

Evidence report

PFAS in UK waters – presence,
detection, and remediation

November 2023

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large class of anthropogenic chemicals that have been used over decades in a wide array of industrial and commercial applications. Estimates suggest more than 10,000 different substances exist and they are popular due to their unique combination of desirable properties, including water-resistance, oil-resistance and thermo-chemical stability.




PFAS are vitally important in life-saving medical devices, our everyday electronic devices, aerospace, fire-fighting foams, weatherproof gear, non-stick cookware and many other consumer product applications and industrial processes that serve to grow the economies of the world and improve our quality of life.

However, there is increasing global concern surrounding this group of chemicals, due to their persistence in the environment over decades, bioaccumulative nature in humans and wildlife, highly mobility, and the health hazards some PFAS have been shown to pose to humans and other animals (US NTP 2016; DWI, 2020; EFSA, 2020; Vo *et al.*, 2020; WHO, 2022; HSE, 2023; US EPA, 2023). Understanding the true risks of adverse effects relies on having good estimates or measures of human and wildlife exposure to PFAS.

Ingesting contaminated drinking water is one of the main pathways by which humans can become exposed to PFAS (Sunderland *et al.*, 2018; Ambaye *et al.*, 2022). Therefore, the presence, detection and remediation of PFAS present in water sources are topics of high importance in national and global chemicals policy. There is limited information on the qualitative and quantitative presence of PFAS in sources of drinking water across the UK, but the data that does exist gives rise to genuine concern.

The analytical methods for detecting individual and total PFAS are not yet standardised, and data are difficult to compare across regions. A range of remediation technologies exist for purifying water but the effectiveness of remediation processes for removing PFAS from water has not been thoroughly investigated.

To highlight and begin to address these gaps in knowledge, the Royal Society of Chemistry has commissioned and undertaken an analysis of currently available PFAS monitoring data for the UK, a review of the scientific literature on the presence, detection and remediation of PFAS, and reports from relevant authorities to determine the answers to three key questions:

-  **1. Presence:** to what extent are PFAS present in sources of UK water?
-  **2. Detection:** what analytical methods exist for detecting PFAS in water?
-  **3. Remediation:** what remediation methods exist for the removal of PFAS from water?

This report brings together this information in one place, with the aim of contributing to a sound evidence base to inform future policy and decision making on this important class of chemicals. In particular, the evidence in this report has been used to inform the **RSC policy position on PFAS in UK drinking water.**

What are PFAS and why is there a concern?

PFAS are defined by the Organisation for Economic Co-operation and Development (OECD) as “**fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)**” (OECD, 2021). Therefore, with a few exceptions, any chemical with at least one perfluorinated methyl group (-CF₃) or one perfluorinated methylene group (-CF₂-) in its structure is considered a PFAS under the OECD definition. Approximately **4,300 chemicals** have been registered as PFAS by the Chemical Abstracts Service, although the precise total number of PFAS that exist is disputed, with estimates exceeding 10,000 (Ambaye *et al.*, 2022; Kidd *et al.*, 2022).

The carbon-fluorine bond present in all PFAS is one of the strongest bonds in organic chemistry, making them **highly chemically and thermally stable** (Ambaye *et al.*, 2022), a desirable property for many products. PFAS are also **amphiphilic** (having both polar and non-polar parts to their structure), causing them to behave like traditional surfactants, and making them both **water and oil repellent** (Krafft and Riess, 2015; Saawarn *et al.*, 2022).

Due to these unique properties, PFAS have been employed extensively since the 1940s in a range of commercial, medical, and industrial products – from aqueous fire-fighting foams and water-repellent clothing to paint additives and non-stick cookware (Wang *et al.*, 2022; Ambaye *et al.*, 2022; Meegoda *et al.*, 2022).

However, the strength of the C-F bond also renders PFAS highly **persistent** (Meegoda *et al.*, 2022), hence the group being commonly dubbed ‘**forever chemicals**’. Once manufactured, PFAS **accumulate** in living organisms and in the environment and will not generally degrade naturally (Kwiatkowski *et al.*, 2020; Sunderland *et al.*, 2018). In addition, they are often highly **mobile**, dispersing across the globe far from their initial source of release (WHO, 2022).

Owing to their widespread use and their stability in and mobility through the environment, PFAS can now be detected almost everywhere (Saawarn *et al.*, 2022). They have been found contaminating soil, land leachates, sludge, surface water, groundwater, seawater, wastewater, drinking water and even the blood of humans and other animals (Vo *et al.*, 2020; Ambaye *et al.*, 2022).

The widespread presence of PFAS in waters around the world and their persistence alone may be enough to raise alarm bells for improving the use and management of PFAS. However, a cause for greater concern is that exposure to some PFAS has been associated with **adverse health effects** in humans and other animals (Kwiatkowski *et al.*, 2020).

These include effects on growth, reproduction, carcinogenesis, thyroid function, cholesterol levels, and immunotoxicity (US NTP, 2016; EFSA, 2020; EA, 2021; Wang *et al.*, 2022).

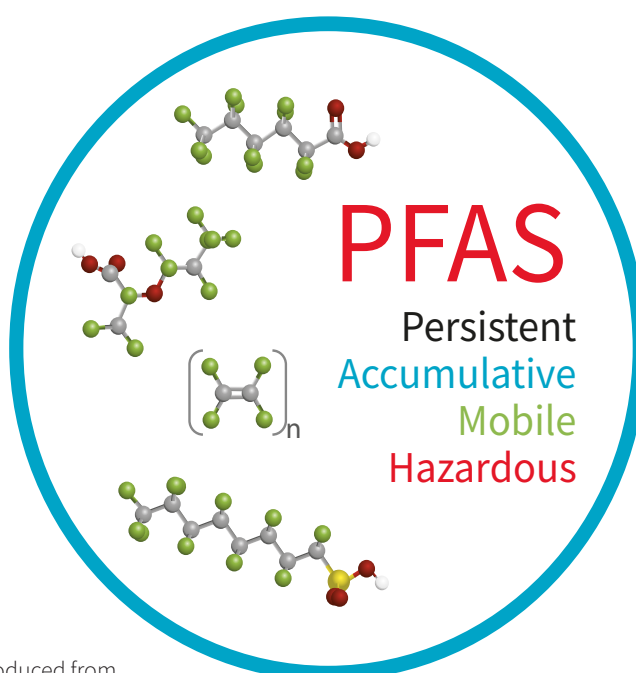


Figure 1. Key properties of PFAS (reproduced from Kwiatkowski *et al.*, 2020)

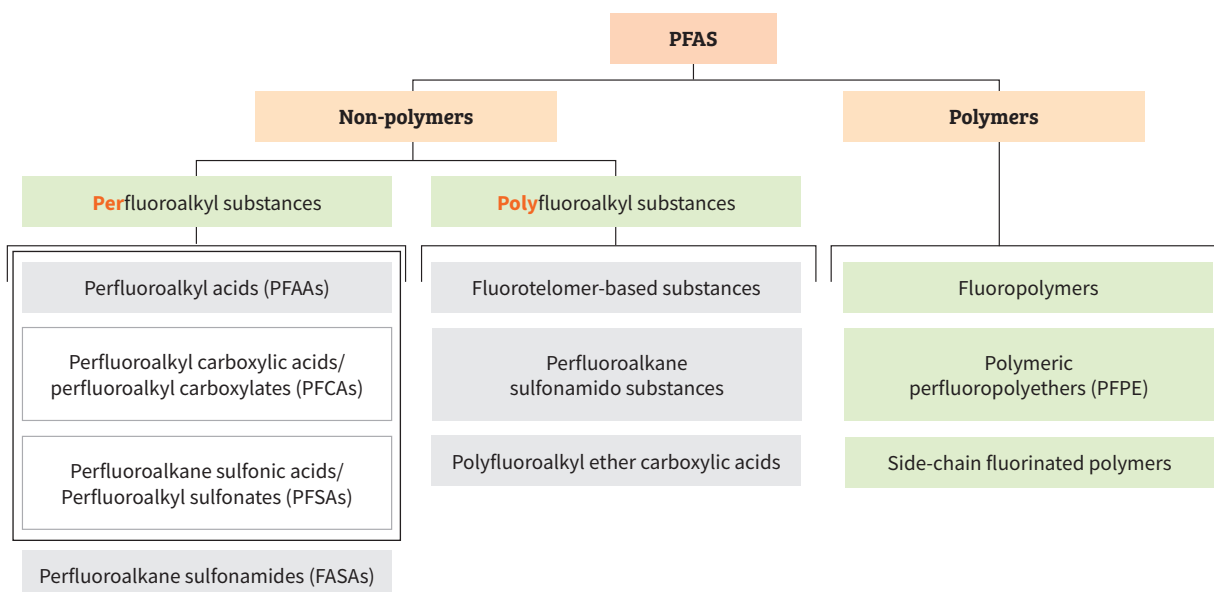


Figure 2. Summary of different groups of PFAS (reproduced from the ITRC naming conventions of PFAS).

However, to date, relatively few PFAS have been subject to extensive toxicity testing, so information on the hazardous properties of individual chemicals from traditional OECD guideline test methods is limited, in reality (EA, 2021). The two most widely studied and historically used PFAS have been perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA).

PFAS can be grouped according to chemical structure in many ways. Arguably the simplest is to consider a substance as short-chain (\geq alkyl carbons), long-chain (>8 alkyl carbons) or in some cases, PFAS can be designated as ‘fluoropolymers’.

Whether or not to include fluoropolymers in regulatory action remains a matter of debate (Henry *et al.*, 2018). The issue is arguably less with the fluoropolymer per se, which is of low bioavailability and toxicity, but with shorter chain processing aids, such as hexafluoropropylene oxide (HFPO) dimer and its ammonium salt (referred to as GenX chemicals), which are designed as alternative processing aids to PFOS and PFOA in the manufacture of fluoropolymers; US Environmental Protection Agency (EPA) evidence on the human health toxicity of GenX is available at <https://www.epa.gov/system/files/documents/2023-03/GenX-Tox-Assessment-technical-factsheet-March-2023-Update.pdf>

A sub-chronic reference dose (RfD) of GenX chemicals, that can be considered safe, relating to the observed liver effects of GenX, was estimated by the EPA to be 30 nanograms per kilogram body weight per day (ng/kg/day). Due to the lack of chronic duration studies, an extra 10-fold uncertainty factors was applied to yield a chronic RfD of 3 ng/kg/day.

GenX would appear to be of lower toxic potency than the sum of four PFAS found in food, as evaluated by the European Food Safety Authority (EFSA), for which a guideline value of 4.4 ng/kg/week was set as a tolerable weekly intake (EFSA, 2020). Nevertheless, the chronic RfD value for GenX is also stringent.

These low values for safe reference doses derived by authoritative bodies give cause for concern. Considering intakes in infants, as the most sensitive group, for a six-month-old child with a mean body weight of 8.8kg (EFSA 2020) drinking 1L of water a day, a RfD value of 3 ng/kg/day would allow for an intake of GenX at 26.4 ng/L/day from all sources. Using the EFSA guideline intake value of 4.4 ng/kg/week, equivalent to 0.63 ng/kg/day, for an infant of 8.8kg, this would allow for an intake of 5.5 ng/L/day. With these low guideline values for intake, we need to know the extent of PFAS levels that could contaminating our drinking water from various sources.

The evidence

1. Presence: to what extent are PFAS present in UK water?

There is clear evidence to show that PFAS are widespread in UK surface and groundwaters, but the data also shows there are regional differences when PFAS have been quantified. Data from the Environment Agency (EA, 2021), and more recently from research by Stéphane Horel at the [Forever Pollution Project](#), presented in *Le Monde* (and other media outlets), indicate that there is widespread PFAS presence in water in the UK and Europe.

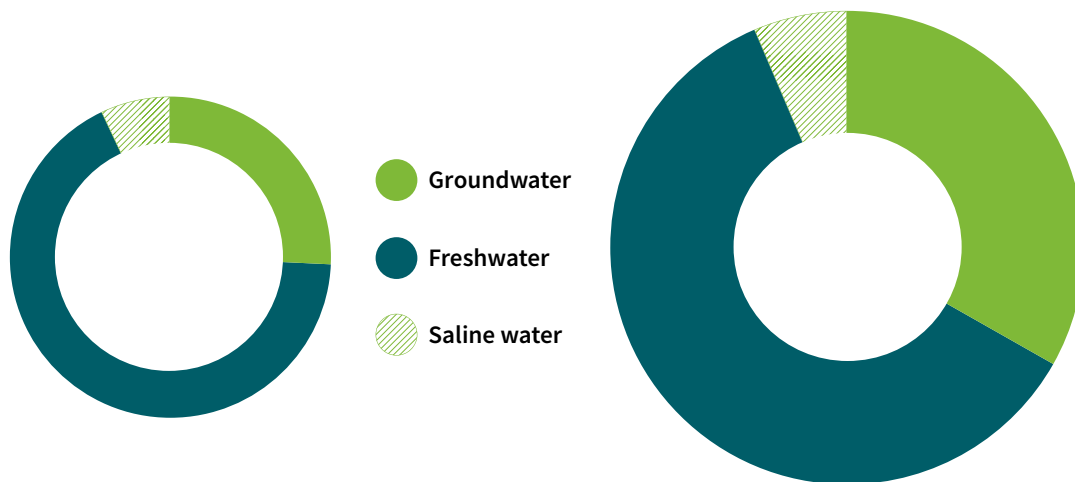
Following presentations at an RSC expert-led event on PFAS in water in November 2022, and the RSC's independent research, there is clear evidence that PFAS are present in UK surface and [groundwaters](#). However, environmental monitoring for PFAS has been patchy and inconsistent, using varied criteria for which types of PFAS are measured, and different analytical methods and limits of detection. This makes it challenging to quantify the extent of the problem of PFAS pollution in UK waters.

ENVIRONMENT AGENCY (ENGLAND AND WALES) DATA

Summary: A semi-quantitative monitoring programme, targeting 16 PFAS was conducted between 2014 and 2019. A fully quantitative monitoring programme for PFOS and PFOA ran between 2016 and 2019. Since 2021, the EA has measured a wider range of PFAS in groundwater samples using methods that can provide some quantitation (EA, 2021). However, it remains challenging to conclude on the impacts of PFAS contamination in quantitative terms. The qualitative presence of multiple PFAS in UK waters is not in doubt.

Semi-quantitative monitoring programme

The Environment Agency (EA) (England and Wales) conducted a semi-quantitative targeted monitoring programme for PFAS between 2014 to 2019 for 16 PFAS substances, all of which are included in the Drinking Water Inspectorate's (DWI) current list of 47 PFAS substances for monitoring. This programme involved sampling of both groundwater and surface water (including fresh, estuarine and coastal water).



Water – (LC-MS scan)

- Target screen
- 2014 to 2019
- ~15 PFAS
- Semi-quantitative

Water – WFD surveillance

- 2016 – 2019
- PFOS and PFOA
- Fully quantitative
- Monthly sampling

Figure 3. Overview of Environment Agency sampling for PFAS 2014-2019. Relative size of sampling programme is represented by circle size

Semi-quantitative monitoring can only screen for the presence or absence of a given PFAS species above the limit of detection (LOD), so is there to help detect emerging contamination issues, rather than give absolute concentration values for individual PFAS (EA, 2021).

The LOD is the lowest quantity of a substance that can be reliably detected using analytical equipment, so the lower the LOD, the better able we are to detect low concentrations of a given PFAS species (John *et al.*, 2022).

Analysis looks at three levels: <10 ng/L, between 10-100 ng/L, and >100 ng/L.

- The EA indicated in its report of the monitoring data (EA, 2021) that LODs down to 0.1 ng/L (freshwater for 8/16 PFASs) and 0.1 ng/L (groundwater for 8/16 PFASs) are achievable. However, for freshwater samples, 20% of the total number samples had no LODs reported. This was markedly better for groundwater samples, for which 4% of samples had no LOD reported. This data had to be omitted.
 - For freshwater samples, there were ~21,000 total PFAS hits across ~3,500 discreet samples.
 - 20% of the freshwater data was omitted due to the units of the LOD not being reported.
 - 42% of the total detections in freshwater samples had a 10 ngww/L LOD.
 - LODs ranged from 0.1 ng/L to 50 ng/L for groundwater samples (37% of the samples were analysed at the 0.1 ng/L level).
 - For groundwater samples, there were ~2,000 total PFAS hits across ~1,000 discreet samples.
 - Only 3.5% of the groundwater data had no LODs or no units for the LOD reported, these data were omitted.
 - Of the 16 PFAS compounds being monitored, eight freshwater and seven groundwater PFAS substances were detected in less than 2% of the samples.
 - Analysis of the data largely supports the EA view that PFAS contamination is widespread, but it is hard to judge the extent and severity of water contamination on environment and health.

Fully quantitative monitoring programme

Between 2016 and 2019, the EA conducted fully quantitative assessments of the levels of the two most extensively studied and manufactured, and therefore most detected PFAS in the environment – PFOS and PFOA – from ~500 sites across England (Ambaye *et al.*, 2022; Meegoda *et al.*, 2022; Figure 4). It concluded that PFAS presence appears widespread, with examples of hotspots. Statements from the EA (2021) report include:

- Approximately **470 freshwater sites** and approximately **55 estuarine and coastal locations** were sampled in England **for PFOS and PFOA**.
- Water samples were **collected monthly** through a routine surveillance monitoring programme.
- Mean measured concentrations of PFOS and PFOA shown geographically (see figure 4).
- This programme sampled a wide range of water quality parameters to support the EA's water body classification decisions.

Face-value observations from maps included in the EA (2021) report:

• PFOS

- PFOS contamination appears widespread, according to the EA monitoring.
- Concentration of PFOS appears maximally to exceed 0.5 µg/L at one sampling site.
- Hotspot locations appear disperse.
- Levels of PFOS appear to be higher than PFOA.

• PFOA

- PFOA contamination appears widespread, according to the EA monitoring.
- All observed concentrations of PFOA appear to be at the 0.05 – 0.1 µg/L level or lower.
- Hotspot location primarily in the North West of England.

Results from the EA (2021) report include:

- Detectable levels of PFOS were found at over 99% of surface water sites sampled.
- Detectable levels of PFOA were found at over 99% of freshwater sites and over 96% of estuarine and coastal sites sampled.
- The data illustrates a wide range of concentrations of both PFOS and PFOA in English waters.
- The data show significant spatial variation in concentrations measured.
- Mean measured concentrations of PFOS in fresh surface waters range from less than the minimum reporting value (MRV) to 0.61 µg/L.
- Mean measured concentrations of PFOA in fresh surface waters range from less than the MRV up to 0.073 µg/l.
- Lower concentrations of PFOS were observed in estuarine and coastal waters than in freshwaters, with reported mean values ranging from 0.04 ng/L to 9.5 ng/L.

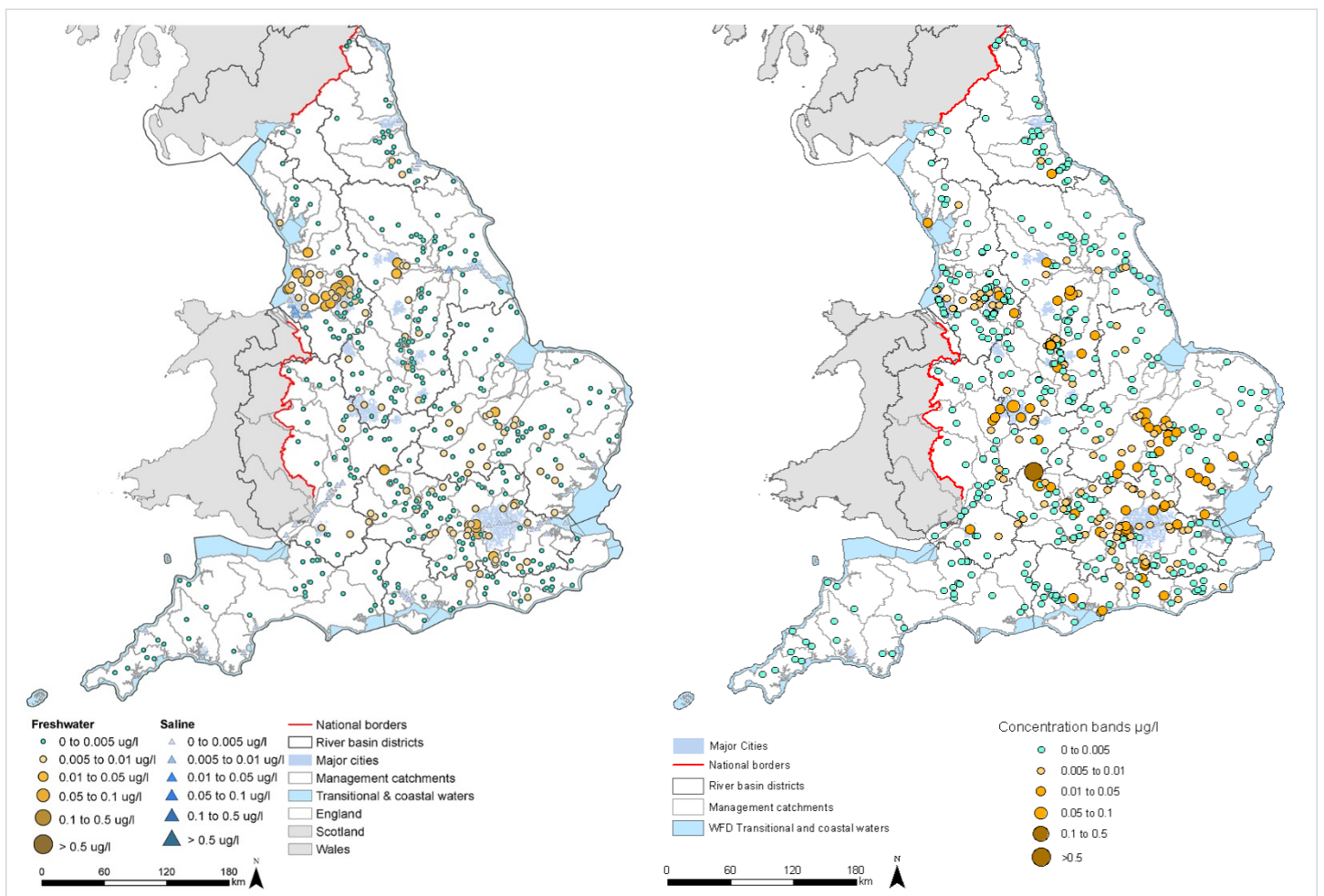


Figure 4 Sampling locations in England and mean measured PFOS (left) and PFOA (right) concentrations from Environment Agency surveillance monitoring programme (from EA, 2021)

Forever Pollution Project data on PFAS in UK waters (2023)

SUMMARY

During the RSC project, PFAS contamination came into the public view by way of media coverage. *Le Monde* published a Map of Forever Pollution using data from the Forever Pollution Project, which is quite possibly the largest quantified EU-wide PFAS dataset to date.

Data from the *Le Monde* map of ~1,700 samples also showed widespread presence of PFAS in the UK (Table 1). For approximately two thirds of sites, measurements of PFOS and PFOA were less than 10 ng/L in surface and ground waters. However, a third of sites measured between 10-100 ng/L of PFOS and PFOA, which has typically been considered by the Drinking Water Inspectorate (DWI) as a 'medium risk' level if found in drinking water, and 3-4% were at levels designated by the DWI as requiring immediate remediation (Dagorn *et al.*, 2023).

	Total number of samples included in analysis	Percentage of samples less than 10 ng/L	Percentage of samples 10 ng/L to 100 ng/L	Percentage of samples greater than 100 ng/L*
PFOS	1,644	63	33	4
PFOA	1,768	65	32	3
Sum of PFAS	1,647	0	89	11

Table 1 Forever Pollution Project data on PFAS in UK water; *In excess of current DWI 'wholesomeness' concentration level.

A similar high-level analysis of the raw Forever Pollution Project dataset was performed to compare with the EA data. From the data it is noted that:

- The dataset is largely based on surface water and ground water (76%-96% across all regions) with sediment generally accounting for the remainder.
- Although six PFAS substances were recorded in the data set, regionally, PFOS and PFOA were the two main substances for which PFAS sum values are based.
- PFAS sum levels were between 10 ng/L and 100 ng/L for upwards of 81% of samples across all regions.
- For PFOA exclusively, on average, 74% of samples were <10 ng/L.
- For PFOS exclusively, on average, 65% of samples were <10 ng/L.
- 37% and 44% of these samples respectively were below 4 ng/L, the proposed US standard.
- It is hard to correlate this data to DWI standards for drinking water, but it gives an idea of the PFAS burden in water generally.
- Based on analysis of the Forever Pollution Project data, 89% of samples (all water matrices – mostly ground water/surface water) contained ‘total PFAS’ levels of between 10 ng/L and 100 ng/L, (i.e. below the European Union (EU) threshold in the Drinking Water Directive, of 0.1 µg/L). 11% of samples are above 100 ng/L and 0% were below 10 ng/L.
- For the same set of data, when judged on PFOS level only, 63% of samples were below 10 ng/L (with 44% of those being below 4 ng/L), 33% were between 10-100 ng/L and 4% were above 100 ng/L.
- When judged on PFOA level only, 65% of samples were below 10 ng/L (with 37% of those being below 4 ng/L), 32% of samples were between 10-100 ng/L and 3% were above 100 ng/L.
- Regional disparity: the sum of PFAS levels were between 10-100 ng/L for upwards of 81% of samples across all regions. This is challenging to attribute to any particular source, and the high mobility of PFAS in water may have an impact.

Sum of PFAS

- 0% of the ~1,700 UK samples recorded PFAS concentrations of <10 ng/L. That is, all samples had a sum level of PFAS greater than this level.
- 89% of UK samples (all water matrices – mostly ground water/surface water) contained between 10 ng/L and 100 ng/L PFAS_sum.
- 11% of samples were above 100 ng/L for the PFAS_sum.
- 63% of samples were detected to be below 10 ng/L (with 44% of those being below a stricter limit of 4 ng/L, as per US EPA guideline value for PFOS).
- 33% were between 10-100 ng/L.
- 4% were above 100 ng/L.
- 65% of samples were below 10 ng/L (with 37% of those being below 4 ng/L, as per the EPA guidelines value for PFOA).
- 32% of samples were between 10-100 ng/L.
- 3% were above 100 ng/L.

Evidence for PFAS in drinking water

A new report from the DWI, entitled *Drinking Water 2022: The Chief Inspector's report for drinking water in England*, has provided summary data of PFAS testing in raw and treated water.

In response to new requirements introduced in 2021 on monitoring 47 PFAS compounds, water companies in England in 2022 submitted test results for PFAS in raw and treated water. Test results were grouped into the DWI's tier system, which uses a risk-based approach (low, medium and high) to manage PFAS.

Tiered actions for controlling risks from PFAS

Tier	Results or Result Risk Assessment	Escalating actions
Tier 1	<0.01 µg/l	Risk assessment and monitoring
Tier 2	<0.1 µg/l	Risk control and consultation
Tier 3	0.1 µg/l	Risk reduction and notification

Table 2. Tiered actions for controlling risks from PFAS (from DWI, 2023). © Crown Copyright

The majority of companies detected PFAS at Tier 2 'medium risk' levels in raw water sources, while only two detected PFAS at Tier 3 'high risk' levels (see table 3).

The number of test results from raw water PFAS monitoring

Company	Total raw water tests analysed	Results below LOD	Tier 1 – <0.01 µg/l	Tier 2 – <0.1 µg/l	Tier 3 ≥0.1 µg/l
AFW	10,652	9,999	14	566	73
ANH	121,732	116,951	4,474	285	22
BRL	2,115	1,987	113	15	0
CAM	2,822	2,807	15	0	0
ISC	799	771	21	7	0
NES	4,136	3,704	418	14	0
PRT	4,608	4,477	119	12	0
SES	366	299	66	1	0
SEW	10,976	10,610	280	86	0
SRN	12,462	11,958	406	98	0
SST	7,627	9,684	295	59	0
SVT	2,538	2,518	20	0	0
SWB	1,739	1,730	9	0	0
TMS	1,037	728	300	9	0
UUT	5,290	4,996	271	23	0
VWP	57	57	0	0	0
WSX	1,116	1,067	43	6	0
YKS	12,403	12,195	206	2	0

Table 3. Number of test results from raw water PFAS monitoring (from DWI, 2023). © Crown Copyright

The data on samples of treated water reveals that consumers are mostly drinking water with PFAS in the 'low risk' Tier 1 level, but some final water still contains PFAS at Tier 2 'medium risk' levels. Two samples were in Tier 3 'high risk' after treatment, but this water was subsequently blended to achieve dilution before it was used (see table 4).

Company	Total raw water tests analysed	Results below LOD	Tier 1 - <0.01 µg/l	Tier 2 - <0.1 µg/l	Tier 3 ≥0.1 µg/l	Tier 3 in supply
AFW	4,118	3,966	9	143	0	–
ANH	120	14	106	0	0	–
BRL	752	634	83	35	0	–
CAM	1,977	1,971	6	0	0	–
ISC	470	454	14	2	0	–
NES	4,535	3,712	774	49	0	–
SES	636	499	136	1	0	–
SRN	83,868	82,067	1,688	111	2	0
SST	6,091	3,567	190	37	0	–
SVT	376	368	8	0	0	–
SWB	2,492	2,486	6	0	0	–
UUT	2,790	2,571	199	20	0	–

Table 4. Number of treated water samples in Tiers 1, 2 and 3 by company (from DWI, 2023). © Crown Copyright

Interestingly, the company with Tier 3 samples in treated water did not report any Tier 3 samples in raw water sources. This example demonstrates the need for more monitoring and testing, as the current data collection is at an early stage.

The data from this report confirms that PFAS are present in UK drinking water, in addition to the environment.

2. Detection: what analytical methods exist for detecting PFAS in water?

Reliable analytical methods for detecting PFAS are essential to understand their presence across various matrices, so that we can more effectively target contaminated sites to protect the environment and human health (De Silva *et al.*, 2020; Ambaye *et al.*, 2022).

In addition, it is critical that methods are highly sensitive, in order to comply with health guidance levels for PFAS in drinking water, some of which require the ability to detect PFAS at the ng/L (part per trillion, ppt) scale.

Detection techniques

Each analytical method uses a particular technique to detect and quantify the PFAS present. These techniques commonly involve **mass spectrometry**, which works by ionising unknown molecules (i.e. giving them a charge), and then accelerating the ions using magnetic and/or electric fields.

The mass analyser measures how the molecules travel after being accelerated, producing a mass:charge ratio (m/z). On the output graph, each chemically distinct molecule creates a 'peak', which enables researchers to identify and quantify the PFAS that were present in the initial sample. Mass spectrometry can either be low resolution (LRMS), high resolution (HRMS) or ultra-high resolution (UHRMS) - which type is used will depend on the category of analytical method being performed. Fourier transform ion cyclotron resonance mass spectroscopy (FTICRMS) has also been used to identify new types of PFAS.

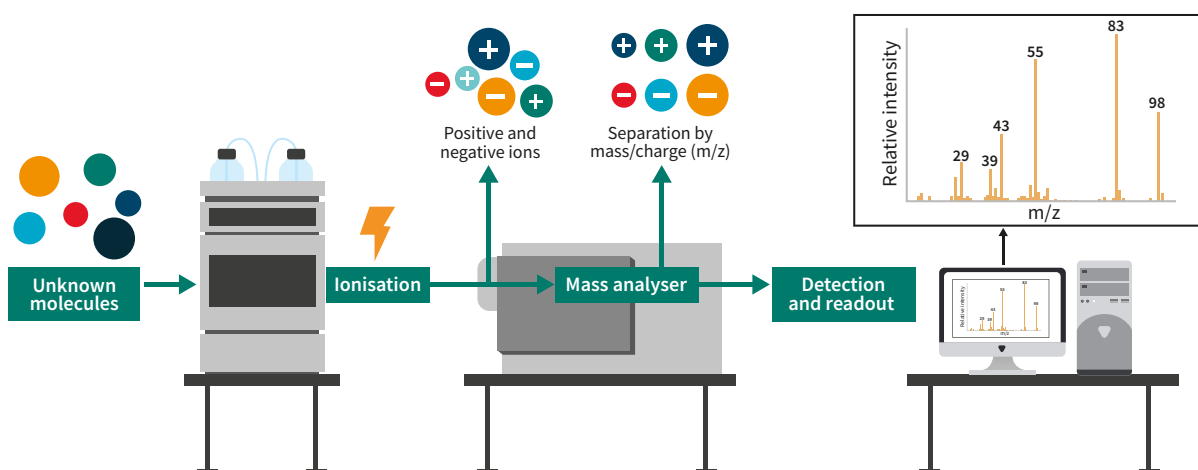


Figure 5. The process of using mass spectrometry to identify unknown PFAS (from US GAO, 2022).

Categories of analytical methods

Initially, most analytical methods were **targeted** to measure the levels of specific known PFAS, including PFOS and PFOA (Nakayama *et al.*, 2019). However, targeted methods are always one step behind the ever-changing chemicals landscape.

As new PFAS chemical structures are introduced into commercial products and subsequently, the environment, the research focus has shifted to developing methods that can detect novel unknown PFAS using **suspect and non-targeted** analyses (Nakayama *et al.*, 2019; Winchell *et al.*, 2021; EA, 2021).

However, even suspect and non-targeted analyses cannot capture the total extent of PFAS contamination. As a result, **surrogate indicators** are increasingly being used to get an indication of the magnitude of PFAS burden. These methods allow us to understand the contributions from unknown PFAS, as well as precursor compounds (De Silva *et al.*, 2020).

These three broad categories of analytical methods for PFAS can be seen in figure 6.

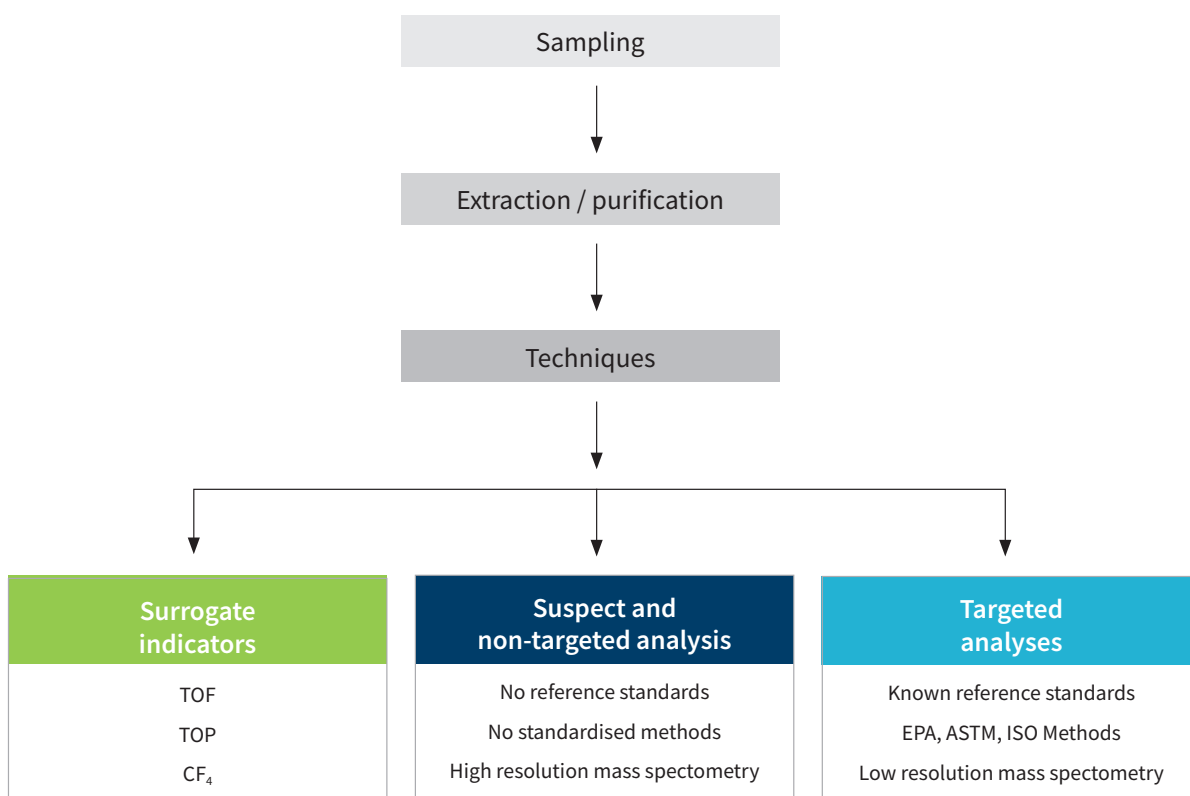


Figure 6. Overview of analytical methods for detecting PFAS, which can be grouped into three key categories: targeted analyses, suspect and non-targeted analyses, and surrogate indicators (from Winchell *et al.*, 2021)

TARGETED ANALYSES

Targeted analyses use **known reference samples** ('analytical standards') to **screen for specified PFAS** species, and therefore only detect PFAS that the researcher 'targets' (Winchell *et al.*, 2021).

The main advantages of targeted analyses are that they enable the concentrations of individual PFAS to be measured **accurately** and at **low levels**. However, the approach is **limited to a finite number of PFAS substances** for which we currently have analytical standards (De Silva *et al.*, 2020).

Most published methods for PFAS analysis are targeted, including those produced by the EPA, ASTM (formerly known as the American Society for Testing and Materials) and the International Organization for Standardization (ISO).

Most studies in the scientific literature that report PFAS concentrations collect their data using targeted approaches (EA, 2021). Targeted analyses benefit from being accurate and highly sensitive, with some methods capable of reliably detecting PFAS at concentrations under 1 part per trillion (ppt) (US GAO, 2022).

There have been substantial improvements to targeted analyses of PFAS in the last few decades, including improved sensitivity of instruments and lowered detection limits (De Silva *et al.*, 2020).

However, to this day, only ~1% (approx. 50 species) of PFAS can be detected using targeted methods, as they rely on a reliable reference sample, known as an 'analytical standard', to compare to so that the PFAS being targeted can be identified and subsequently quantified (US GAO, 2022).

Fewer than 100 analytical standards for PFAS exist. Therefore, outputs from targeted analyses are unable to detect the thousands of other PFAS that may be present in a sample, so cannot give a comprehensive picture of the magnitude of PFAS that have been discharged into the environment, nor capture potential PFAS formed due to the transformation of precursors over time (Kidd *et al.*, 2022; Kuzniewski, 2022).

Published methods

In the United States, the EPA is responsible for providing sampling and analytical methodologies of emerging contaminants, such as PFAS. EPA methods undergo multi-lab validation before being published. Both within the US and internationally, many agencies, state departments, labs and public research universities rely on these methods to detect and measure PFAS (Kidd *et al.*, 2022).

The EPA has two published methods for the analysis of PFAS in drinking water: **EPA 537.1** and **EPA 533**. Using these methods combined, a total of 29 unique PFAS can be measured (US GAO, 2022). **EPA 537.1** is able to detect and quantify 18 PFAS and is an improved version of the previous method 537, which could only detect 14 (Kuzniewski, 2022).

EPA 533 complements EPA 537.1 and can be used to detect an additional 11 PFAS (25 in total). It has only recently been validated and focuses on detecting PFAS with carbon chain lengths below 12 (Winchell *et al.*, 2021; US GAO, 2022).

Both methods are highly sensitive, with detection ranges far below the EPA's current 70 parts per trillion (ppt) Health Advisory (HA) levels for PFAS (Kuzniewski, 2022). See Table 5 for lowest concentration minimum reporting limits (LCMRLs) for each method.

The EPA has developed another method for non-potable water (e.g. wastewater, untreated surface water, groundwater), **EPA 8327**, which can detect 24 PFAS (US GAO, 2022). This method can also be used to test for PFAS in soil and solid waste. The detection range for PFAS is reported as the lower limit of quantification (LLOQ), which is the lowest concentration of the analyte (i.e. PFAS species) that can be measured and reported with a degree of confidence (Kuzniewski, 2022).

The EPA is also currently drafting another method for PFAS analyses in wastewater, surface water, and groundwater, **EPA 1633**. This method will also be able to detect PFAS in other matrices, including soil, biosolids, landfill leachates and fish tissue, and is currently undergoing a multi-laboratory validation study (US GAO, 2022). The EPA expects to publish the final version of the method in late 2023.

EPA method	Types of PFAS detected	Matrix tested in	Detection range
537.1	18 PFAS acids	Drinking water	LCMRL* of 0.53-6.3 ppt
533	25 PFAS with 12 or fewer carbons (11 PFAS are additional to 537.1)	Drinking water	LCMRL of 1.6-9.1 ppt
8327	24 PFAS	Non-potable water, soil, and solid waste	Not applicable; uses LLOQ**
Draft method 1633	40 PFAS	Wastewater, surface water, groundwater, biosolids, landfill leachates, fish tissue	Not applicable; typical reporting limits for aqueous: 1.6-40 ppt

*Lowest concentration minimum reporting limits. **Lower limit of quantification.

Table 5. A summary of EPA methods used to detect PFAS in water (adapted from Kuzniewski, 2022).

Aside from the EPA, various other organisations have also developed analytical methods for PFAS, such as the American Society for Testing and Materials' method **ASTM D7979** for analysing PFAS in water by direct injection, and the ISO's water quality PFAS testing method, **ISO 21675** (Winchell *et al.*, 2021).

The DWI, a body that provides independent reassurance to consumers in England and Wales about the safety of drinking water supplies, require data for 47 PFAS to be submitted (DWI, 2020). Of these substances, 34 can be analysed by using existing validated methods (EPA 533, EPA 537.1 or ISO 21675) (Winchell *et al.*, 2021).

Detection technique = LRMS

Targeted analyses use **low-resolution mass spectrometry (LRMS)**, such as triple quadrupole (QqQ, i.e. MS/MS) instruments (Winchell *et al.*, 2021). These work by comparing the mass:charge (m/z) ratio from compounds in the output to analytical standards of specific known PFAS species, to identify whether those targeted PFAS were present in the sample being tested. LRMS does not provide the mass accuracy or sensitivity needed to identify and quantify suspect or novel PFAS, and therefore can only be used to detect PFAS for which we already have reference analytical standards.

SUSPECT AND NON-TARGETED ANALYSES

Suspect and non-targeted analyses can detect the presence of **both known and unknown PFAS** present in the environment (Fiedler *et al.*, 2020). This includes novel PFAS produced as a result of industrial processes (intentionally or not), as well as PFAS transformation products formed in natural engineered systems (De Silva *et al.*, 2020).

However, these methods are **qualitative, not quantitative**, and can only identify the species of PFAS present, not their relative concentrations.

As yet, there are **no published, standardised methods** (e.g. EPA methods) for suspect and non-targeted analyses.

These analyses use **high resolution mass spectrometry**, a very accurate technique which allows researchers to narrow down the possible structures and formulas for an unknown molecule. They are able to do this **without the need for analytical standards**, thereby overcoming a key limitation of targeted analysis.

Recent improvements to the sensitivity of mass analysers have permitted researchers to conduct so-called ‘suspect’ and ‘non-targeted’ analyses, which can detect unknown PFAS. *Suspect analyses* broadly screen for **‘known unknowns’** i.e. PFAS that are suspected to be found in a given sample, by comparing detected mass measurements to those which have been previously reported (US GAO, 2022; Winchell *et al.*, 2021).

Non-targeted analyses can detect **‘complete unknowns’** i.e. novel molecular structures. These analyses are particularly useful as they are capable of discovering emerging PFAS contaminants (EA, 2021). For example, EPA researchers in Alabama used non-targeted screening to reveal 19 PFAS being emitted as by-products downstream of manufacturing facilities (US GAO, 2022).

Suspect and non-targeted analyses, however, can only *identify* the PFAS present and are **unable to accurately quantify** their relative amounts. However, in theory, once these analyses have been used to detect unknown PFAS, this knowledge can be subsequently incorporated into targeted analyses to measure the concentration of each PFAS present (Winchell *et al.*, 2021).

To date, there are no finalised published methods (e.g. EPA methods) which use suspect or non-targeted approaches. This has resulted in a general **lack of standardisation**, with researchers independently developing a variety of different approaches that are difficult to compare (US GAO, 2022).

Detection technique = HRMS

High resolution mass spectrometry (HRMS) methods are most effective when using high resolution time-of-flight (HRTof), orbitrap or Fourier transform ion cyclotron resonance (FTICR) instruments (Winchell *et al.*, 2021; Fiedler *et al.*, 2020; Young *et al.*, 2022).

HRMS is capable of a greater mass accuracy than low resolution mass spectrometry (LRMS), being able to determine the mass of compounds present in a given sample to several decimal places. This increased accuracy allows the molecular formulas of unknown chemicals to be narrowed down to only a few possibilities (Brunn *et al.*, 2023). For this reason, HRMS **does not rely on analytical standards** to identify PFAS.

PFAS can be identified in samples by comparing the mass spectra detected in a sample against spectral libraries (e.g. NIST ref; Place, 2021) (suspect screening), or by using software to interpret the mass spectra independently of a library to identify potential PFAS, e.g. Fluoromatch (non-targeted analysis).⁵

Another key advantage of HRMS is that you can go back to the data later and conduct **post-analysis**. This allows analytes that were unable to be identified at the time of analysis to be recorded retrospectively (Winchell *et al.*, 2021). However, in practice, the utility of suspect and non-targeted analyses are limited by the data processing capabilities of HRMS.

Analysing the data is labour-intensive, and requires specially trained analysts (De Silva *et al.*, 2020; US GAO, 2022). It is not always possible to detect all the chemicals present in a sample as some chemicals will be inadvertently omitted during sampling, sample preparation and analysis. These methods are often large and expensive, and not all institutions will be able to implement HRMS methods.

SURROGATE INDICATORS: QUANTIFYING TOTAL PFAS BURDEN

Surrogate indicator methods aim to **quantify the total burden of PFAS** in environmental and biological samples by using **proxy measures** for PFAS, instead of attempting to identify individual compounds.

The most common surrogate indicators for PFAS are **total organic fluorine (TOF)** methods, which estimate total PFAS using measurements of total organic fluorine (the TOF assay), extractable organic fluorine (EOF), or adsorbable organic fluorine (AOF). Alternatively, the **total oxidisable precursors (TOP)** assay aims to assess the burden of unknown PFAS precursor molecules.

These indicators give a more accurate picture of total contamination by PFAS, and therefore enable **faster identification of contaminated PFAS ‘hotspots’** and better assessment of individuals’ exposure levels (De Silva *et al.*, 2020). They are also **relatively inexpensive** to operate and **do not rely on having analytical standards** for individual PFAS chemicals, which targeted analysis requires (EA, 2021; Karmann *et al.*, 2021).

However, these indicators can only give a general picture of the extent of contamination and **cannot identify the specific PFAS** in a sample. There are also **no standardised or multilaboratory-validated methods**. Most methods are not widely available.

Detection techniques for TOF methods include combustion ion chromatography (CIC), particle-induced gamma ray emission (PIGE) spectroscopy, and fluorine-19 Nuclear Magnetic Resonance (NMR) spectroscopy. For the TOP assay, standard LC-MS/MS (low resolution mass spectrometry) from targeted analysis is used.

Targeted and suspect screening/non-targeted analyses, whilst useful approaches for identifying individual PFAS species, vastly underestimate the total PFAS load in a given sample. Instead of trying to detect which compounds are present, surrogate indicator methods (also known as total indices or sum parameters) use proxy measures in an attempt **to estimate the true concentration of PFAS present** (Winchell *et al.*, 2021). As well as their ability to reveal the presence previously ‘hidden’ PFAS, some of these methods benefit from being **lower-cost alternatives** to targeted/other analyses (Kidd *et al.*, 2022), although the TOP assay is still quite an expensive option.

⁵ See Innovative Omics for further detail: <https://innovativeomics.com/software/fluoromatch-flow-covers-entire-pfas-workflow/>

However, despite the utility of surrogate indicators in determining the extent of PFAS contamination in a particular area, they **lack in sensitivity and specificity** (Kidd *et al.*, 2022). Unless these analyses are paired with other types of methods, the identities of specific PFAS or precursors remain unknown (Winchell *et al.*, 2021). These approaches also destroy the organic molecules in the process of testing for them, so **do not allow retrospective identification of specific PFAS compounds** (Fiedler *et al.*, 2020).

In addition, **other sources of fluorine in the environment pose a limitation** to some of these methods, as fluorine detected cannot always be attributed to PFAS. For instance, a number of pharmaceutical compounds and pesticides are also organofluorine compounds and therefore are detected by these methods, which may lead to overestimates of the extent of PFAS contamination (US GAO, 2022). The presence of background inorganic fluorine can also influence the accuracy of some results (Winchell *et al.*, 2021).

Total organic fluorine

The term ‘organic fluorine’ or ‘organofluorine’ refers to a compound that contains fluorine bonded to carbon atoms (US GAO, 2022). Measuring the total amount of organic fluorine in a sample can act as a useful proxy for measuring total PFAS levels (EA, 2021). As a consequence of the high energy C-F bond they have, these compounds are very rare in nature, and almost always man-made, so high levels of organic fluorine are likely indicative of large quantities of PFAS (De Silva *et al.*, 2020).

The outcome of total organic fluorine (TOF) analyses can be compared to the quantity of PFAS detected in a sample by a targeted method, for example, EPA Method 537.1. The results often reveal that targeted methods fail to identify significant amounts of organofluorine compounds (and therefore PFAS).

The ‘known’ PFAS in a sample from targeted analyses may range from as low as 2% to 60% of the true total value (Winchell *et al.*, 2021; EA, 2021). To date, there are no standard multi-lab validated methods for measuring TOF, however, several different practices have been developed, which are detailed below (Winchell *et al.*, 2021; EA, 2021).

TOF assay

The TOF assay indicates the total mass of organic fluorine present in the sample, most often calculated using the difference between total fluorine and inorganic fluorine measurements. The assay works by adsorbing PFAS (most often onto activated carbon), and then conducting combustion ion chromatography (CIC) to determine the quantity of organic fluorine in the sample (see detection techniques for further details).

Depending on the type of media being sampled, two common adaptations of the TOF assay are used: the adsorbable organic fluorine (AOF) assay for aqueous matrices; and the extractable organic fluorine (EOF) assay for a variety of matrices, including seawater, freshwater, sediments and soils (Winchell *et al.*, 2021). These adaptations are much more sensitive, with AOF and EOF both having limits of detection (LOD) orders of magnitude lower than the TOF assay (US EPA, 2020).

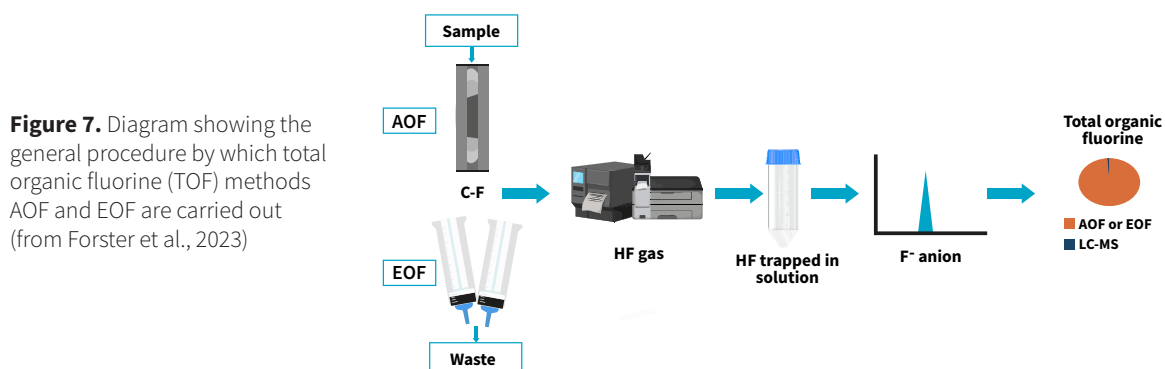


Figure 7. Diagram showing the general procedure by which total organic fluorine (TOF) methods AOF and EOF are carried out (from Forster *et al.*, 2023)

Adsorbable Organic Fluorine assay

Adsorbable Organic Fluorine (AOF) methods determine the total organic fluorine levels in **aqueous matrices** by measuring the quantity of organofluorine compounds that are **adsorbed onto granular activated carbon (GAC)** (Karmann *et al.*, 2021; Jones *et al.*, 2022; Brunn *et al.*, 2023). This method typically retains longer chain PFAS ranging in carbon-chain lengths of 4-10 and both ionic and neutral PFAS but fails to retain small carbon chain PFAS (Jones *et al.*, 2022).

Inorganic fluorine species (typically fluoride or its complexes with Al^{3+}) can also adsorb onto GAC, so these are removed from the extract by washing it with a nitrate solution, to avoid ending up with falsely high values for AOF (Karmann *et al.*, 2021). Following this, **combustion ion chromatography (CIC)** is commonly used to determine the quantity of organic fluorine remaining.

There is increasing demand and stakeholder interest in aggregate methods like AOF. The EPA is in the process of multi-laboratory validating a test method for AOF (**Draft Method 1621**) to determine concentrations of organofluorines in wastewaters and surface waters, which is expected to be finalised in late 2023 (US EPA, 2020).

The EPA decided to develop an AOF method rather than a TOF assay method because the results of AOF analysis are less impacted by inorganic fluorine than the TOF assay (US EPA, 2020). In addition, AOF methods are far more sensitive than TOF assay methods, in general achieving analytical limits of detection (LOD) of 1.3 ug F/L and an LOQ (limit of quantification) of 2.0 ug F/L (Brunn *et al.*, 2023).

Extractable Organic Fluorine assay

Extractable Organic Fluorine (EOF) methods can be used to detect organofluorine in **many different matrices**, including water, sediment, soil, sludge, consumer products and biological tissue samples (Brunn *et al.*, 2023; Karmann *et al.*, 2021).

The PFAS in the sample are first isolated typically using solvents or solid-phase extraction (SPE) (Brunn *et al.*, 2023; Ateia *et al.*, 2023). The eluate is then **combusted** at a high temperature and the fluorine formed is quantified by **combustion ion chromatography (CIC)**, in a similar manner to AOF (Aro *et al.*, 2022; Brunn *et al.*, 2023).

The EOF approach captures **all organofluorine substances** extracted from a sample (Karmann *et al.*, 2021). However, there may be poor recoveries for certain PFAS compounds (e.g. neutral PFAS) using EOF, depending on the selectivity of the sorbent used (Brunn *et al.*, 2023; Jones *et al.*, 2022). As yet, there has been little standardisation of EOF methods (Karmann *et al.*, 2021).

Detection techniques = CIC, PIGE, ^{19}F -NMR

There are three key detection techniques that can be used in TOF methods to measure total fluorine:

The most common of these is **combustion ion chromatography (CIC)**. CIC involves combusting the adsorbent/eluate containing the PFAS at 900°C-1,000°C in a humid, oxygen-rich environment (Winchell *et al.*, 2021; Kidd *et al.*, 2022).

These conditions oxidise the PFAS, break their C-F bonds, and form hydrofluoric acid (HF), which dissociates into H^+ and F^- ions when in aqueous solution. Ion chromatography is used to measure the concentration of fluoride ions (F^-) by separating the ions by their interaction with a resin (Winchell *et al.*, 2021; US GAO, 2022).

The resulting measurement is taken to be equivalent to the amount of organic fluorine present in the original sample (assuming background inorganic F^- was previously measured and removed) (Kidd *et al.*, 2022). CIC does not require expensive specialised equipment (US GAO, 2022).

Particle-induced gamma-ray emission (PIGE) spectroscopy is another total fluorine technique, primarily used for surface analysis of solid matrices. In theory, this could be expanded to encompass water samples if they are dried and the residue measured (Jones *et al.*, 2022).

This technology has the potential to be useful for PFAS analysis, being both sensitive and high throughput (it can process >20 samples an hour) (US GAO, 2022). However, it is not yet widely available, and has not been refined for use with environmental samples (Jones *et al.*, 2022; US GAO, 2022).

In addition, it can only detect fluorine to the depth that a gamma beam can penetrate the surface of the sample. What's more, there is currently no reliable method for separating inorganic and organic fluorine during PIGE analysis, and the technique is expensive, requiring complex instrumentation including a proton beam accelerator (US EPA, 2020).

Finally, **fluorine-19 nuclear magnetic resonance (¹⁹F-NMR) spectroscopy** can be used to characterise and quantify PFAS with minimal background signal interferences at the chemical shifts expected for PFAS (Camdzic *et al.*, 2021). ¹⁹F is the only naturally occurring isotope of fluorine, and organofluorine compounds are rare in the environment.

This technique monitors the chemical shift associated with terminal CF₃ group of a PFAS (Jones *et al.*, 2022). Due to the distinguishable ¹⁹F signal from the terminal CF₃ moiety on PFAS, ¹⁹F-NMR can differentiate PFAS from non-PFAS compounds and from F⁻ ions (Camdzic *et al.*, 2021).

This is a key advantage of this technique, as it can eliminate most interferences from other classes of organofluorine compounds like pesticides, or from inorganic fluorine (Jones *et al.*, 2022). However, like PIGE, the instrumentation required for this technique is expensive, and is not often found in commercial laboratories, limiting the ability to scale it up (US EPA, 2020).

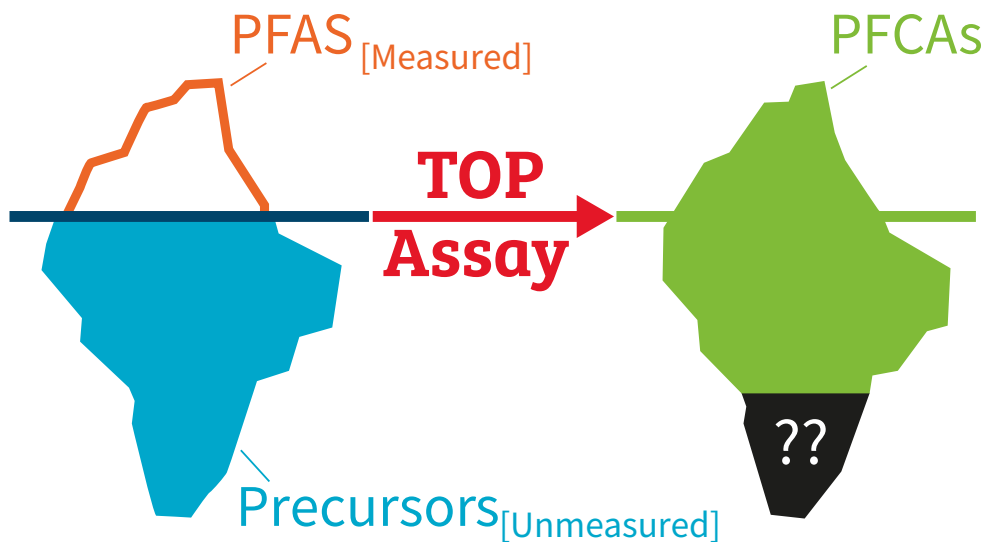
Total Oxidisable Precursors

PFAS precursors are chemicals that can degrade into a certain class of PFAS called **perfluoroalkyl acids (PFAAs)** under certain conditions (Ateia *et al.*, 2023). PFAAs include perfluoroalkyl carboxylic acids (PFCAs), such as PFOS, and perfluoroalkyl sulfonic acids (PFSAs), such as PFOA (Ateia *et al.*, 2023; Kuzniewski, 2022). Unlike some other classes of PFAS, PFAAs are very unlikely to break down in the environment, due to their stable C-F bonds and the oxidised state of their polar head groups (Ateia *et al.*, 2023).

Many of the PFAS that cannot be detected by targeted methods ('unknown PFAS') are PFAS precursors (Ateia *et al.*, 2023). Therefore, it is critical that we can identify and measure these precursors in order to fully understand the extent of PFAS contamination in environmental samples.

The Total Oxidisable Precursor (TOP) assay is able to estimate the total concentration of PFAS precursors by oxidising them into stable PFAS compounds that can be detected through targeted methods (Ateia *et al.*, 2023; US GAO, 2022). To undertake the assay, duplicate samples are collected and tested (Ateia *et al.*, 2023).

- 1) The first sample has a strong **oxidising agent** (e.g. heat- and alkaline-activated persulfate) added, which **converts any PFAS precursors present into terminal PFAA oxidation products**, e.g. PFCAs (Brunn *et al.*, 2023; Ateia *et al.*, 2023; Kuzniewski, 2022; Kidd *et al.*, 2022; John *et al.*, 2022). The second sample remains untreated.
- 2) Both samples then undergo **targeted analysis by LC-MS/MS** (Ateia *et al.*, 2023) and the concentration of PFAS detected is compared. Any heightened PFAS concentration in the sample that underwent the oxidation process can be assumed to be caused by precursors that were converted into PFAAs (EA, 2021).



Key practical considerations when using TOP Assay

Figure 8. Diagram illustrating how the TOP assay can convert unmeasurable PFAS precursors (blue) into stable, easily measurable PFCAs (green). Reprinted (adapted) with permission from Ateia *et al.*, 2023. Copyright 2023 American Chemical Society.

Alternatively, a single sample can be taken, and first undergo targeted analysis to establish the background PFAS levels, before undergoing the oxidation step to assess the change in PFAS concentration (and therefore the quantity of precursors present) (John *et al.*, 2022).

The TOP assay has many advantages. As well as revealing the presence of previously unidentifiable precursors, it is **significantly more sensitive** than other surrogate indicators like AOF and EOF, and able to detect PFAS at concentrations of 0.1-1 ng/L (ppt) (Winchell *et al.*, 2021; Brunn *et al.*, 2023; US GAO, 2022).

The assay also **uses the same analytical instrumentation as targeted analysis**, so can theoretically be applied to diverse matrices (including aqueous, solid and animal tissue), and is more accessible to laboratories by removing the need for them to invest in extra equipment (Kidd *et al.*, 2022; Brunn *et al.*, 2023; Ateia *et al.*, 2023).

However, there are several limitations to the TOP assay. For example, there are concerns that **some precursors** such as those in fluoropolymers are incompletely oxidised into PFCAs (Fiedler *et al.*, 2020; Brunn *et al.*, 2023). This may lead to the assay underestimating the true concentration of precursors in a sample (Winchell *et al.*, 2021).

Conversely, lab-imposed conditions for oxidation may be too harsh and not indicative of the environment, so results might represent a ‘worst-case scenario’ of the potential oxidised products that can be formed by precursors (Winchell *et al.*, 2021). In addition, the assay does not distinguish among PFAS, and **individual precursor compounds cannot be identified** (Kidd *et al.*, 2022; US GAO, 2022).

The assay is also **expensive** to carry out, as each sample must be analysed twice by LC-MS/MS to get a measure of PFAS levels before and after oxidation has occurred (Winchell *et al.*, 2021; Kuzniewski, 2022; Kidd *et al.*, 2022). Finally, issues with repeatability of measurements have meant that the assay has **only been reliably applied to aqueous matrices** so far (Kidd *et al.*, 2022).

No standard published procedure exists for the TOP assay as yet. This has resulted in some inconsistencies in the results obtained by different laboratories (Camdzic *et al.*, 2021; Winchell *et al.*, 2021).

Detection technique: LC-MS/MS (the TOP assay uses the same instrumentation as targeted analysis).

Total organic fluorine (TOF)		Total organic precursors (TOP)	
Non-targeted method and enables the total PFAS level to be determined, if data is available for the known PFAS then it is possible to establish the unknown PFAS burden		Targeted to PFAAs, and converts any PFAS precursors into their respective PFAAs	
Advantages	Disadvantages	Advantages	Disadvantages
Generates sum of PFAS value	Non-targeted – interpretation of results is unclear	Estimates total load of known PFAS from PFAA precursors	Interpretation of results is unclear
Relatively low cost compared to LC-MS/MS	Interference from ‘non-PFAS’ such as pharmaceuticals and pesticides	Can provide indicative data on PFA chain length which may aid source identification	Does not account for non PFAA precursors and novel/next generation PFAS such as Gen-X
EOF – all matrices	AOF – aqueous samples only	Theoretically can be applied to diverse matrices	In practice only reliably applied to aqueous matrices
Good screening approach to get an idea of overall contamination	Lack of standardised methods leads to variable results between labs. (potential bias from sample extraction)	Sensitive (0.1 – 1ng/l)	Variable recoveries/ potential bias from sample extraction
	Uncertain if it its sufficiently sensitive (0.1 – 0.5µg/l)		Non-representative end-products

Table 6. Summary of the advantages and disadvantages of TOF and TOP methods (created with information from EA, 2021)

Challenges of PFAS in water analysis

There are a number of challenges associated with detecting and quantifying PFAS contamination:

- **Large number of PFAS:** there are thousands of individual PFAS and precursors currently present in the environment (EA, 2021). Therefore, there is no ‘one size fits all’ method to approach PFAS analysis.
- **Novel emerging PFAS:** new PFAS are constantly being introduced by man-made treatments and environmental degradation (Winchell *et al.*, 2021).
- **Diverse and complex chemistry:** PFAS are a broad, complex family of compounds with a wide variety of chemical properties. This diversity means that multiple analytical approaches are often required to reveal the overall nature and scale of PFAS contamination (Winchell *et al.*, 2021).
- **Lack of analytical standards:** EPA methods are all targeted to detect specific PFAS, and thus require analytical standards to confirm the identity of each PFAS. Reliable analytical standards are not available for the vast majority of PFAS species. Of the thousands of PFAS, fewer than 100 analytical standards exist at present, and EPA methods can only detect and quantify 50 of these (US GAO, 2022). This limits the ability to determine the extent of PFAS contamination at a site using targeted methods.
- **Contamination of samples:** PFAS can leach from lab equipment, skewing detection levels from samples to be higher than their true value. Using glassware is also unsuitable, as PFAS have a high affinity for glass, meaning that the observed PFAS level in a sample can be reduced from its true value.
- **Instrument sensitivity:** PFAS have been found to be harmful to humans at very low exposure levels, thus, highly sensitive instruments are needed in order to detect whether the compounds are present in a variety of environmental matrices, even at extremely low concentrations (Winchell *et al.*, 2021; Kidd *et al.*, 2022).
- **Cost:** costs of PFAS analysis were a key challenge identified by academics and agencies in a survey conducted by the US Government Accountability Office. For example, mass spectrometry instrumentation can cost over \$500,000 to acquire and set up. These kinds of costs are likely to be prohibitive for smaller utilities (US GAO, 2022).
- **Lack of non- targeted/surrogate indicator methods:** unfortunately, suspect and non-targeted and surrogate indicator methods are largely still in development or not widely available (US GAO, 2022).
- **Lack of portability of test methods and the time needed to perform analysis:** in an ideal world real-time and in situ measurement would be the goal, but equipment is bulky and costly.

Estimating PFAS levels in human blood when PFAS is found in drinking water

A new tool from the US Agency for Toxic Substances and Disease Registry (ATSDR) has been provided to estimate PFAS levels in human blood⁶, which it describes as follows:

“The Centers for Disease Control and Prevention (CDC) and the Agency for Toxic Substances and Disease Registry (ATSDR) developed the per- and polyfluoroalkyl substances (PFAS) Blood Level Estimation Tool for community members with exposure to PFAS through drinking water who would like more information about levels of perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorohexanesulfonic acid (PFHxS), and perfluorononanoic acid (PFNA) in their blood. Because blood tests for PFAS are not widely available, the estimates from this tool might be helpful when considering ways you might be exposed to PFAS and options for reducing your exposure, or when speaking with your healthcare provider. This tool is not intended to replace actual PFAS blood testing.”

Whilst these data are based on US National Health and Nutrition Examination Survey (NHANES) biomonitoring data in US populations⁷, there is no reason that UK populations or EU populations would be physiologically different, or that background levels in UK populations would be significantly higher or lower than in the US.

The use of representative reference data is a normal practice. The UK Health and Safety Executive (HSE) already uses European data as a proxy for the UK, as there is no human biomonitoring data for PFAS available for UK populations to date.

When using this modelling tool, by inputting the current UK DWI guidance value of 100 ng/L (100 ppt) which could potentially be allowable for any individual PFAS (in this tool PFOA, PFOS, PFHxS and PFNA) the estimated blood levels (µg PFAS/L) are calculated to be as presented in figure 9.

Using the US ATSDR modelling tool, PFAS blood levels were calculated for a 50-year-old female of 70kg body weight at a level of 100 ng/L in drinking water, i.e. at the current UK DWI guideline value for any individual PFAS (see figure 9). This predicted blood levels that could be significantly higher than measured levels in US populations.

The calculations were repeated using a level of 10 ng/L in drinking water, i.e. 10-fold lower than the current UK DWI guideline value for any individual PFAS (see figure 10). This predicted blood concentrations reduced to lower levels for each PFAS that are within historic ranges, albeit at the high end for PFHxS and PFNA, preventing significant bioaccumulation potential.

The population biomonitoring data for these calculations was based on the US NHANES survey data from 2017 and 2018.

⁶ The tool can be accessed at <https://www.atsdr.cdc.gov/pfas/resources/estimating-pfas-blood.html>

⁷ <https://www.cdc.gov/nchs/nhanes/index.htm>

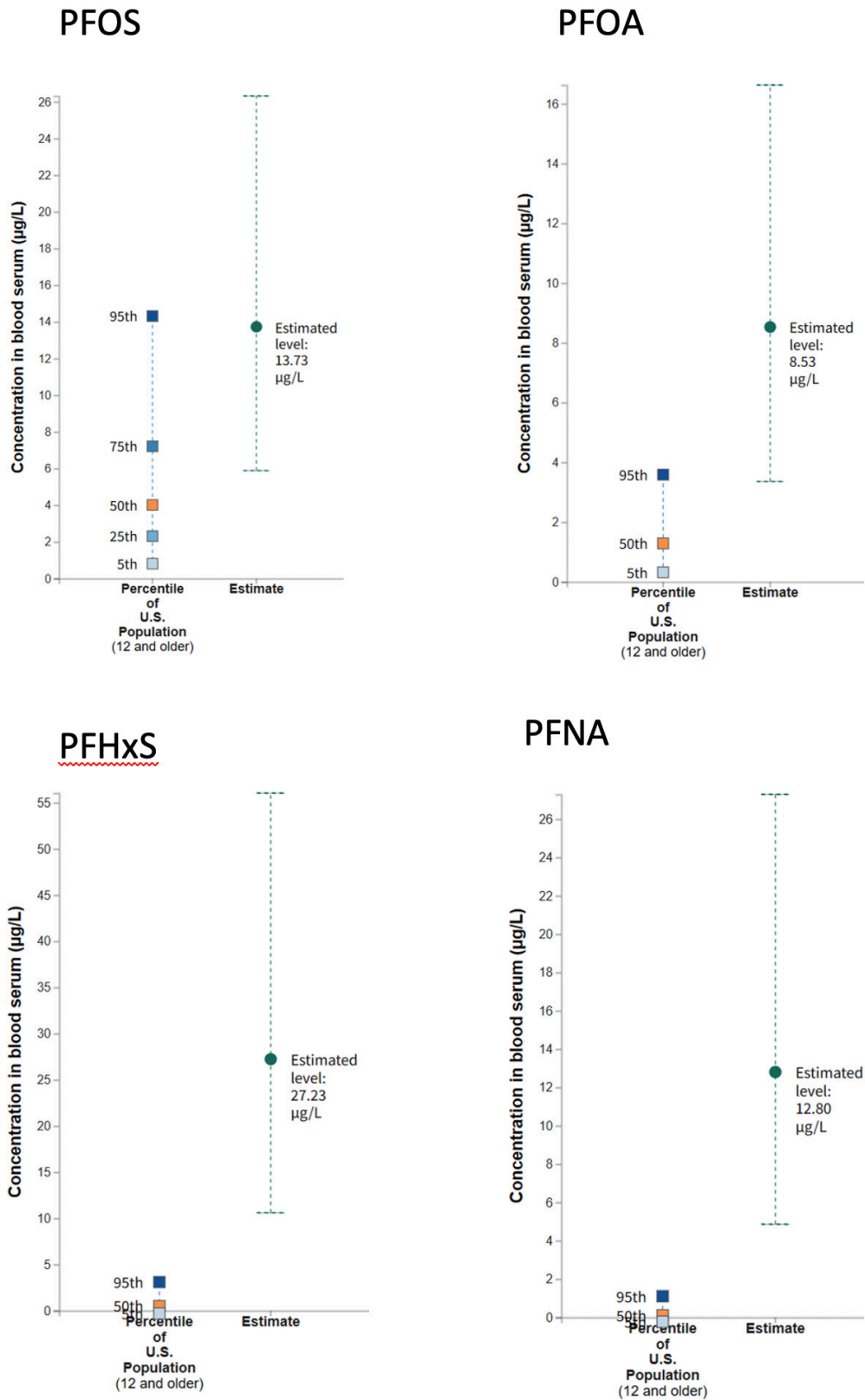
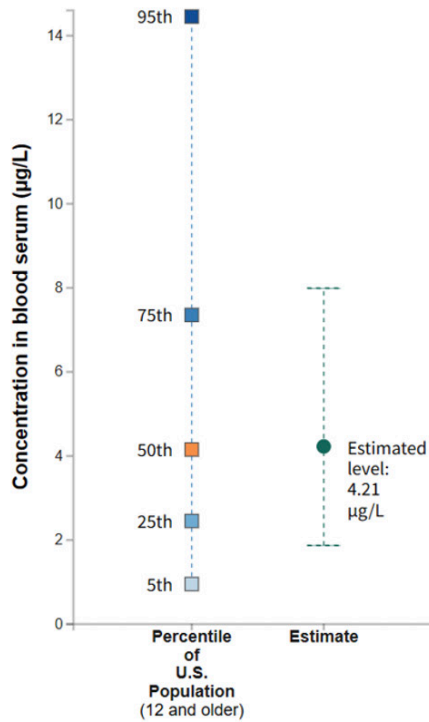
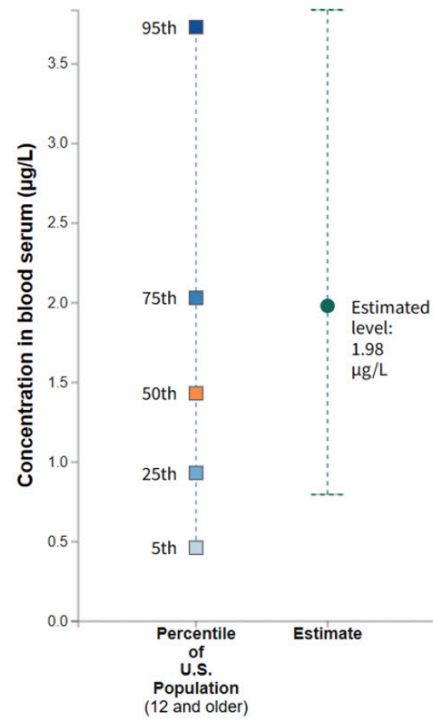


Figure 9. Outputs from the US ATSDR modelling tool for predicting PFAS blood levels ($\mu\text{g/L}$) in a 50-year old female of 70kg body weight, using assumed drinking water levels of PFOS, PFOA, PFHxS and PFNA at 100 ng/L (100 ppt), the current UK DWI guideline.

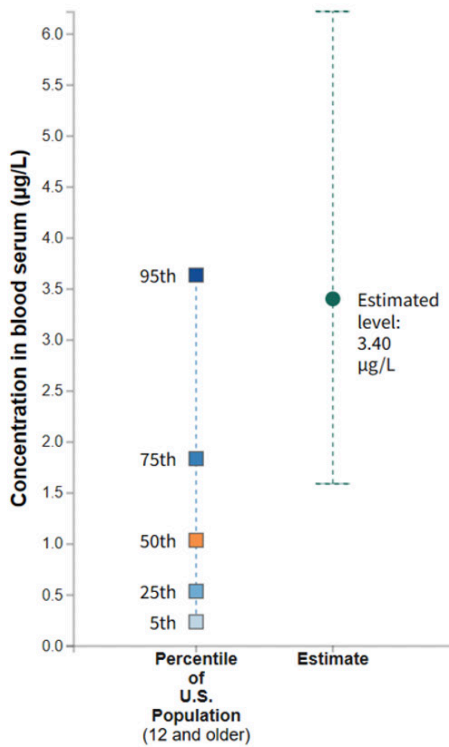
PFOS



PFOA



PFHxS



PFNA

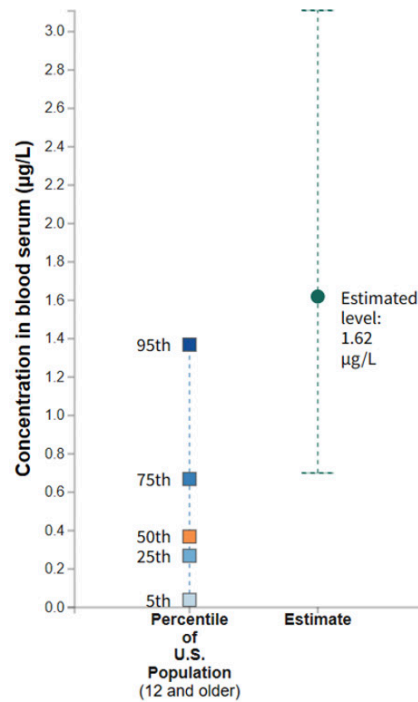


Figure 10. Outputs from the US ATSDR modelling tool for predicting PFAS blood levels ($\mu\text{g/L}$) in a 50-year-old female of 70kg body weight, using assumed drinking water levels of PFOS, PFOA, PFHxS and PFNA at 10 ng/L (100 ppt), 10-fold lower than the current UK DWI guideline.

3. Remediation: what methods exist for the removal of PFAS from water?

Even if PFAS production stopped immediately, the many decades of historic use of these chemicals means that a legacy of environmental contamination exists that will not naturally degrade and thus requires active remediation (EA, 2021).

Owing to the high stability of PFAS compounds, many conventional drinking water treatment processes such as coagulation, flocculation, and disinfection are unable to effectively remove PFAS from water (efficiencies reported to be in the range of 0%-5%) (Saawarn *et al.*, 2022; WHO, 2022).

As a result, several remediation methods specific to PFAS have been developed, which fall into two categories depending on their desired outcome: either to separate and concentrate the PFAS from aqueous matrices (**non-destructive methods**), or to target the C-F bond and thus entirely remove the PFAS from existence (**destructive methods**) (Vo *et al.*, 2020). At present, non-destructive methods are deployed more commonly and at a larger scale than destructive methods.

An overview of the most common currently used remediation methods follows below. For the precise efficiencies of these processes see **Table 7**, which summarises the range of removal rates achievable for each treatment method, as well as their key advantages and disadvantages. In addition, there is a discussion of more **niche methods**, and the **'treatment train'** approach, whereby non-destructive and destructive methods can be combined in situ to achieve optimal complete remediation of PFAS.

Non-destructive methods

SUMMARY

Non-destructive methods aim to separate PFAS from the media they are found in, thus preventing humans from coming into contact with the chemicals (Meegoda *et al.*, 2022). However, whilst such separation methods may remove PFAS from drinking water, they generate PFAS-contaminated residuals in the process, and ultimately fail to remove PFAS from the environment, where the chemicals can continue to cycle through and pose health risks (Winchell, 2022).

Methods can broadly be split into **adsorption** (which includes the use of activated carbon and ion exchange resins) and **membrane filtration** (which includes reverse osmosis and nanofiltration), although a new generation of advanced polymer-based and synthesised materials has recently been tested for PFAS removal (Vo *et al.*, 2020). Adsorption methods generally have lower efficacies than membrane methods, but are cheaper to run. Currently, the most common non-destructive method is adsorption using granular activated carbon (GAC).

Adsorption

Adsorption is a process whereby contaminants are removed from the aqueous phase onto solid media (WHO, 2022). It is a widely used technology for the remediation of PFAS. The process is highly efficient, relatively cheap to run, has low-energy requirements, and is easy to operate (O'Connor, 2022). Adsorption is a particularly effective remediation method for long chain (high molecular weight) and hydrophobic PFAS (WHO, 2022). However, competition for removal with co-contaminants such as ions and organics can compromise the performance of adsorbents (Vo *et al.*, 2020).

Granular and powdered activated carbon and ion exchange resins are the most common adsorbents, although other adsorbents exist, e.g. biochar, polymer-based, and synthesised material.

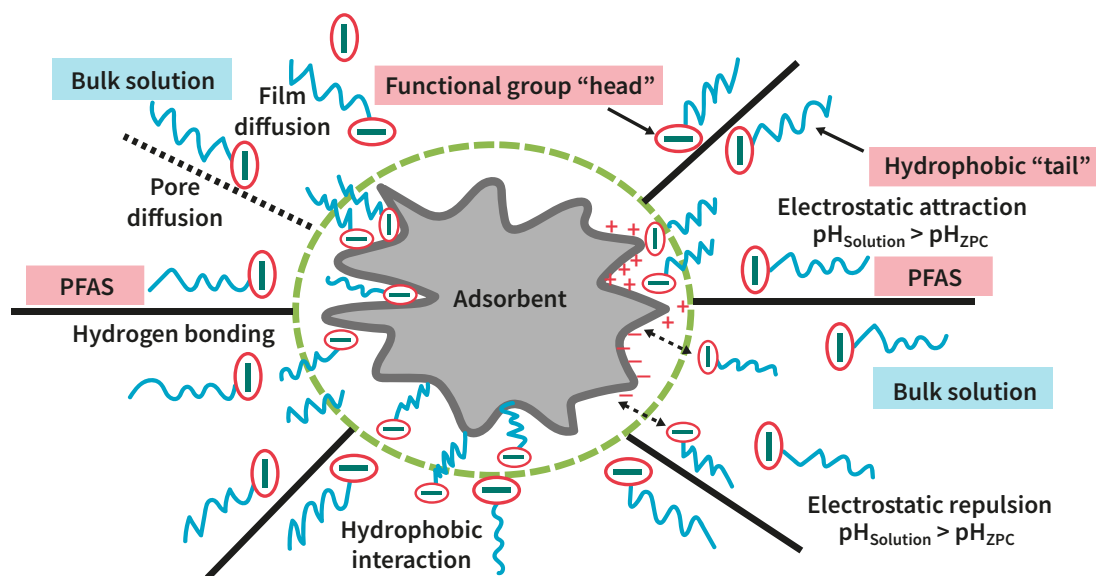


Figure 11. Removal of PFAS compounds from aqueous matrices via adsorption (from Saawarn *et al.*, 2022).

Activated carbon

Two forms of activated carbon are available for use as adsorbents – either granular (1-2mm diameter) or powdered (<0.1mm diameter) (WHO, 2022).

Granular activated carbon (GAC) is a more widely used method than powdered activated carbon (PAC) and is normally employed for the removal of PFOS and PFOA, although to a lesser degree it is also used for the remediation of other PFAS (DWI, 2020). In general, GAC is used in filtration beds downstream of clarification and depth filtration processes (WHO, 2022). After exhaustion, GAC requires thermal regeneration at 800°C-1,000°C and media top-up (DWI, 2020).

In addition, a challenge remains for what to do with used carbon filters containing GAC with adsorbed PFAS. Sending these to landfill can cause PFAS to leach into the underlying soil (Saawarn *et al.*, 2022).

Powdered activated carbon (PAC) generally works by being dosed into the water supply at an early stage of water treatment, and later removed by coagulation, clarification and filtration processes (WHO, 2022). Unlike GAC, PAC is used only once prior to being disposed of with the water treatment sludge, and typically is not reactivated (DWI, 2020).

Some studies find PAC to be more effective than GAC at removing PFAS from aqueous matrices, potentially due to PAC's larger surface area and the presence of many sorption sites and functional groups on its surface (Yu *et al.*, 2009; Saawarn *et al.*, 2022).

Ion exchange

Ion exchange (IEX) processes are an established technology for the removal of contaminants such as nitrate and arsenic during the treatment of surface and groundwater sources (DWI, 2020). IEX has also been shown to be effective for the removal of charged PFAS.

At ambient pHs, PFAS species in drinking water are typically negatively charged anions, therefore most research has focused on **anionic exchange resins** (WHO, 2022). This method works by the exchange of anions (e.g. OH^- , Cl^- , HCO_3^-) present on the resin surface with the solution, and vice versa (Saawarn *et al.*, 2022).

While this is effective at remediating negatively charged PFAS, positively charged PFAS are poorly removed by anionic exchange resins. In addition, IEX resins are often single use, making the process operationally costly and requiring the disposal of used resin (WHO, 2022).

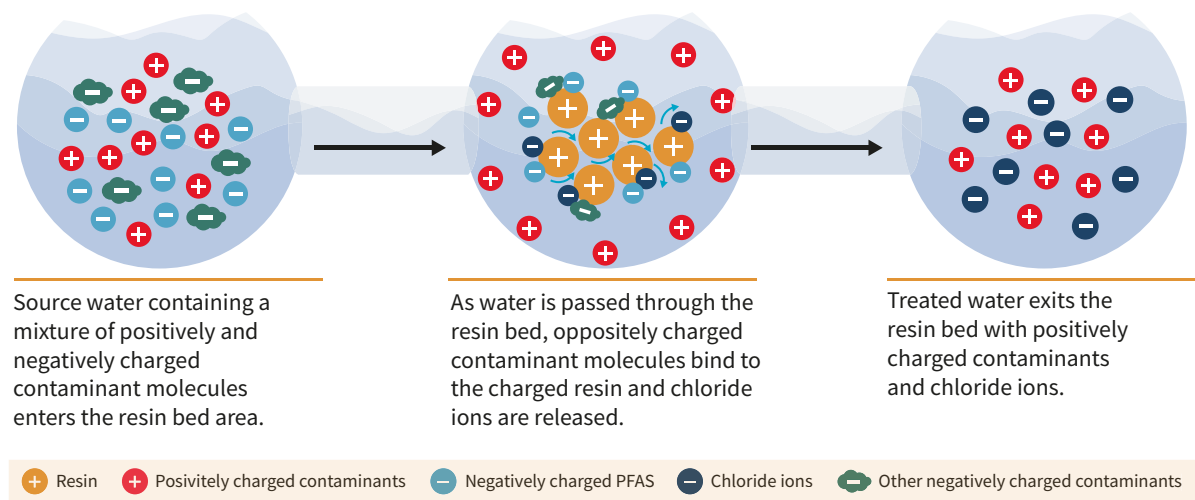


Figure 12. How ion exchange removes PFAS (from US GAO, 2022).

Membrane filtration

Membrane filtration separates PFAS from contaminated media in a **pressure-driven process**, whereby a semi-permeable or porous membrane selectively eliminates PFAS solutes from solvents (Saawarn *et al.*, 2022). This usually works through **size exclusion**, although it can also involve electrostatic repulsion, diffusion, and cake layer filtration (Vo *et al.*, 2020).

Membrane separation processes can be either low or high pressure. Low pressure methods, such as microfiltration and ultrafiltration, use filters with large pore sizes (100-400 nm and ~10 nm, respectively) and are therefore unsuitable for removing PFAS molecules, which have an effective diameter of ~1 nm. The high pressure methods **reverse osmosis (RO)** and **nanofiltration (NF)** are suitable for PFAS remediation, owing to their smaller respective pore sizes of <1nm and 1-10nm (Saawarn *et al.*, 2022). Between the two, RO has higher removal efficiencies than NF, although both are extremely effective at rejecting a range of PFAS (WHO, 2022). Using these methods, many studies report the removal of more than 99% PFAS from contaminated media at high concentrations of up to 1000 mg/L (Vo *et al.*, 2020; Ambaye *et al.*, 2022). In addition, membrane methods provide an absolute barrier for PFAS removal when operated correctly, meaning they are more stable and reliable than adsorption (WHO, 2022).

However, high pressure membranes require lots of energy and water resources to operate, resulting in high costs which limit their large-scale application (WHO, 2022; Saawarn *et al.*, 2022). The methods also suffer from technical issues, principally fouling, caused by humic acid and inorganic particles in polluted water which can compromise PFAS rejection efficiency (Vo *et al.*, 2020).

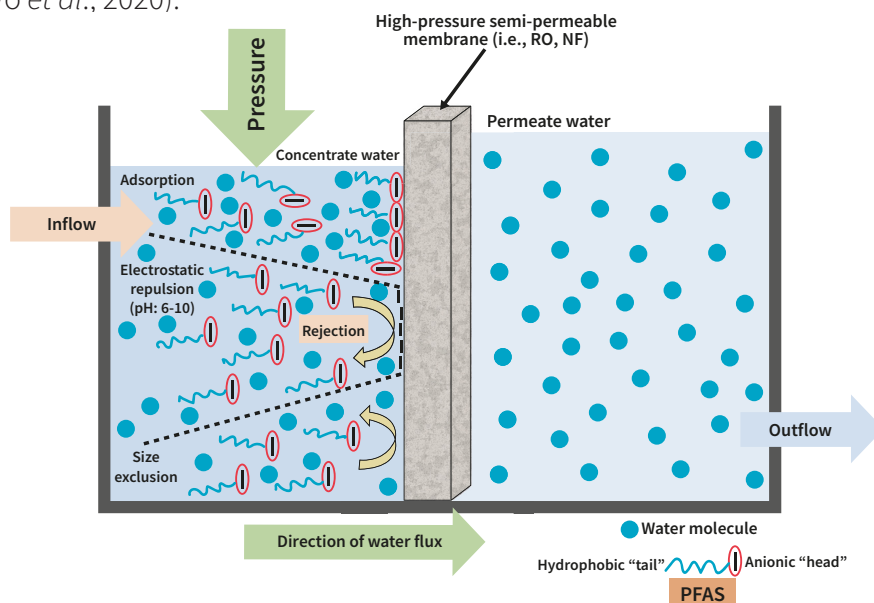


Figure 13. Mechanism of membrane filtration for PFAS removal (from Saawarn *et al.*, 2022).

Destructive methods

SUMMARY

Destructive methods break the strong C-F bonds present in PFAS molecules, thus destroying the chemicals and permanently removing them from the environment (Meegoda *et al.*, 2022). Many destructive methods exist, including **advanced oxidative processes (AOPs), plasma and incineration**.

They represent a critical research area, given their powerful ability to break PFAS cycling through different environmental media and address society’s urgent need to fully remediate the chemicals (Vo *et al.*, 2020).

However, these methods are currently limited in the scale at which they can be employed. Due to the large amount of energy required to overcome the C-F bond, destructive methods are typically accompanied by high running costs and require sophisticated operating systems.

Advanced oxidation processes

Advanced oxidation processes (AOPs) encompass various methods, such as photocatalysis, sonolysis, super critical water oxidation, ozonation, catalyst-supported UV, and electrochemical oxidation (Vo *et al.*, 2020). They function by generating **OH• radicals** - powerful oxidants that can cleave carbon-carbon, carbon-nitrogen and other chemical bonds. The radicals react with organic pollutants like PFAS, breaking them into smaller non-toxic molecules or even fully mineralising them to CO₂ and H₂O (Wanninayake, 2021).

These $\text{OH}\cdot$ radicals are formed using oxidising chemical catalysts such as hydrogen peroxide, ozone, potassium permanganate and ammonium persulfate, with or without energy sources such as UV irradiation (Saawarn *et al.*, 2022).

AOPs are becoming an increasingly popular technology due to their rapid action and ease of use (Yadav *et al.*, 2022). However, AOPs still have limited performance when it comes to degrading PFAS. For example, UV/H₂O₂ methods can only reach efficiencies of up to 15% using application conditions considered feasible for drinking water treatment systems (WHO, 2022).

In addition, AOPs are expensive to operate, cannot yet deal efficiently with short chain PFAS, and can sometimes form toxic by-products such as hydrogen, fluorine, and chlorine gas (Kuzniewski, 2022; Vo *et al.*, 2020; Yadav *et al.*, 2022). Alarmingly, oxidative processes may even result in an increased concentration of PFAS in the finished water by oxidising polyfluorinated precursor chemicals that are present in raw water (WHO, 2022). Further research is needed to improve reaction rates and degradation efficiency, allowing AOPs to be scaled up and function in real field scenarios (Saawarn *et al.*, 2022), and considerations made regarding sustainability of processes.

Two examples of AOPs (photocatalysis and sonolysis) are summarised below:

Photocatalysis

Photocatalysis involves three components: a light source, an oxidant and a catalyst. Together these undergo a cyclic reaction that degrades the PFAS chain and ultimately regenerates the photocatalyst such that it can be recycled at the end of the cycle (Yadav *et al.*, 2022).

Several catalysts can work as photocatalysts, including TiO₂, In₂O₃, Fe₂O₃, ZnO, CdS, and Ga₂O₃ (Meegoda *et al.*, 2022). In particular, TiO₂-based catalysts are widely used because they are readily available, non-toxic, and chemically stable, as well for their ability to satisfactorily degrade organic pollutants (like PFAS) at a relatively low cost compared to other catalysts (Yadav *et al.*, 2022).

Photocatalysis can be performed at ambient temperatures, requires little energy, and is able to consume green energy, rendering it a highly sustainable process.

However, it has relatively low degradation efficiencies compared to other destructive methods for PFAS, is much more effective for the destruction of PFOA than PFOS and generates toxic intermediate reaction products. In addition, photocatalysis is impacted by the presence of co-contaminants, and TiO₂ is very tricky to recover from treated solutions (Meegoda *et al.*, 2022).

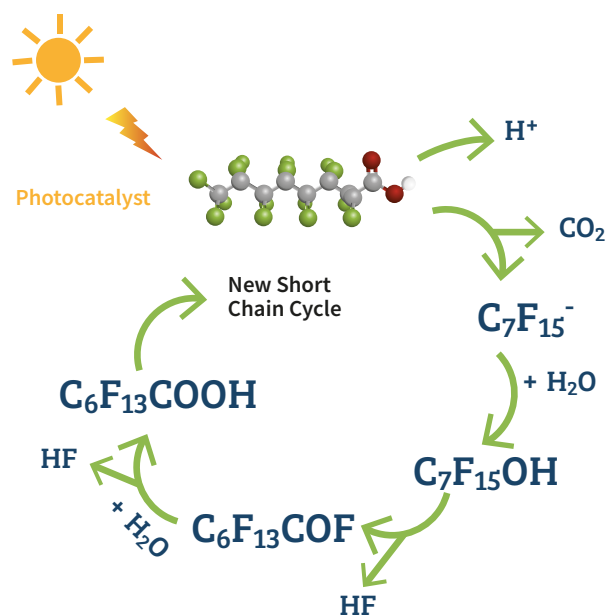


Figure 14. Photocatalytic method for PFAS degradation (from Meegoda *et al.*, 2022).

Sonolysis

Sonolysis uses sonowaves (soundwaves) as the main driving force to destroy PFAS present in aqueous matrices (Saawarn *et al.*, 2022). Soundwaves cause bubbles to form in the solution, which enlarge and eventually collapse, resulting in very high localised temperatures $\sim 5,000\text{K}$.

The heat generated from bubble collapse creates the conditions for pyrolysis and causes water vapour to convert into free radicals such as $\text{OH}\cdot$ and $\text{H}\cdot$ (Vo *et al.*, 2020; Meegoda *et al.*, 2022). These radicals react with PFAS compounds at the bubble-water interface, causing them to break down into degradation products such as CO_2 and F^- ions (Saawarn *et al.*, 2022).

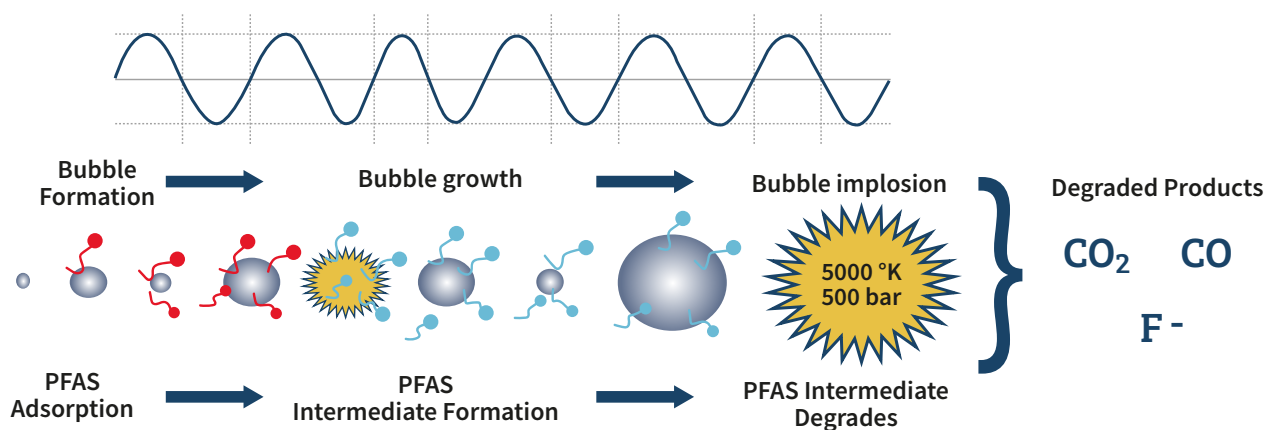


Figure 15. Schematic view of PFAS destruction with sonolysis (from Meegoda *et al.*, 2022).

Advantages of the technique include being able to achieve complete defluorination of PFAS without pre-treatment or the need for chemical additives. In addition, experiments have shown that co-contaminants don't impact the efficiency of sonolysis for PFOS and PFOA degradation (Meegoda *et al.*, 2022).

However, the technique consumes large amounts of energy and has high capital costs. As yet, sonolysis has only been performed at laboratory-scale and not scaled up for commercial use (Verma *et al.*, 2021). Additional studies are needed to address factors such as power density and size of transducer, the frequency and geometry of the reaction, and the physicochemical properties of environmental matrices (Meegoda *et al.*, 2022).

Plasma

Plasma is a treatment technology that uses high voltages to break down PFAS (Vo *et al.*, 2020). Plasma is created when adequate energy is added to a gas (e.g. argon, He and H_2), inducing ionisation of the atoms and the production of electrically charged gas ("plasma") (Yadav *et al.*, 2022; Verma *et al.*, 2021).

Highly reactive oxidative and reductive species (such as $\cdot\text{OH}$, $\cdot\text{O}$, $\text{H}\cdot$, $\text{O}_2\cdot$) and aqueous electrons (e^-_{aq}) are formed as a result of the electrical discharge in the vicinity of liquid water (Meegoda *et al.*, 2022; Vo *et al.*, 2020) (see figure 16). These reactive species make C-F bonds unstable, mineralising PFAS contaminants into their component parts (Verma *et al.*, 2021).

Plasma can be categorised into two treatment types: **thermal plasma** and **non-thermal/cold plasma**:

Thermal plasma (TP) is characterised by a thermodynamic equilibrium between the species in the gas and the electrons, and requires higher energy and pressures to operate (Yadav *et al.*, 2022).

Non-thermal plasma (NTP) is preferable to thermal plasma for treating PFAS-contaminated water, due to its lower energy requirements and higher excitation selectivity (Verma *et al.*, 2021; Meegoda *et al.*, 2022). It is characterised by a non-equilibrium state between the electrons and the other heavy species in the gas (ions and neutrals), with the temperature of the electrons being much higher than other particles in the gas (Yadav *et al.*, 2022). As a result, the electrons will constantly collide with the gas's atoms, generating electrons, radicals, ions, and photons (Meegoda *et al.*, 2022).

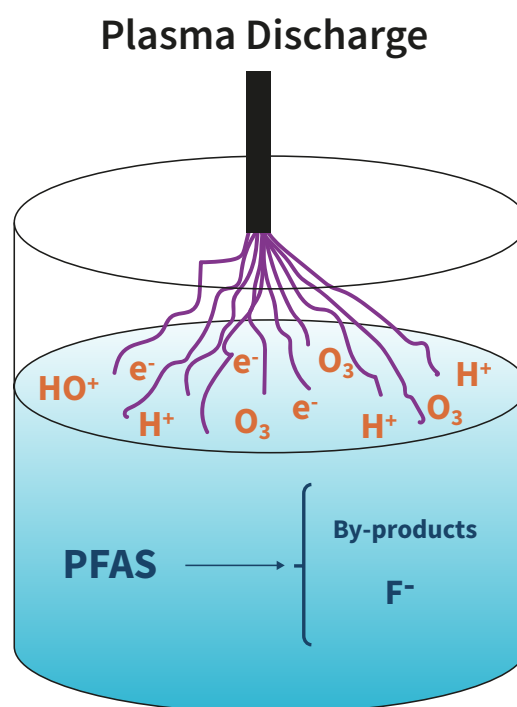


Figure 16. Non-thermal plasma approach for PFAS destruction (from Meegoda *et al.*, 2022).

Pilot studies have revealed that plasma can deal with PFAS precursors, has short treatment times, can remove both short and long-chain PFAS, and is not affected by the presence of co-contaminants (Vo *et al.*, 2020; Yadav *et al.*, 2022; Meegoda *et al.*, 2022). However, the high voltage required to operate plasma (up to 30 kV) is of major concern, as it brings with it significant costs and safety concerns (Vo *et al.*, 2020).

Plasma also makes treated water acidic, requiring subsequent pH corrections before it can be used, and often forms shorter-chain PFAS (Meegoda *et al.*, 2022). Finally, the mechanism by which plasma mineralises PFAS is not yet fully understood (Meegoda *et al.*, 2022). As such, plasma is currently in the research stage, and not ready for full-scale application (Verma *et al.*, 2021).

Incineration

Incineration is a method that uses high temperatures (up to 1,200°C) to defluorinate and thus destroy PFAS (Meegoda *et al.*, 2022). Before incineration can be applied to PFAS in aqueous matrices, the contaminants must be separated from the water using non-destructive methods such as adsorption and membrane filtration (Vo *et al.*, 2020).

Under ideal conditions, the complete destruction of PFAS by incineration results in final products such as carbon monoxide, carbon dioxide, water, hydrogen fluoride, etc. (Meegoda *et al.*, 2022). However, incomplete combustion can lead to the release of toxic gases such as dioxin, furan, and fluorocarbon emissions as well as other unknown by-products which may be problematic (O'Connor, 2022). In addition, any untreated PFAS are released directly into the environment, so there is a high risk of secondary air and soil pollution (Meegoda *et al.*, 2022).

There are limited studies available that relate to PFAS incineration in full-scale operating facilities, so there is much that is still not clearly understood, including the effectiveness of incineration as a PFAS-destruction method and the fate of by-products that are produced (Meegoda *et al.*, 2022). The sustainability and energy intensive nature of this method also needs to be considered.

Despite the many unanswered questions, incineration facilities are well-established and already widely deployed to manage other contaminants present in solids, liquids or gases. Therefore, the initial cost of implementing this method is very low compared to other destructive technologies, and further research is critical to establish how effectively existing facilities remediate PFAS (Meegoda *et al.*, 2022).

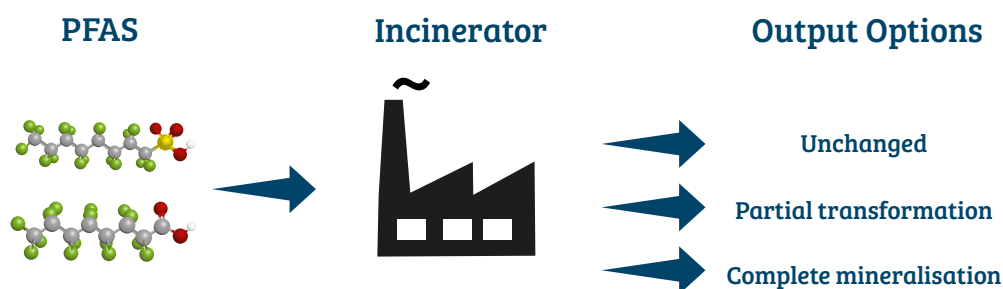


Figure 17. PFAS destruction pathway through incineration (from Meegoda *et al.*, 2022)

Treatment method	Range of removal rates achievable	Advantages	Disadvantages
Activated Carbon (GAC/PAC)	PFOS 0% to $\geq 90\%$, PFOA 0% to $\geq 90\%$ (Depending on age of GAC)	Widely used; environmentally friendly; low-cost; easy to operate; high removal rates possible; household applications possible.	Variable removal efficiency observed; competitive adsorption with contaminants e.g. natural organic matter; PAC is used only once before disposal; GAC requires thermal regeneration and media top-up; disposal of waste carbon required; optimisation required for PFAS removal.
Ion-Exchange (IEX)	PFOS $\geq 90\%$, PFOA 10%-90%	Good removal of PFOS; sorption rates dependent on polymer matrix and porosity; some removal of PFOA possible.	Single use of IEX resin after exhaustion makes process expensive; disposal of used resin required; rate of exchange influenced by many parameters, including influent PFAS concentration; competition for removal between other water contaminants; surface water may need clarification or filtration prior to use; less effective for removal of uncharged, positively charged and short-chain PFAS.
Membrane Filtration (RO & NF only)	PFOS $\geq 99\%$, PFOA $\geq 92\%$ -99%, $>93\%$ for range of species	High levels of removal; can be combined with GAC for higher removal rates; effective for multi-contaminant removal; household applications possible.	Waste must be treated before disposal; high capital and running costs; susceptible to fouling and pre-treatment and post treatment may be needed.
Advanced Oxidation Processes (AOPs)	PFOS 10%-50%, PFOA $<10\%$	Can oxidise numerous contaminants to degradation products using reactive hydroxyl radicals.	Less effective than other methods; significant energy input needed to achieve moderate removal; may oxidise polyfluorinated precursor chemicals present in the raw water, which could result in an increased concentration of PFOS and PFOA in the finished water.
Photocatalysis (AOP)	31%-99% (scale not given, assume small)	Low energy consumption; performed at ambient temperatures; sustainable technology; it can be recycled.	Low degradation efficiency; inefficient for sulfonic groups; toxic intermediate products; additional treatment is needed; affected by co-contaminants.
Sonolysis (AOP)	28%-99% (small scale)	Effective for long-chain and short-chain PFAS; effective for highly concentrated PFAS; effective against co-contaminants; no chemical additives are needed; does not require pre-treatment.	Widescale application; high energy consumption; its mechanism is not well understood; optimisation of ultrasonic and geometric parameters are needed to scaling up of technology.
Plasma	Up to 99% (lab scale)	Can deal with PFAS precursors; effective for long-chain and short-chain PFAS; low energy consumption; no chemical additives are needed; short treatment time; effective for highly concentrated PFAS; effective against Co-contaminants.	Affects water's pH, making it acidic; forms short-chain PFAS; its mechanism is not well understood; longer time for short-chain treatment; the addition of chemicals is required; non-targeted reactions can result in longer treatment time.
Incineration	Not reported, limitation with partial combustion	Widescale application; reduced capital cost; effective for long-chain PFAS.	Toxic intermediate and final products; high environmental impact; air and soil contamination; toxic by-products.

Niche methods

SUMMARY

As our understanding of the potential harm posed by PFAS chemicals has grown, research into remediation methods has been rapidly developing in line with the increasing global demand for effective technologies.

As a result, many new methods have recently emerged, which have potential to be part of the future solution to the PFAS problem, but which are not yet ready for full-scale application. Some of these 'niche' methods, including **biodegradation** and **foam fractionation**, are summarised below.

Biodegradation

In general, PFAS are highly resistant to biodegradation due to the strength of their C-F bonds and high negativity in F- (Wanninayake, 2021; Saawarn *et al.*, 2022). However, recently, novel options for biological remediation have emerged, including bacterial, phytological, and enzymatic methods.

Bacterial remediation

Under standard environmental conditions, the energy demand for breaking C-F bonds is too high for microorganisms to oxidise PFAS (Saawarn *et al.*, 2022). However, it has recently been discovered that some bacterial strains are capable of degrading PFAS in anammox and anaerobic conditions (Vo *et al.*, 2020).

For example, one study showed 60% removal of PFOS and PFOA by *Acidimicrobium* A6 within 100 days (Saawarn *et al.*, 2022). Other researchers have shown that different bacterial strains, such as *Pseudomonas aeruginosa* and *Pseudomonas parafulva* can degrade PFAS under aerobic conditions (Saawarn *et al.*, 2022).

Despite these successes, there are many challenges before bacterial remediation is a viable treatment option for PFAS, including the significant amount of time needed for bacteria to break down PFAS (Verma *et al.*, 2021; Vo *et al.*, 2020).

Phytoremediation

Phytoremediation is the process by which plants take up (and thus remove) PFAS compounds. It is a non-destructive method that works in a similar way to adsorption – the PFAS are localised to plant matter and then need to be subsequently dealt with.

Existing studies have used wetland plants to remediate PFAS from various environmental matrices and have shown significant PFAS accumulation in different plant parts, such as roots, stems, leaves and grains (Saawarn *et al.*, 2022).

Despite research on phytoremediation being in its infancy, its economic feasibility and environmental sustainability make it an appealing future option for PFAS removal (Saawarn *et al.*, 2022).

Enzymatic remediation

Enzymatic methods could be an exciting low-energy alternative to presently used high-energy methods for destroying PFAS. In recent years, some enzymes have been shown to be capable of remediating PFAS at an exceptionally fast pace (Wanninayake, 2021). For example, those extracted from *Cannabis sativa* L. can degrade 98% of PFOS and PFHxS in just one hour, significantly faster than microorganisms. The plant protein does this by altering its secondary structure (increasing β -turns and decreasing random coils, α -helix and β -sheets) which helps it to adsorb PFAS at the hydrophobic site of protein and the side chain of amino acid (Vo *et al.*, 2020).

Foam fractionation

Foam fractionation dates back to the 1940s and is a widely-used technology for the treatment of a range of contaminants, including waste from the textile and milk industries (Yadav *et al.*, 2022). It has recently shown potential for the non-destructive removal of PFAS, although it has not yet been applied for continuous drinking water treatment on the scale of other existing technologies (WHO, 2022).

The method works by introducing bubbles (usually air or nitrogen) into contaminated solutions which rise through and attach to any surface-active substances (e.g. PFAS) present, which the bubbles have a high affinity for (Yadav *et al.*, 2022). The bubbles eventually rise to the top, forming a foam layer that is extracted from the solution and treated using a low-pressure evaporation system (or any other destructive process). The rest of the treated solution can either be discharged or treated by another process (Yadav *et al.*, 2022).

This technique benefits from being quick, low-cost, low-energy and space-efficient. From a commercial perspective, because foam fractionation has already been implemented by wastewater treatment plants that process PFAS-contaminated water, this technology can easily be scaled-up. In addition, it leaves behind small residual concentrations of contaminants, and prevents the continued circulation or transport of PFAS, unlike other non-destructive methods like ion exchange (Yadav *et al.*, 2022). However, whilst foam fractionation is very efficient at removing long-chain PFAS, it has poor efficiencies for short-chain PFAS, which are highly soluble in water and have low surfactant abilities (Yadav *et al.*, 2022).

Treatment train approach

SUMMARY

The treatment train is a **novel, hybrid approach** which aims to overcome the inadequacies of single remediation technologies by combining multiple methods simultaneously, therefore achieving **more effective overall remediation of PFAS** than any one individual technique (Saawarn *et al.*, 2022; Yadav *et al.*, 2022; Verma *et al.*, 2021).

Despite there being many existing techniques that are effective at remediating PFAS, all of them suffer from various shortcomings, such that no one method clearly stands out as superior to the rest.

The overall appeal of a remediation method depends on many factors: not only its PFAS removal efficiency, but its cost-effectiveness, energy-intensiveness, duration of treatment, susceptibility to interference by co-contaminants, ability to be scaled up easily, whether it produces hazardous intermediates, and whether it is environmentally friendly (Yadav *et al.*, 2022; Saawarn *et al.*, 2022).

The treatment train approach combines different treatment methods to achieve greater overall PFAS removal efficiency and practical feasibility (Saawarn *et al.*, 2022). It consists of an initial **concentrating phase** (i.e. a non-destructive method) which removes PFAS from a contaminated solution, followed by an on-site **degradation phase** (i.e. a destructive method) to break C-F bonds and mineralise the compounds in the reject stream entirely (Yadav *et al.*, 2022).

Using this two-step technique reduces the requirement for extreme operating conditions. It is also logistically easier, by removing the need to transport the reject stream from one site to another (Yadav *et al.*, 2022).

An example of a treatment train process has been visualised in figure 18, which shows how membrane processes (nanofiltration) and advanced oxidation processes (electrooxidation) can be combined to remove a PFAS (PFHxA) from industrial process water.

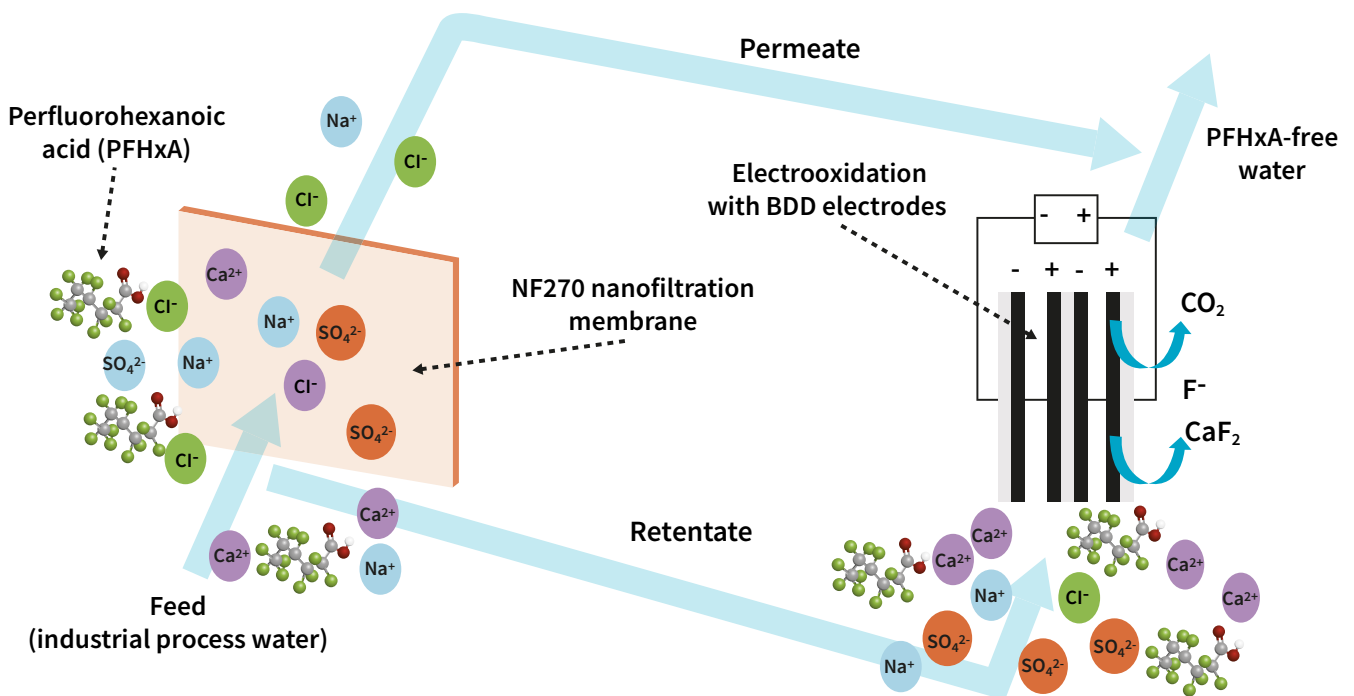


Figure 18. Example of a treatment train process using membrane and oxidative processes to remove and destroy PFAS (from Thompson *et al.*, 2011).

Conclusions

Hundreds, if not thousands, of persistent PFAS have been used over decades and are still entering our environment today.

Some are known to be highly toxic with guideline intake values for the most potent to date in the 0.67 to 3 ng/kg/day range. This presents a legacy, current and future pollution and human health issue.

Many surface and ground water sources of drinking water are contaminated by varying levels and types of PFAS. One major route of PFAS exposure is from PFAS contamination of drinking water and direct daily oral ingestion, but we do not have sufficient data to know whether the levels of PFAS in water sources lead to levels of concern in drinking water.

If drinking water contamination is not managed well, it could lead to bioaccumulation of PFAS in humans and wildlife over the coming years with increasing human blood levels being seen with potentially adverse consequences.

The availability of environmental monitoring test methods is limited to approximately 50 PFAS, and even these are not standardised making it difficult to compare concentrations of PFAS in source waters across regions. More investment and standardisation of commercially available test methods is needed.

There are many technical approaches available to remove PFAS from water but all have their own challenges and limitations in terms of making them practicable and economically viable for the water sector to implement. The evidence in this report acts as the basis for the development of an RSC policy position on PFAS in drinking water.

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