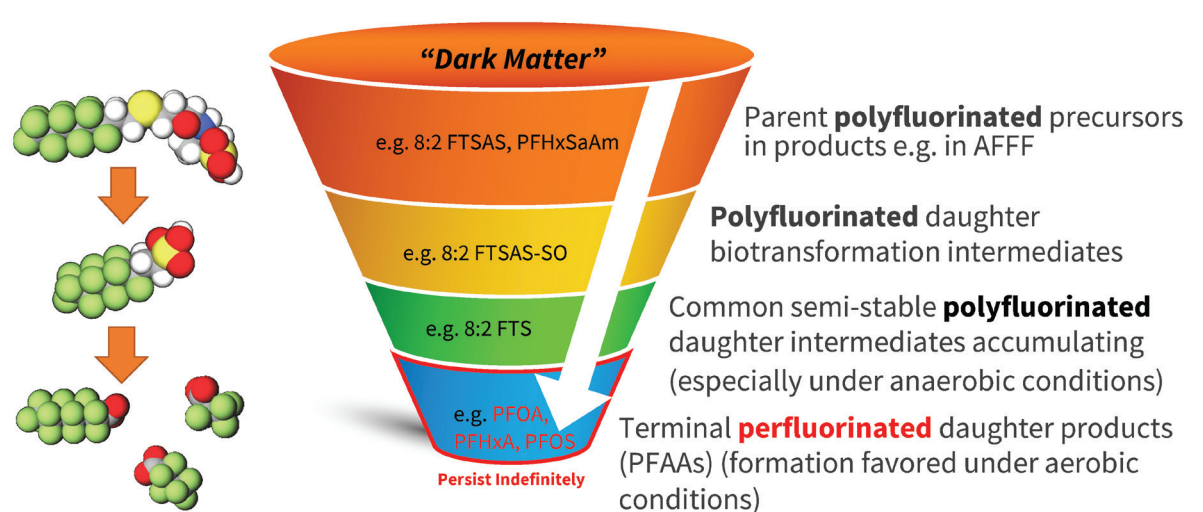


Figure 1. Environmental Transformation of Polyfluoroalkyl PFAS to Create Persistent PFAAs

## PFAS Uncloaking

The PFAS present in all fluorinated firefighting foams comprise a mixture of perfluoroalkyl substances such as PFOS and polyfluoroalkyl substances, with foams still currently in use being dominated by polyfluoroalkyl substances. The polyfluoroalkyl substances tend to be proprietary molecules which cannot be detected using conventional chemical analyses, but they biotransform in the environment, to create the detectable and regulated perfluoroalkyl substances, such as PFOS, PFOA and shorter chain, more mobile PFAS such as perfluorohexanoic acid (PFHxA). These perfluoroalkyl substances are collectively termed perfluoroalkyl acids (PFAAs) and include PFOS, PFOA, PFNA, PFHxS and PFHxA. The polyfluoroalkyl substances have been termed PFAA-precursors as they create PFAAs and the fact that these precursors remain hidden from conventional chemical analyses has led to them being termed as "Dark Matter". [11]. A biotransformation funnel showing the generation of PFAAs via common daughter products from a parent PFAA-precursor found in some fluorinated firefighting foams called 6:2 fluoromercaptoalkylamido sulphonate (6:2FTSAS) is shown in Figure 1.

## PFAS Source Bleeding

The PFAAs are extremely persistent in the environment, tend to be negatively charged (anionic) thus highly mobile and their mobility increases as the length of the perfluoroalkyl chain decreases, so shorter chains can travel further in groundwater. The polyfluoroalkyl substances can be positively charged (cationic) or have a combination of charges (zwitterionic) meaning they are retained by most soils and aquifers, thus they can remain in locations where firefighting foams have been applied, such as fire training areas. They can then represent an ongoing source of PFAAs, as charge switching can occur as these PFAA-precursors biotransform, meaning they are converted from less mobile cationic and zwitterionic forms to much more mobile anions, such as PFOS, PFOA, PFHxS, PFNA and PFHxA. The further complexity is that amphiphilic PFAS, self-assembled in bilayer structures which can stack into multiple layers, such that multi-layered coatings can be present on surfaces. Amphiphilic PFAS have been shown to concentrate on concrete surfaces which then act as source of PFAAs for decades to come.

PFAS have been shown to be associated with the air water interface, and can also be stored on the surface of groundwater [12]. So, whilst many PFAS are highly mobile and subject to long range transport, there can also be a significant reservoir



## PFAS Source Zone and Plumes - Generic Conceptual Site Model

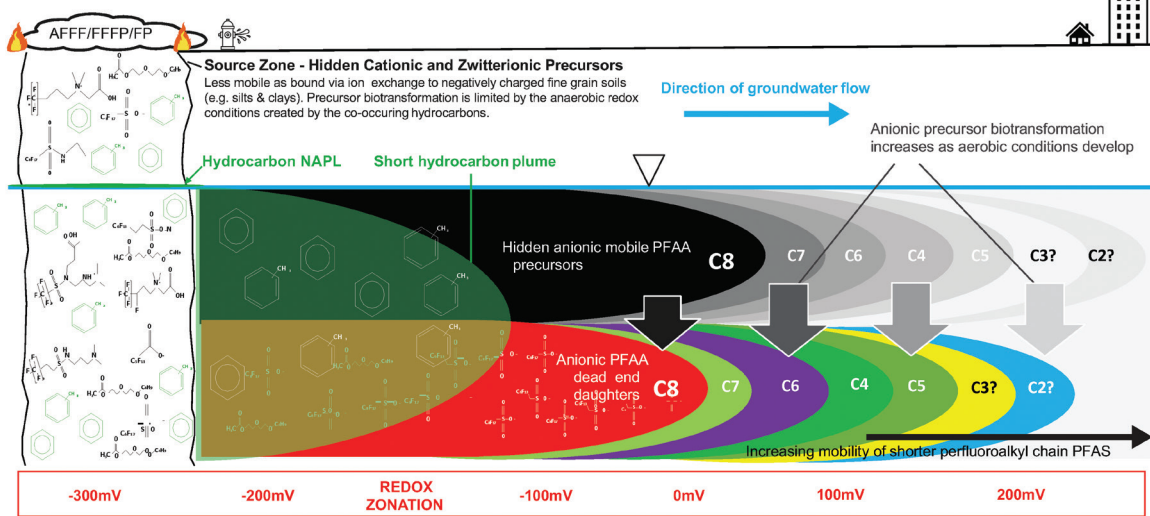


Figure 2 Generic Conceptual Site Model Considering PFAS Fate and Transport [13].

remaining at the source (e.g. fire training areas), associated with surficial soils, concrete and the capillary fringe (or smear zone) where the water table fluctuates. The presence of high levels of undetectable PFAA-precursors in soils can have significant implications when selecting remedial technologies as the “Dark Matter” can mean certain remedial approaches are potentially ineffective unless their performance on the PFAA-precursors is proven. A generic conceptual site model (CSM) describing PFAS fate and transport is presented below in Figure 2. Tetra tech is applying a specialist cleaning agent termed PFAScrub® to remove PFAS from soils and this has been demonstrated to remove an order of magnitude more PFAS than using water alone.

### Chemical Analyses

Analytical methods to assess the presence of the polyfluorinated precursors and PFAAs, such as the total oxidisable precursor (TOP) assay have been commercially available since 2015. This method can detect a wide range of PFAA precursors indirectly, by converting them into PFAAs using a chemical oxidant, so the resulting PFAAs can then be detected, as their chemical analysis is often possible. For the TOP assay to be applied to detect PFAA-precursors in soils some additional extraction methods are required which focus on removing cations and zwitterions, so that they can then be quantified. Recent research has shown that 97% of the PFAS in soil sources remain undetected [14]. The TOP assay could be described as the PFAS uncloaking tool, but care needs to be taken ensuring that the published data quality objectives are met [15] and that interpretation is accurate.

### PFAS Water Treatment

When considering treatment of PFAS impacted waters such as groundwater and surface water, characterising the water using TOP assay can be essential to allow design of the treatment solution. Estimation of the sorptive capacity of a water treatment system

may be flawed if only a fraction of the PFAS in the water has been assessed. This can be more important when considering water that is being extracted from an area close to a PFAS source, as there will have been less time for the PFAA-precursors to have been transformed via biological activity. Activated carbon is more effective for treatment of the longer chain (more hydrophobic) PFAAs such as PFOS and PFOA, as opposed to the shorter chains such as PFHxA. For shorter chain anionic PFAS, ion exchange resins are generally more successful, as electrostatic interactions can be used to remove them from water. Characterising the water that needs treating for natural organic matter and common anions, such as sulphate, can be very important to determine the likelihood of successful treatment. Running small scale column studies and water treatment laboratory scale or field pilots can be used to design treatment systems.

Other technologies that are developing to remove PFAS from water include multiple proprietary sorbent media and foam fractionation, to remove PFAS from solution and concentrate it. Treatment methods that apply oxidants, such as ozofractionation, which applies ozone in foam fractionation, will convert PFAA precursors into PFAAs, meaning that some of the amphiphilic PFAA precursor that could readily be separated by the foam fractionation process are instead oxidised into a short chain PFAAs that are not as easily removed [16]. Application of oxidants, such as ozone, or biological attack on common PFAA-precursors, known as fluorotelomers, leads to the generation of a series of short chain PFAAs, including some termed ultrashort PFAAs (with 1 to 3 carbon atoms in their chain), that are not detected using commercially available analyses. The generation of a third of the mass of precursors as ultrashort chains has been reported when oxidants are applied [17]. Transformation of a fluorosurfactant found in certain AFFFs, through 6:2FTS (6:2fluorotelomer sulphonate) is shown in Figure 3. This process will occur if oxidants or aerobic biological treatment processes are applied to treat PFAS which often includes PFAA-precursors. So, application of water treatment technologies using aerobic biological processes and chemical oxidants may lead to the formation of

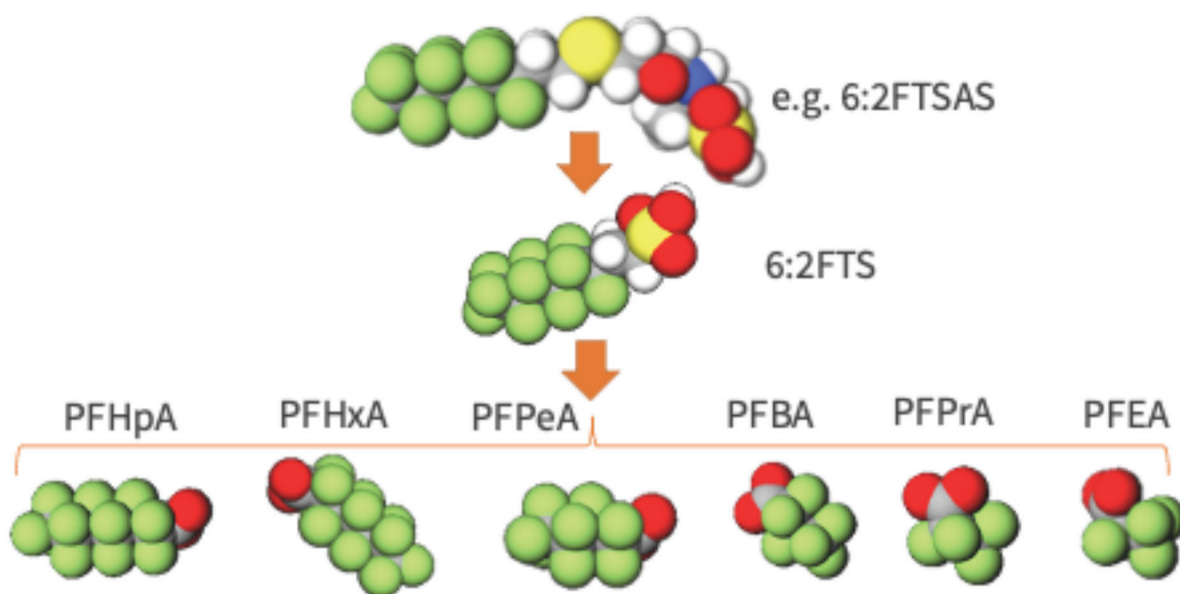


Figure 3 Conversion of PFAA precursors to a range of PFAAs via chemical oxidation or biotransformation.

more mobile PFAS.

A series of remedial technologies that separate and destroy PFAS are being developed, with Tetra Tech leading the way in scaling up destructive approaches such as sonolysis, electron beams and use of supercritical water oxidation.

### Summary

Management of PFAS impacts to ground requires a detailed understanding of the unique behaviours of this class of compounds, where physical, chemical, and biological processes can act to retain or mobilise PFAS from soils into groundwater or surface waters which can impact drinking water supplies. As regulations become increasingly comprehensive and stringent, the risks posed by a wide range of PFAS will need to be considered. When considering remediation of soils impacted by PFAS, there are significant uncertainties characterising PFAS, which is an essential step before embarking on a remedial approach. Tetra Tech can assist with characterising and treating PFAS, as a result of experience characterising, risk assessing and treating this class of contaminants since 2005.

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