

PFAS – Groundwater’s Dark Matter

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Kabwe well field, Zambia
(D Lapworth BGS © UKRI).

Thousands of per- and polyfluoroalkyl substances (PFAS) compounds have been produced — many at industrial scale — since the early part of the 20th century.^{1,2} They have been used in various applications including non-stick cookware and firefighting foams, and by well-known brands such as Teflon® and Gore-Tex®. The extreme persistence of PFAS has earned them the name ‘forever chemicals’. There are various sources of PFAS which end up in the environment, including in groundwater, as shown in **Figure 1**. Events which may lead to contamination include runoff from sites where a certain kind of firefighting foam was used or releases of untreated industrial process water. PFAS also spread around the globe by airborne transport.

The potential for long-term adverse human and environmental health impacts related to PFAS exposure has come into focus in the last few years. PFAS exposure may affect the immune system, may increase cholesterol levels and may increase the risk of kidney or testicular cancer³. At this time, however, the health effects of short- and long-term exposures to mixtures of different PFAS are poorly understood. Many PFAS compounds are now banned or are being phased out.

The unique chemistry of PFAS compounds results in different fate and transport pathways in the natural environment, which are poorly understood compared to better studied organic chemical contaminants such as organic solvents and fuels. In response to this, a large number of research projects are under way around the world to better understand the environmental and health consequences of PFAS, especially in groundwater. This overview paper describes the chemistry and detection of PFAS in groundwater samples, their current water quality limits, and potential treatment options for PFAS polluted water.

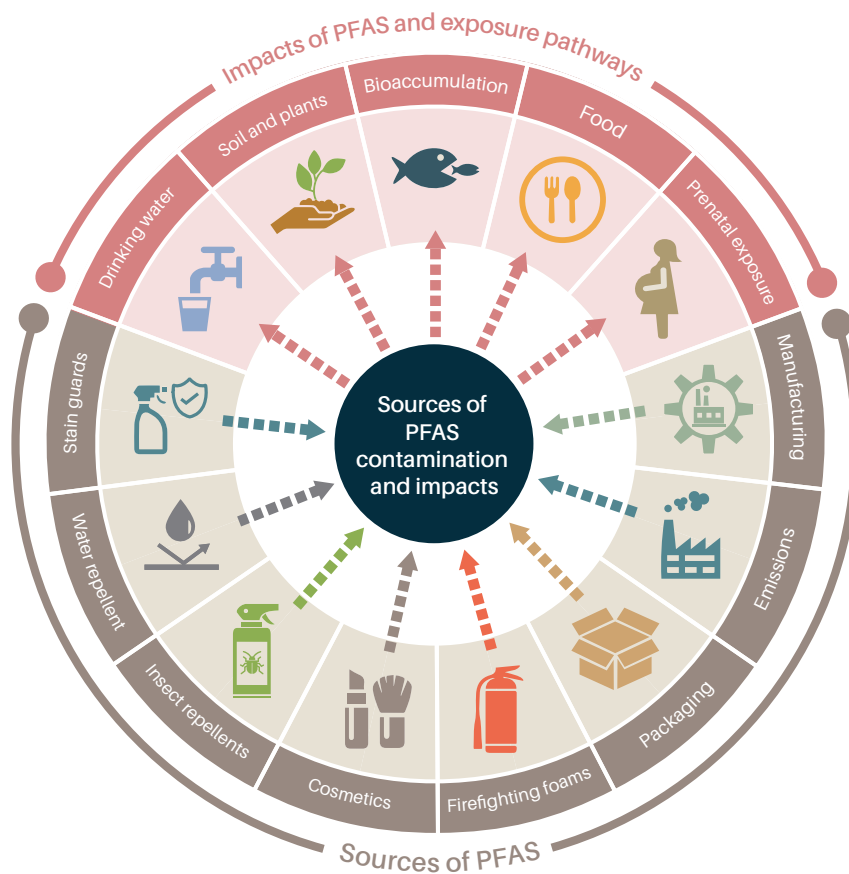


Figure 1 Sources of PFAS compounds in the environment (Design: Cashman 2022 & D Lapworth BGS © UKRI).

PFAS Chemistry and Detection in Waters

The basic chemical structure of PFAS compounds is a chain of carbon atoms and carbon-fluoride bonds. The bond between carbon and fluoride is the strongest bond in organic chemistry and makes PFAS highly resistant to degradation in the environment. The thousands of PFAS compounds are divided into sub-groups, each having unique chemical properties. A major PFAS subgroup are surfactants (i.e., compounds that consist of a water repelling tail and a water attracting head). Two prominent compounds in this PFAS sub-group are perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS).

The widespread use of PFAS in industrial processes and consumer products has resulted in the release of PFAS into the global environment and their ubiquitous detection in living organisms,⁴ groundwater and drinking water.⁵⁻⁷ There are some notable case studies of PFAS contaminated sites, some of which are highlighted in **Box 1**.

The Buncefield incident in the UK, 2005

In December 2005, a fire destroyed the UK's fifth largest oil-product storage facility at Buncefield, in Hertfordshire. The fire burnt for 5 days and has been described as the 'largest incident of its kind in peacetime Europe'. Fire fighting foam and fuel product runoff from the site caused pollution of soils and groundwater. Fighting this fire consumed much of the UK's inventory of PFOS-related fire-fighting foam, more than 750 000 litres of foam concentrate⁸. Even though much of the runoff was recovered, PFAS compounds (primarily PFOS) were later detected in the local soil and groundwater. The polluted soil and the aquifer have been undergoing treatment: as of 2017, an estimated 1 kg of PFOS has been removed from the aquifer.⁸

Exposure to PFAS from water sources in China

PFAS contamination was detected in groundwater sources used for drinking water around a fluorochemical industrial park in Fuxin, China⁹. PFOA and perfluorobutane sulfonate (PFBS) were found in groundwater at maximum concentrations of $>20 \mu\text{g/L}$, as well as in vegetables and eggs harvested around the industrial park, highlighting ubiquitous contamination by PFAS. A recent study¹⁰ found that drinking waters across urban centres in China were exposing people to potentially harmful levels of PFAS. Over 500 drinking water samples, including groundwater sources, across 66 cities found high concentrations of PFOA and PFOS. PFAS were present at concentrations $>20 \text{ ng/L}$ in water from more than 20% of cities studied.



Figure 2 The Buncefield fire, UK 2005, which needed c.0.75 million litre of foam concentrate to control, resulting in soil and groundwater pollution.

Regulation	Compound	Limit (ng/L)
U.S. EPA (Interim updated Health Advisory) ¹⁵	PFOA	0.004
	PFOS	0.02
	PFBS	2000
	'GenX chemicals'	10
U.S. state level (example of Illinois) ¹⁶	PFOA	2
	PFOS	14
U.S state level (example of Massachusetts) ¹⁶	Six PFAS substances combined (PFOA, PFOS, PFHxS, PFNA, PFHpA, and PFDA)	20
European Commission Drinking Water Directive ¹⁷	Total PFAS	500
	List of 20 PFAS	100
UK Drinking Water Inspectorate ¹⁸	PFOA and PFOS trigger level above which further monitoring for PFAS must be undertaken. All UK drinking water utilities were required to screen for 47 PFAS compounds from October 2021	10
Government of Australia — Drinking water quality guideline value ¹⁹	Total PFOS+PFHxS	70
	PFOA	560

Table 1 Recommended limits for PFAS in the U.S., Australia, and Europe for drinking water.

The global distribution of PFAS in the environment is influenced by their physicochemical properties, such as their solubility in water or chemical structure. Although these compounds have been circulating in the environment for decades, PFAS were not widely documented in environmental samples until the early 2000s. This is because the detection of PFAS was difficult with the analytical equipment available at that time.¹¹ Since then, government laboratories and others have developed and validated a series of methods for PFAS. Today, commercial laboratories routinely detect 40 or more PFAS compounds in groundwater and other environmental matrices.^{12,13} Still, many PFAS cannot be detected by these methods and require even more sophisticated analytical methods and equipment. A further complication that hinders the quantification of individual PFAS compounds is the lack of distinct chemical standards, which are only available for a very limited number of the many thousands of PFAS released to the environment. For that reason, indirect and screening methods have been developed which measure how much organic fluorine is contained in a PFAS-contaminated water sample.¹⁴



Figure 3 Water sampling in India (T Boving, University of Rhode Island). *(left)*

Figure 4 Urban groundwater sampling, Zambia (S Pedley, University of Surrey). *(right)*

In addition to the difficulties in detecting and quantifying PFAS compounds in environmental samples, their widespread use in many everyday items, including laboratory supplies and reagents, resulted in the problem of PFAS background contamination. For example, background contamination can result from PFAS unintentionally introduced into a sample by a person wearing PFAS containing clothing, like Gore-Tex® or using equipment containing Teflon® parts. Consequently, great care must be taken to avoid contamination during sample preparation, which could otherwise result in the false detection of certain PFAS.² With the right equipment and quality assurance procedures in place, PFAS detection limits in aqueous samples are very low, in the parts per quadrillion (ppq) range — equivalent to one drop of water in 20 Olympic sized swimming pools.

PFAS Water Quality Limits

Typical PFAS concentrations in polluted groundwater range from picograms per litre to micrograms per litre (note that one picogram per litre is equal to one ppq). However, PFOS concentrations several thousand times higher (> 1,000 mg/L) have been reported in wastewater.^{5, 20} Many countries and states are at various stages in developing regulatory frameworks for PFAS in water, soils, and other environmental matrices. For instance, the US EPA¹⁶ has established a non-enforceable health advisory level while an array of widely varying standards and regulations exist in individual states (Table 1). In Europe, the European Commission¹⁷ limits total PFAS in water at 500 nanograms per litre. Increasingly stringent PFAS groundwater quality regulations are anticipated in the near future. Similar limits exist in other countries.^{18, 19}

Potential PFAS Treatments

Treating PFAS in waters is challenging and costly. Current treatment options for PFAS contaminated environmental matrices can be broadly classified as either destructive or nondestructive. Non-destructive technologies remove PFAS from groundwater via sorption to activated carbon or specially designed sorbents but, as the name implies, do not destroy PFAS. Therefore, spent sorbents must be treated by incineration or properly disposed of in hazardous waste landfills. All these options are costly and can have a large carbon footprint. Destructive treatments seek to break up the PFAS molecules into benign compounds. One promising destructive PFAS treatment option for contaminated water is based on chemical oxidation processes.²¹ This application relies on powerful oxidants, such as ozone or persulfate, used in combination with other processes (e.g. electrochemistry). Ultimately, the goal is to degrade PFAS and their intermediates to just fluoride and carbon dioxide.²² However, there are concerns about the effectiveness of oxidation technologies and the fate of intermediates or the formation of harmful and undesired treatment by-products.²³ Therefore, it is likely that PFAS treatment will need to use a combination of both destructive and non-destructive methods.²⁴

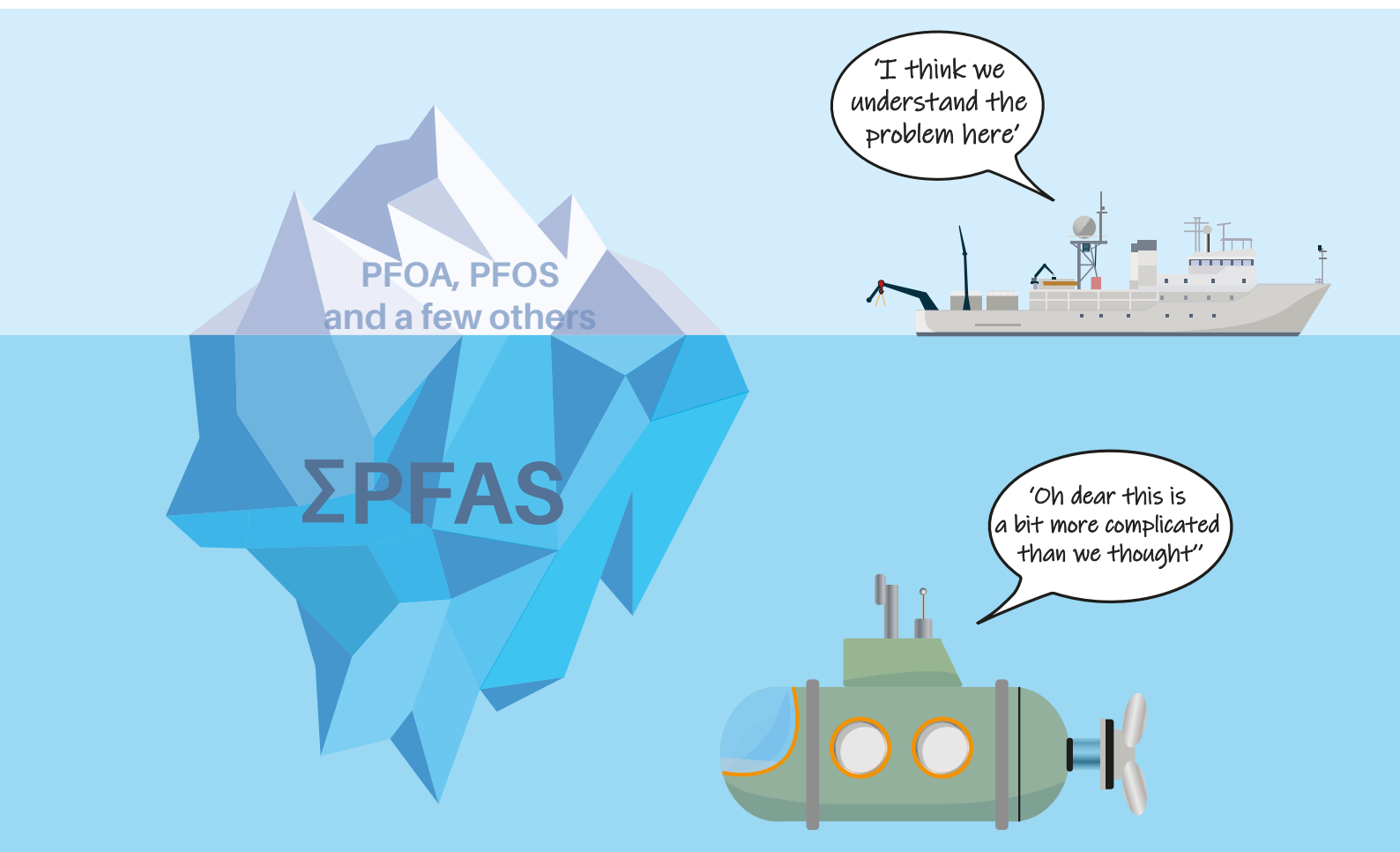


Figure 5 Although much progress has been made in the understanding of PFAS in the environment, a lot needs to be discovered still (Design: BGS © UKRI 2022).



Figure 6 Groundwater sampling in Kabwe, Zambia for Emerging Contaminants (D Lapworth BGS © UKRI). *(left)*

Figure 7 Rivers of India (D Lapworth BGS © UKRI). *(right)*

Future Outlook

PFAS will remain a major groundwater quality issue in the coming years and decades. The ubiquitous distribution of PFAS around the globe has the potential to significantly impact the quality and availability of water resources in many regions. The pervasive presence of PFAS in the environment raises concerns about impacts to ecosystem and human health. Further developments in affordable screening and treatment solutions will be necessary to tackle this insidious contamination.

FURTHER INFORMATION

The U.S. Center for Disease Control (CDC)²⁵ and the U.S. Agency for Toxic Substances and Disease Registry (ATSDR)²⁶ websites provide summaries of the current knowledge about PFAS health effects and offer links to other PFAS related sites. The global distribution of PFAS in groundwater was recently described.²⁷ The Environmental Working Group (EWG), an American activist group, provides an overview and maps of PFAS detections in U.S. drinking water systems.²⁸ In Europe, the European Commission²⁹ as well as individual countries, such as the UK,³⁰ provide further information about PFAS. Environmental agencies, such as the US EPA,^{13,14} frequently revise and improve PFAS detection methods. Overviews of PFAS water testing techniques are available from various sources.^{31,32} The treatment of PFAS and examples of destructive and nondestructive remediation technologies are illustrated on the website of the Environmental Security Technology Certification Program (ESTCP),³³ which is the US Department of Defense environmental technology demonstration and validation program. Educational resources about PFAS range from videos to classroom talking points.^{34,35}

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