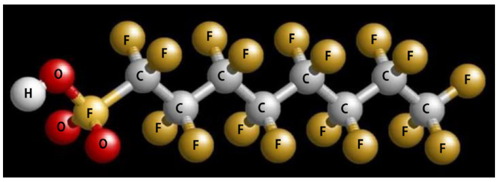
Water Research Australia

Fact Sheet
Perfluorinated chemicals in water

PFAS — Per- and Poly-FluoroAlkyl Substances

PFAS are hydrocarbon molecules with fluorine in place of most or all of the hydrogen atoms normally found on the hydrocarbon backbone.



Extremely strong carbon-fluorine covalent bonds give them unique properties such as high chemical and thermal stability and hydrophobicity (water repellence) and lipophobicity (fat/oil repellence). PFAS are highly water soluble and resistant to degradation and hence widely present in the environment. Historically, the PFAS with the highest production volumes were perfluorooctane sulfonate (PFOS), and perfluorooctanoic acid (PFOA).

World production and use

PFAS were first developed in the 1940s by 3M in the US, and the first commercial application was as a fabric stain repellent in 1956. The heat stability and water and oil repellence of PFAS made them useful for a wide range of applications. DuPont was the second major manufacturer of these compounds in the US, and other major producers were established in in France, Germany and Japan.

Common uses for PFAS in consumer products included non-stick coatings on cookware, stain resistant and water proofing treatments on fabrics, additives in cleaning products and floor polish, and grease resistant packaging for some foodstuffs. PFAS were widely used in the aerospace, automotive, construction, and electronics industries for mechanical components, protective coatings and sealants, additives to hydraulic fluids and lubricants, emulsifiers, wetting agents and mist-suppressing agents. PFAS were also used as herbicides and insecticides, and as active ingredients in firefighting foams.

Points to note about PFAS in Australia

- PFAS are water soluble and are consequently widely present in the environment.
- A study of the levels of PFAS in Australian blood donors from South East Queensland showed that PFAS levels have dropped by >50% between 2002/3 - 2010/11.
- There is a poor understanding of the mechanism/s by which PFAS could have adverse health effects.
- PFAS are still manufactured in a number of countries, but their use is generally being phased out both here and overseas.
- The Australian Department of Defence is investigating a number of its bases to determine the impact of the historic use of PFAS on the surrounding environment.
- FSANZ’s *Hazard Assessment Report—PFOS, PFOA and PFHxS* of April 2017 gives recommendations for Australia’s final health-based guidance values for use during site investigations in Australia.

Current status and prevalence

In the early 2000s concerns over possible health and environmental effects resulted in progressive restrictions on use. Under pressure from the US EPA, 3M had ceased production of both PFOS and PFOA by 2002, however other manufacturers continued to make PFOA. A US EPA spokesman at the time cited evidence of prolonged environmental persistence, detection of PFOS in human and wildlife tissues around the world, and demonstrated toxicity in rodent studies as factors which led to the conclusion that the chemical could potentially pose a risk to human health and the environment over the long term.

The phase-out of PFOA under a global stewardship program was initiated by the US EPA in 2006, with the aim of reducing emissions and product content by 95% in 2010 and eliminating emissions and product content by 2015. Regulatory measures to reduce the manufacture, importation and use of long chain PFAS, and to require industries to seek alternative, safer substitutes have been progressively implemented not only in the US, but also in many other countries.

While production and use of PFAS in Japan, Western Europe and the US has fallen sharply since 2000, there has been a rapid increase in production in China, India, Poland and Russia. Some estimates suggest that global emissions from production of PFAS and fluoropolymers are now at similar levels to those in the 1990s, although it is reported that emission controls and cleaner production methods are now being introduced in some of the new manufacturing countries. Even in countries where regulatory measures have been taken, exposure to PFOS and PFOA from existing treated consumer goods and products, contaminated sites and stored chemicals may still occur.

While not manufactured in Australia, PFAS have been widely used in a number of products and activities.

PFAS in the environment

Unlike other environmentally persistent organic chemicals, PFOS and PFOA bind poorly to soil and organic material, and therefore exist mainly in solution in surface and ground waters.

> Research on mechanisms of environmental transport suggest that low levels of PFAS - even in pristine wilderness areas - can be attributed to long distance transport by rivers and ocean currents, and airborne dispersion.

Studies have indicated that long chain PFAS bioaccumulate in freshwater and marine ecosystems. The lack of controls on airborne emissions and solid or liquid waste disposal (prior to the regulation of PFAS) resulted in significant localised pollution around production facilities and manufacturing plants where these chemicals were used. Pollution is also present at many facilities where firefighting foams containing PFAS were frequently used.

PFAS in humans

The widespread presence of PFAS in human populations was first suggested in a 1976 publication[2]. Researchers who had been studying the effects of water fluoridation on fluoride levels in the body detected organic fluorocompounds tightly bound to the albumin protein in nearly all tested samples of pooled human plasma from blood donors, in addition to the expected ionic form of fluoride. The researchers hypothesised that these organic compounds might originate from the perfluorinated chemicals in consumer products, however, analytical methods available then could not identify specific organic fluorocompounds. Other studies in the US, China, Argentina and Japan during the 1970s and 1980s also reported detection of organic fluorine compounds in human blood, but could not identify the specific chemicals detected.

Since regulatory action was initiated, a large international research effort has sought to characterise human exposure sources and better understand the toxicology of perfluorinated chemicals, but scientific knowledge is still relatively limited. It is now known that the highest levels of PFOS and PFOA are found in the liver, followed by the kidneys and lungs. Both compounds are transferred across the placenta to the foetus, and both are found in breast milk. Both compounds are filtered into urine in the kidney, but are then largely reabsorbed during passage through the renal tubules so that only a small proportion remains in the final urine. This internal recycling is believed to contribute to the long half-lives of both PFOS (estimated at 4.1 to 8.7 years) and PFOA (2.3 years) in humans.

A significant contribution to epidemiological information was made by the C8 Health Project which investigated the impacts of PFOA pollution (from a DuPont manufacturing plant) of several public drinking water supplies in West Virginia and Ohio. A class-action lawsuit resulted in DuPont funding independent medical testing and epidemiological studies of the exposed residents. Blood samples and questionnaire data were collected from over 69,000 people, with 40,000 people agreeing to participate in a five year follow up cohort study.

The blood testing program undertaken in 2005/2006 showed the average PFOA level in exposed people was 83 µg/L, compared to levels of 2 µg/L to 5 µg/L in the general US population. Levels of PFOA in public drinking water in the affected area ranged from 0.03 to 3.5 µg/L at this time. In private drinking water supplies levels as high as 22 µg/L were detected.

The health data were analysed by a team of scientists and then evaluated by a panel of three independent expert epidemiologists who concluded that a 'probable link'[3] existed between PFOA exposure and kidney cancer, testicular cancer, ulcerative colitis, thyroid disease, pregnancy induced hypertension and hypercholesterolemia. No probable links were found for over 40 other health outcomes. The method used by the C8 expert panel to make judgements on health effects was defined in terms of the legal settlement and is not the same as the process used by regulatory agencies.

Testing of pooled sera from one group of Australian blood donors (in south-east Queensland) showed evidence of declining exposure, with average levels for PFOS and PFOA in most age groups dropping more than 50% between 2002/03 and 2010/11. The levels were higher in the Australian group than those in the US, however the sample was not nationally representative[4].

Can PFOS or PFOA cause cancer?

The mode(s) of action by which PFOS or PFOA may cause adverse biological effects have still not been established. There is no evidence that these compounds can directly interact with DNA to cause damage, and their chemical properties make this possibility unlikely. However, a number of indirect mechanisms of action could lead to changes in DNA replication or cell division and thus increase cancer risk - and may also play a role in non-cancer adverse effects.

Studies of workers involved in the manufacture or use of PFOS and PFOA have investigated whether there is any link between these chemicals and the development of prostate, bladder and liver cancer in humans. There have been no consistent findings in these studies.

The International Agency for Cancer Research (IARC) has classified PFOA as possibly causing some cancers. Other studies have concluded that the evidence does not support an association between human cancer and either PFOS or PFOA exposure.

A 2016 evaluation of the available evidence, by the US EPA, resulted in classification of both PFOS and PFAS as having 'suggestive evidence of carcinogenic potential'. This is the middle level of a five-level scale for classifying whether a substance does or does not cause cancer in humans.

PFAS in Australia

The National Industrial Chemicals Notification and Assessment Scheme (NICNAS), which has monitored PFOS and PFOA use in Australia through four national surveys, shows that these chemicals are not manufactured in Australia.

PFOS and related compounds are however imported, mainly for use as mist suppressants in the metal plating industry, hydraulic fluid in the aviation industry and surfactants in the photography industry.

PFOA and related chemicals were previously imported into Australia and used in the local manufacture of non-stick cookware. These chemicals are not present in the finished cookware.

In Australia, the importation and use of PFOS and PFOA has declined significantly since 2000, and use of long chain compounds has been restricted in line with international practices.

PFOS and PFOA may be present in a range of imported consumer products, although many countries have phased out, or are progressively phasing out the use of PFOS and PFOA due to concerns about their persistence, bioaccumulation and environmental toxicity.

NICNAS has recommended since 2002 that Australian industries should actively seek alternatives to PFAS and PFAS-related substances. The alternative chemicals should be less toxic and not persist in the environment.[5]

PFOS and PFOA were used extensively in firefighting foams by both civilian and Defence Force firefighters around Australia. These chemicals subsequently leaked from the foams into soils, surface and ground waters.

From 2004, the Australian Department of Defence began phasing out its use of firefighting foams containing PFOS and PFOA as active ingredients. According to the Department website, the foam now used by Defence is a more environmentally safe product. Defence has also changed the method of use to ensure that the risk of environmental impact is minimised. The Department of Defence has commenced a national program to review its estate and investigate and implement a comprehensive approach to manage the impacts of PFAS on, and in the vicinity of, some of its bases around Australia. Six sites are currently under investigation, with a further 12 pending.[6]

Environmental contamination by perfluorinated chemicals has had a relatively low profile in Australia, however the issue has been publicised in recent years. In 2014 residents near the Oakey Army Aviation base in Queensland were notified of the presence of PFOS and PFOA in groundwater, and advised not to drink the water while further investigations were undertaken. In March 2015 the Victorian Country Fire Authority training facility at Fiskville was permanently closed following the discovery of extensive PFOS contamination at the site. Later in 2015, contamination from the Williamtown Royal Australian Air Force Base in New South Wales caused closure of commercial fisheries and warnings to residents in an area of over 60 square kilometres near the base. Householders were advised to avoid drinking or preparing food with bore water, and not to eat eggs from chickens, or drink milk from cows or goats kept in the area.

Implications for the water industry

In June 2016, the Commonwealth Department of Health commissioned Food Standards Australia New Zealand (FSANZ) to develop final health-based guidance values for perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonate (PFHxS).

On 3 April 2017 the Australian Government's Chief Medical Officer announced new tolerable daily intake levels (TDIs) of polyfluoroalkyl substances (PFAS) which are now in line with US standards. FSANZ's *Hazard Assessment Report—PFOS, PFOA and PFHxS*[7] gives recommendations for Australia's final health-based guidance values. These values will be used consistently in undertaking human health risk assessments across Australia.

FSANZ advises that the final health-based guidance values are protective of human health; are precautionary measures for use when conducting site investigations; and assist in providing advice to affected communities on how to minimise exposure to PFAS.

In its statement on 3rd April the Department of Health stated "it is important to note that these new TDIs are precautionary measures given that there is no consistent evidence that exposure to PFAS causes adverse human health effects."

The health-based guidance values are shown below:

Toxicity reference value	PFOS		PFOA	
	ng	ug	ng	ug
Tolerable Daily Intake (ng or µg / kg bw/d)	20	0.02	160	0.16
Drinking Water Quality Guideline (ng or µg /L)	70	0.07	560	0.56
Recreational Water Quality Guideline (ng or µg /L)	700	0.7	5,600	5.6

Note: bw = body weight, ng = nanograms, µg = micrograms

The recommended health-based guidance values have replaced the Environmental Health Standing Committee's (enHealth) interim human health reference values which had been in place since June 2016. At the time there was concern the levels had been set in line with European guidance values, rather than the lower US limits, which were put in place in May 2016.

The current Australian Drinking Water Guidelines do not include guideline values for either PFOS or PFOA, and there are no formally recognised Australian health or ecological screening levels for PFOA, PFOS or PFAS in soil, natural waters or other media.

Water Treatment options

Removal of PFAS by conventional water treatment processes is problematic. The properties that make these compounds useful means they are relatively hydrophilic, resistant to biotransformation and chemically inert, which significantly reduces effectiveness of some water treatment technologies.

We gratefully acknowledge the input and advice provided by a number of WaterRA Member researchers and experts in the compliation of this fact sheet. The intention of the fact sheet is to provide an overview of the issue with the best available information at this time.

Evaluation of water treatment methods has indicated that nanofiltration and reverse osmosis filtration appear to be most effective for removal of PFAS from drinking water supplies, although the performance of nanofiltration has been verified only in small scale applications. Granular activated carbon (GAC) and anion exchange techniques can remove long chain compounds but are less effective for shorter PFAS. The available evidence also suggests that GAC filters may require frequent regeneration or replacement to remain effective. Given the high cost of reverse osmosis treatment and the potential problems of dealing with contaminated RO reject water, many utilities may find blending of sources or switching to alternative supplies to be a more economic option to reduce PFAS levels.[8]

Sources:

A large part of this fact sheet has been summarised from the feature article [1] *"Perfluorinated Chemicals In Water"* published in Health Stream issue 82, July 2016. For more information on this topic refer to the original article.

Additional reference material from:

[2] *Organic Fluorocompounds in Human Plasma: Prevalence and Characterisation* ACS Symposium Series: Washington, DC, 1976

[3] "Probable link", the criterion by which the C8 Science Panel evaluates the evidence is defined in the Class-action Settlement Agreement to *"mean that based upon the weight of available scientific evidence, it is more likely than not that there is a link between exposure to C-8 and a particular human disease among Class members"*. This determination is made by the three expert scientists who make up C8 Science Panel and may not conform to the decision making processes of regulatory agencies. http://www.c8sciencepanel.org/index.html

[4] Toms, LM et al. (2014). *Decline in perfluorooctane sulfonate and perfluorooctanoate serum concentrations in an Australian population from 2002 to 2011*. Environment International 71: 74-80

[5] *Per- and poly-fluoroalkyl substances (PFAS) Fact Sheet,* Australian Health Protection Principal Committee (June 2016)

[6] *http://www.defence.gov.au/id/PFOSPFOA/*

[7] *Health Based Guidance Values for PFAS for use in site investigations in Australia Fact Sheet, http://www.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-hbgv.htm#FSANZ*

[8] *Background technical Information for Poly- and Perfluoroalkyl Substances (PFASs or PFCs)* Alice Fulmer, Water Research Foundation, May 2016