



PFAS basics

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1. What are PFAS

Per- and polyfluoroalkyl substances (PFAS) are a large group of chemicals that have been used since the 1950s. The chemical structure of PFAS gives them useful properties, such as thermal stability and the ability to repel water and oil, that makes them valuable in a wide variety of industrial and consumer applications. They have been used in the manufacture of non-stick cookware, fabric, furniture and carpet stain protection applications, food packaging and in some types of firefighting foam (Table 1.1).

This group of chemicals was formerly known as *perfluorinated compounds*, or *PFCs*, but the name has been changed to avoid confusion with another group of chemicals that are relevant to climate change, which are also known as PFCs.

The best-known examples of PFAS are:

- perfluorooctane sulfonate, also known as PFOS; and
- perfluorooctanoic acid, also known as PFOA.

Perfluorohexane sulfonate (PFHxS) is another chemical of the PFAS group and is present in some firefighting foams.

PFAS are not manufactured in Australia but have been used here for many years in a wide range of manufacturing processes. PFOS and related compounds are imported into Australia mainly for use as mist suppressants in the metal plating industry, hydraulic fluid in the aviation industry and surfactants in the photography industry. PFOS and PFOA firefighting foams were used extensively worldwide from 1970s by both civilian and military authorities due to their effectiveness in extinguishing liquid fuel fires.

Prior to the regulation of PFAS, there were no controls associated with the waste disposal activities from manufacturing plants using these chemicals which can result in solid, liquid or airborne emission of PFAS. Pollution is also present at many facilities where firefighting foams containing PFAS have been heavily used.

PFOS and PFOA may be present in a range of imported consumer products, although many countries have phased out, or are in the process of phasing out the use of PFOS and PFOA. Some countries, including Poland, India, China and Russia are still manufacturing PFAS.

Table 1.1: List of historical applications of PFAS

Industry branch	PFAS application
Aviation, aerospace & defense	additive in aviation hydraulic fluid; insulators; solder sleeves
Biocides	active ingredient in plant growth regulators or ant baits, enhancers in pesticide formulation
Construction products	additives in paints and coatings; coating architectural materials
Electronics	flame retardants
Firefighting	film formers in AFFF and FFFP; protective clothing
Household products	wetting agent in floor polishes
Metal plating	wetting agent, mist suppressing agent

Oil production	surfactants in oil well stimulation
Polymerization	emulsion polymerization processing aids
Automotive	lubricants and low friction bearings and seals
cable and wiring	coating for weathering, flame and soil resistance
Electronics	insulators, solder sleeves
Energy	film to aid weatherability solar collectors
Food processing	fabrication materials
Household products	nonstick coating
Medical articles	grafts and implants; coatings for surgical drapes and gowns
Paper and packaging	oil and grease repellent
Semiconductors	working fluids in mechanical vacuum pumps
Textiles, leather and apparel	oil and water-repellent stain release; raw materials for highly porous fabrics

Source: OECD (2013), OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD.

2. What is the concern?

During the manufacturing process of some PFAS, and the use of PFAS products, PFOA and PFOS have been released to the air, water and soil throughout the world. Unlike many other organic chemicals PFOS and PFOA do not bind strongly to soil and organic materials. This means that they are readily transported in solution in surface and groundwaters. Consequently, a plume of contamination in groundwater may be up to 100 times as extensive as other contaminants.¹

PFAS have been detected in isolated parts of the world indicating that they are very long lived in the environment with half lives of 2 to 4 years for PFOA, 5 to 6 years for PFOS and 8 to 9 years for PFHxS.¹ They may be transported over large distances by rivers and ocean currents and through airborne dispersion. Studies have indicated that PFAS bioaccumulate in freshwater and marine ecosystems.²

For most people, the main exposure pathway for PFAS is through ingestion³, such as:

- Drinking contaminated water
- Eating food contaminated with PFAS, such as fish or shellfish
- Eating food packaged in materials containing PFAS (e.g. greaseproof packaging such as popcorn bags, pizza boxes)
- Hand to mouth transfer in babies and toddlers from stain resistant materials containing PFAS.

¹ <https://www.ienvi.com.au/pfas-frequently-asked-questions/>

² e.g. Ahrens (2011) Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate J. Environ. Monit., 13, 20–31

³ National Center for Environmental Health Agency for Toxic Substances and Disease Registry, An Overview of Perfluoroalkyl and Polyfluoroalkyl Substances and Interim Guidance for Clinicians Responding to Patient Exposure Concerns Interim Guidance Revised on 5/07/2018

Exposure to PFOS and PFOA from inhalation and dermal routes during showering and bathing has been assessed as negligible⁴. Skin absorption studies have also suggested that under typical conditions, skin is resistant to PFOS and PFOA transport⁵.

"While there have been many studies into the health effects of PFAS it is uncertain whether PFAS are harmful to human health. In the few areas in which there is evidence for a possibly causal association of PFAS with an effect on human health the association is either uncertain or apparently weak."

The PFAS Health Study: Systematic Literature Review⁴.

The biological half-life in human serum varies with the type of PFAS, with estimates of 3.8 years for PFOA, 5.4 years for PFOS and 8.5 years for PFHxS⁶.

A recent review⁶ examined published research to February 2017 on the health effects of exposure to PFAS chemicals on the human body. The research included people that had a higher than usual exposure of PFAS, such as manufacturing workers, firefighters and people exposed through contaminated water supplies.

The reported health effects⁷ were:

- increased levels of cholesterol in the blood;
- increased levels of uric acid in the blood;
- reduced kidney function, although it is possible that poor kidney function caused by something else causes increase in PFAS levels in blood;
- alterations in some indicators of immune response;
- altered levels of thyroid hormones and sex hormones;
- later age for starting menstruation in girls, and earlier menopause; and
- lower birth weight in babies.

However, the differences in the reported health effects between people who have the highest exposure to PFAS and those who have had low exposure were small. The level of health effects reported in people with the highest exposure was generally still within the normal ranges for the whole population. The panel found inadequate evidence that PFAS caused other health effects.

Many jurisdictions have opted to take a conservative approach to the regulation of PFAS on the assumption that future studies may yield evidence for a causal link between exposure and adverse health effects. This approach is a precautionary response to allay fears in the community that are stoked by media reports such as those in which PFAS chemicals have been described as "the new asbestos".⁸

⁴ Health Canada (2016) Draft guidelines for public consultation: Perfluorooctanoic acid (PFOA) in Drinking Water. Health Canada (2016) Draft guidelines for public consultation: Perfluorooctane Sulfonate (PFOS) in Drinking Water.

⁵ Franko, J., Meade, B.J., Frasch, H.F., Barbero, A.M. and Anderson, S.E. (2012). Dermal penetration potential of perfluorooctanoic acid (PFOA) in human and mouse skin. *J. Toxicol. Environ. Health A.*, 75(1): 50–62.

⁶ Kirk M, Smurthwaite K, Bräunig J, Trevenar S, D'Este C, Lucas R, Lal A, Korda R, Clements A, Mueller J, Armstrong B. The PFAS Health Study: Systematic Literature Review. Canberra: The Australian National University. 2018.

⁷ Summary of the PFAS Expert Health Panel – Report to the Minister, March 2018

⁸ <https://www.abc.net.au/4corners/contamination/9032140>



3. Limits in Queensland

The two limits that are relevant to water and sewage in Queensland are the limits for water and limits for biosolids.

The limits in drinking water in Australia, which apply to Queensland water supplies, have been set out in the Australian Drinking Water Guidelines⁹. The Guidelines have recently been updated to include specific health-based guidance values for PFAS in drinking water. These guidance values are the same as that published by the Australian Government Department of Health as follows¹⁰. Similarly, the guidelines for recreational waters have been recently updated to reflect a revised exposure calculation methodology from the tolerable daily intake values, which remain unchanged.

Table 3.1: Health based guidance values for PFAS

PFOS/PFHxS	PFOA	Description	Source
0.02 µg/kg body weight/day	0.16 µg/kg body weight/day	Tolerable daily intake	FSANZ ¹¹
0.07 µg/L	0.56 µg/L	Drinking water	Australian Government Department of Health ¹⁰ and Australian Drinking Water Guidelines ⁹
2 µg/L	10 µg/L	Recreational water	NHMRC ¹²

For biosolids and their reuse, there is a separate standard that appears in the recently updated Queensland Department of Environment and Science End of Waste Code¹³.

Table 3.2: End of waste code maximum contaminant limits for PFAS

Application	TOF Limit	Comment
Biosolids	0.39 mg/kg (dry mass)	Where TOF analysis is not available, the sum of oxidizable precursors (TOPA C4-C14) and analysed PFAS (PFBS, PFHxS, PFOS, PFOSA, PFDcS) is taken to be a surrogate for TOF
Soil (after biosolids application and mixing)	0.005 mg/kg (dry mass)	Where TOF analysis is not available, the sum of oxidizable precursors (TOPA C4-C14) and analysed PFAS (PFBS, PFHxS, PFOS, PFOSA, PFDcS) is taken to be a surrogate for TOF

⁹ NHMRC, NRMCC, (2011) Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra. Version 3.5 Updated August 2018

¹⁰ Australian Government Department of Health, (2017). Health based guidance values for PFAS for use in site investigations in Australia. <https://www1.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-hbgv.htm>

¹¹ <http://www.foodstandards.gov.au/consumer/chemicals/Pages/Perfluorinated-compounds.aspx>

¹² NHMRC (2019) Guidance on Per and Polyfluoroalkyl (PFAS) in Recreational Water. National Health and Medical Research Council, Canberra. Updated August 2019

¹³ Queensland Government Department of Environment and Science, (2018). End of Waste Code Biosolids (ENEW07359617) <https://environment.des.qld.gov.au/assets/documents/regulation/wr-eowc-approved-biosolids.pdf>

4. Where are they found?

There are several sites in Queensland that have been investigated for PFAS contamination due to their association (current or historical) with aviation, defence or fire and emergency services. PFAS is a major constituent of AFFF firefighting foams that have been in use in Australia since the 1950s. The need for training of personnel in firefighting techniques has resulted in repeated use of the foams which in turn has resulted in contamination of some sites. These sites include areas where bores used for drinking water supply have been found to contain detectable levels of PFAS¹⁴.

In Australia PFAS have been ubiquitously detected to be present in low concentrations in wastewater influent and effluent, and biosolids¹⁵ and in the leachate from landfill sites¹⁶. The source of the PFAS is more enigmatic but is most likely to be from products containing PFAS that are disposed to landfill, potentially PFAS-contaminated trade waste (liquid and solid), and from dispersion into wastewater through normal household cleaning and washing.

Wastewater treatment processes only provide partial removal of some water soluble PFAS. It is also recognised that wastewater treatment breaks down PFAS precursor chemicals to produce PFOA. Thus, wastewater treatment processes can appear to increase the total amount of PFAS in effluent compared with an influent stream.

¹⁴ <https://www.qld.gov.au/environment/pollution/management/disasters/investigation-pfas/sites>

¹⁵ Gallen, C., Eaglesham, G., Drage, D., Nguyen, T. Hue and Mueller, J.F. (2018). A mass estimate of perfluoroalkyl substance (PFAS) release from Australian wastewater treatment plants. *Chemosphere* 208 975-983.

¹⁶ Gallen, C., Drage, D., Eaglesham, G., Grant, S., Bowman, M. and Mueller, J.F. (2017) Australia-wide assessment of perfluoroalkyl substances (PFASs) in landfill leachates. *Journal of Hazardous Materials* 331, 132–141.

5. Analysis

The PFAS National Environmental Management Plan provides a concise analysis of the standard methods of analysis for PFAS¹⁷. The table has been reproduced below (Table 5.1) for completeness.

In summary:

- It is recommended that total PFAS can be estimated using a combination of the appropriate US EPA method (for liquid or solid samples) with either a TOFA (total organic fluorine assay) or TOPA (total oxidisable precursor assay) analysis.
- TOFA considers the total mass of organic fluorine while TOPA considers PFAS with perfluorinated carbon chain lengths from C4 to C14.
- TOFA has a significantly higher limit of reporting compared to that usually available with TOPA, because of the limitation of the analytical technique for TOFA
- TOFA can be used to check the degree to which TOPA analysis accounts for potential precursors, noting that any PFAS with a carbon chain length shorter than C4 and longer than C14 would be missed by either TOPA or standard LC-MS/MS analysis.

Caution must be applied in the interpretation of results for the following reasons:

- Traditional PFAS analysis only targets the specific analytes (for example the thirteen PFAS chemicals listed in Table 5.1 for US EPA Method 537) and therefore may underestimate the presence of total PFAS chemicals in the environment.
- The TOP Assay looks at the perfluorinated or polyfluorinated compounds that are sometimes termed “precursors” because they can bio-transform to form simpler perfluoroalkyl acids such as PFOA.
- The way the environment oxidizes PFAS into potentially harmful forms may be more conservative than the TOP assay processes in the laboratory.

The PFAS NEMP is currently in the consultation phase of a revision to a new version. One of the concerning statements in the revised draft is the following:

"Attention should be given to the range of products that can cause PFAS contamination of samples, including new clothing, footwear, PPE and treated fabrics stain and water resistant products, sunscreen, moisturisers, cosmetics, fast food wrappers, Teflon®, sampling containers with Teflon®-lined lids, foil, glazed ceramics, stickers and labels, inks, sticky notes, waterproof papers, drilling fluids, decontamination solutions and reusable freezer blocks. These should not be worn or used during any stage of sampling (at site, during transport etc.) where sample contamination could affect analytical results."

Many of these items are commonplace in the field sampler's kit and everyday life. This highlights the importance of good sampling protocols including duplicate samples and trip blanks to assess the extent to which contamination from external sources might be present.

¹⁷

https://www.epa.vic.gov.au/~media/Files/Your%20environment/Land%20and%20groundwater/PFAS%20in%20Victoria/PFAS%20NEMP/FINAL_PFAS-NEMP-20180110.pdf



Table 5.1: PFAS standard methods of analysis

Methods of PFAS analysis	Method Analytes	Sample type	How can the method be used?	Limitations	References
US EPA Method 537.1 Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and LCMS/MS	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, PFBS, PFOS, NMeFOSAA, NEtFOSAA HFPO-DA, 11Cl-PF3OUdS, 9Cl-PF3ONS, ADONA	Drinking water, ground and surface water	To analyse for specific analytes	Only detects specific PFAS Does not require results to be corrected for Internal Standard recovery Limited internal standards Further details in the reference	Shoemaker <i>et al.</i> 2018
US EPA Method EPA821-R-11-007 Draft Procedure for Analysis of Perfluorinated Carboxylic Acids and Sulfonic Acids in Sewage Sludge and Biosolids by HPLC/MS/MS December 2011	PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, PFBS, PFHxS, PFHpS, PFOS, PFOSA, NMeFOSA, NEtFOSA, NMeFOSE, N-EtFOSE	Sewage sludge and biosolids	To analyse for specific analytes	Only detects specific PFAS Further details in the reference	US EPA Method EPA821-R-11-007
Total Oxidisable Precursor Assay (TOPA)	Total PFAS chains (C4-C14)	Water samples and extracts including soil, biota, AFFF products and wastes	Can be used in conjunction with a US EPA method to estimate the total PFAS in a sample, and in some circumstances, the approximate end point PFAS. Can help inform risk assessments.	Cannot be used to target exact PFAS precursors, as it is a semiquantitative method. Allows for some inferences as to precursor chain length	Houtz <i>et al.</i> 2012
Total Organic Fluorine Assay (TOF) as combustion ion chromatography (the most common available)	Total fluoride in organic and inorganic forms	Water samples and extracts including soil, biota, AFFF products and wastes	Can be used in conjunction with a US EPA method to understand the total presence of organic fluorine in a sample and compare this to the organic fluorine equivalent detected by the US EPA method.	Cannot be used to target exact PFAS precursor compounds	Laboratory reported methods only



6. What does it mean for the water and sewerage industry?

As an industry we can expect to see greater regulation and ongoing attention to PFAS as an “emerging contaminant”.

The attention will come despite the current lack of a recognised substantial risk to human health. The underlying principle for this is outlined in the NEMP2 published by the heads of EPA of Australia and New Zealand.

We can expect that as analytical methods improve, there will be increased ability and potentially requirements to characterise greater numbers of PFAS compounds.

Attention may shift to newer, presently unrecognised compounds that are not regulated, but have been potentially used to replace many PFAS compounds in manufacturing processes.