

In this Issue:

Perfluorinated Chemicals In Water	1
Update On Flint Water Crisis	2
News Items	7
From The Literature	8
Antibiotic Resistance	
Arsenic	
Disinfection Byproducts	
Environmental Impacts	
Gastric Cancer	
Household Water Treatment	
Lead	
Lithium	
Microbial Source Tracking	
Microbial Surrogates	
Perfluorinated Chemicals	
POU Treatment	
Sialolithiasis	
Uranium	
Water Intake	
Water Quality	
Water Supply	

Editor Martha Sinclair
Assistant Editor Pam Hayes

www.waterra.com.au

Perfluorinated Chemicals In Water

In May this year, the US Environmental Protection Agency (US EPA) released new Drinking Water Health Advisories for perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA) following an assessment of the latest peer-reviewed scientific evidence on the health risks of these chemicals (1). Both substances are members of a large group of man-made chemicals known as per- and poly-fluoroalkyl substances (PFASs) which were widely used in the manufacture of consumer and industrial products from the 1950s until the early 2000s when concerns over possible health and environmental effects resulted in progressive restrictions on use (2). The Health Advisory levels of 70 parts per trillion (0.070 µg/L) for both chemicals (alone or combined) are not enforceable regulatory limits, but are expected to guide public water suppliers and state agencies responsible for drinking water safety in their efforts to assess and manage potential health risks. These levels in drinking water are considered to provide a margin of protection against adverse health effects over a lifetime, assuming that drinking water constitutes 20% of total exposure. The new levels are 3- to 6-fold lower than the previous US EPA Health Advisories of 0.20 µg/L for PFOS and 0.40 µg/L for PFOA set in 2009, and are also considerably lower than most existing regulations or guidance values in other countries.

The basic structure of PFASs is that of organic hydrocarbon molecules where fluorine has been substituted in place of most or all of the hydrogen atoms normally found on the hydrocarbon backbone. In perfluorinated compounds, fluorine is substituted in all possible positions that could be occupied,

except on the essential functional group(s) present on the molecule. In polyfluorinated compounds, there are additional carbon atoms not fully substituted with fluorine. Although PFASs are classified as organic chemicals, the extremely strong carbon-fluorine covalent bonds confer properties that are distinct from other organic molecules, including high chemical and thermal stability as well as hydrophobic and lipophobic qualities. PFASs can be classified into polymeric and non-polymeric substances, and each of these categories can be further divided according to features of the chemical structure, including the length of the molecule, whether it is straight or branched, and the functional groups which are present. As a group, PFASs are resistant to degradation in the environment, however those with shorter carbon chain length and/or branched structures tend to have shorter persistence.

PFASs were developed in the 1940s by the 3M Company in the US, and their first commercial application was in the form of a stain repellent coating for fabrics introduced to the market in 1956. The useful properties of PFASs resulted in them being adopted for a wide range of applications in industry and consumer products over subsequent decades. The DuPont Company became the second major manufacturer of these compounds in the US, and other major production companies were established in France, Germany and Japan. Common uses for PFASs in consumer products included non-stick coatings on cookware, stain resistant treatments for furniture and carpets, water proofing on clothing and mattresses, additives in cleaning products and floor polish, and grease resistant packaging for some foodstuffs. PFASs were also 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. PFASs were also used as herbicides and insecticides, as active ingredients in firefighting foams designed for suppressing fuel fires, and in protective clothing for firefighters.

Historically, the two PFASs with the highest production volumes were perfluorooctane sulfonate (PFOS), and perfluorooctanoic acid (PFOA). Both of

these compounds are non-polymeric PFASs with a simple unbranched structure based on an 8-carbon backbone fully substituted with fluorine. The PFOS molecule contains a terminal sulphonic acid group, while the PFOA molecule has a terminal carboxylic acid group. PFOS was mainly used directly in consumer and industrial products, while PFOA (sometime referred to as C8) was used mainly in the production of fluoroelastomers and fluoropolymers. Both PFOS and PFOA can also be formed in the environment from some fluorochemical precursor molecules.

The widespread presence of PFASs in human populations was first suggested in a 1976 publication by researchers who had been studying the effects of water fluoridation on fluoride levels in the body. They 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 average levels of ionic fluoride correlated with the fluoride levels in the drinking water supplies of the donor populations, but levels of the organic form of fluorine did not. The researchers hypothesised that these organic compounds might originate from the perfluorinated chemicals used in consumer products, and were able to show that their characteristics under nuclear magnetic resonance spectroscopy analysis were consistent with this hypothesis. However, the analytical methods available at that time were not capable of unequivocally identify specific organic fluorocompounds. Several other studies in the US, China, Argentina and Japan during the 1970s and 1980s reported similar findings regarding detection of organic fluorine compounds in human blood, but also did not identify the specific chemicals detected.

A public release of internal documents from the 3M Company later showed that the company had begun to monitor levels of organic fluorine in the blood of some of their production workers soon after the 1976 publication. In 1979 more sophisticated analytical techniques were used to test for PFOS in samples from five workers, and the results confirmed that the majority of the organic fluorine detected in the blood samples was PFOS. In 1980, researchers from 3M published the first evidence of prolonged biological

persistence for these compounds, with half-life estimates of 365 to 530 days based on monitoring concentrations in the blood of retired production workers.

The company commenced a more extensive monitoring program in 1994, using high performance liquid chromatography-mass spectrophotometry to specifically detect PFOS, PFOA and other compounds in the blood of workers. The detection limit for this technique was about 100-fold lower than the previous testing method, and in 1997 the 3M scientists detected PFOS in samples from US blood donors which had been obtained for use as a negative controls when testing workers. This suggested that PFOS was commonly present in the blood of people in the general population, although at lower concentrations than occupationally exposed groups. Over the following months the 3M Company undertook testing of pooled blood bank samples from several different locations in the US, as well as samples collected in two remote rural provinces in China during 1984 and 1994, and samples that had been collected from US military recruits between 1948 and 1951. A range of PFASs were detected in all sample groups except those that had been collected from the military recruits prior to release of these chemicals onto the market. These results confirming the ubiquity of PFASs in blood samples of people in the general population appear to have prompted the company to approach the US EPA in late 1998 and provide some of its unpublished data on toxicology studies in animals and PFOS persistence in the environment.

Over the next year, the EPA assessed the available data on PFOS and engaged in discussions with the 3M Company over the potential hazards of continued use of the chemical. In addition, 3M carried out studies investigating PFASs in foodstuffs, rivers and lakes, sediment, fish, drinking water sources, tap water, influent and treated effluent from wastewater treatment plants, sludge, and municipal landfill leachate which confirmed the widespread environmental distribution of these synthetic chemicals. In May 2000 the 3M Company issued a press release stating that it had decided to phase out the use of *“perfluorooctanyl chemistry used to*

manufacture certain repellent and surfactant products” over the course of the next two years in anticipation of *“increasing attention on the appropriate use and management of persistent materials”*. Only two days later, the New York Times newspaper revealed that this decision was prompted by pressure from the US EPA, which was considering action to compel removal of PFOS from the market. A US EPA spokesman 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.

In subsequent years, evidence emerged of similar concerns about PFOA and other long chain PFASs (classified as perfluoroalkane sulfonates with six or more carbons, and perfluoroalkyl carboxylic acids with eight or more carbons). These compounds exhibit greater toxicity and bioaccumulative tendencies than smaller PFAS compounds. While 3M had ceased production of both PFOS and PFOA in 2002, other manufacturers continued to make PFOA. 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 PFASs, and to require industries to seek alternative, safer substitutes have been progressively implemented not only in the US, but also in many other countries. However, while production and use of PFASs in Japan, Western Europe and the US has fallen dramatically 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 PFASs 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 PFAS from existing treated consumer goods and products, contaminated sites and stored chemicals may still occur.

Unlike most other environmentally persistent organic chemicals, PFOS and PFOA bind poorly to soil and organic material, and therefore exist mainly in the dissolved phase in surface waters. At pH values above pH 4 they exist in dissociated anionic form and may bind electrostatically to positively charged particles. Research on mechanisms of environmental transport suggest that the presence of low levels of PFASs even in pristine wilderness areas can be attributed to long distance transport of these chemicals by rivers and ocean currents, as well as atmospheric dispersion of airborne emissions, and dispersion and transformation of precursor molecules. A number of studies have indicated that long chain PFASs exhibit bioaccumulation in both freshwater and marine ecosystems. The lack of controls on airborne emissions and solid or liquid waste disposal prior to the regulation of these chemicals 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 PFASs were frequently used.

In the years since regulatory action was initiated, a large international research effort has been undertaken to characterise human exposure sources and better understand the toxicology of perfluorinated chemicals, however scientific knowledge is still relatively limited. A significant contribution to epidemiological information has been made by the C8 Health Project which investigated the impacts of PFOA pollution of several public drinking water supplies in West Virginia and Ohio. Contamination from airborne releases, leaching from landfills and liquid waste discharges to surface water from a DuPont manufacturing plant on the Ohio River which forms the border between the two states began in the 1950s and continued until 2002. As was the case for the 3M Company and PFOS, it later emerged that DuPont had been conducting exposure monitoring and toxicological research on PFOA for decades before concerns about health effects became public. In addition, DuPont had detected PFOA in public tap water supplies of nearby communities as early as 1984, but did not inform health or environmental agencies, water suppliers or the public about the contamination.

A class-action lawsuit against the company resulted in a legal settlement in 2004 under which DuPont agreed to fund independent medical testing and epidemiological studies of the exposed residents, as well as paying for installation of carbon filtration plants to remove contaminants from the water supplies. Blood samples and questionnaire data were collected from over 69,000 people for a cross-sectional health assessment, and 40,000 people agreed to participate in a five year follow up cohort study. The diseases and conditions studied included cancer, heart disease, low birth weight and pregnancy loss, as well as thyroid, liver and immune dysfunction. The blood testing program undertaken in 2005/2006 showed the mean 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 3.49 µg/L at this time. In private drinking water supplies levels as high as 22.1 µg/L were detected.

The health data were analysed by a team of scientists 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 (including preeclampsia) and hypercholesterolemia. No probable links were found for over 40 other health outcomes. To date over 3,500 lawsuits against DuPont have been filed by individuals seeking compensation for a range of illnesses allegedly caused by PFOA exposure from the West Virginia manufacturing plant, but only a few have so far reached the courts.

Both PFOS and PFOA are readily absorbed from the gut after ingestion, but little is known about the contribution of inhalation or dermal contact to total exposure. These chemicals are not metabolised by humans or animals, and are excreted in unchanged form, mainly in the urine. They bind electrostatically to multiple sites on the albumin protein in the bloodstream, and may also bind to other proteins in the body. Although both compounds are filtered freely into urine in the glomeruli of the kidney, they are then efficiently 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 8.67 years in humans, 121 days in monkeys, 48 days in rats, and 37 days in mice) and PFOA (2.3 years in humans, 20.5 days in monkeys, 11.5 days in rats, and 15.6 days in mice). Within the body, the highest levels of both compounds are found in the liver, followed by the kidneys and lungs. Both PFOS and PFOA are transferred across the placenta to the developing foetus, and both are found in breast milk.

Animal toxicology studies have shown a range of adverse impacts including liver cancer, liver toxicity, developmental toxicity and impacts on immune function that are common to both compounds. Other effects are less well characterised and may differ between the two substances. For non-cancer effects, animal research indicates that foetal development is the most sensitive aspect for both PFOS and PFOA. Some human studies suggest an association between PFOS exposure and bladder, colon, and prostate cancer, but the results are not consistent and other risk factors such as smoking were sometimes not assessed. For PFOA, associations with testicular and kidney cancer have been suggested by human studies. Evaluation of the available evidence under the US EPA's *Guidelines for Carcinogen Risk Assessment* (2005), resulted in classification of both PFOS and PFAS as having "suggestive evidence of carcinogenic potential". For PFOA, the data were sufficient to permit a quantitative estimate of cancer risk in humans, but for PFOS the study limitations and inconsistencies in dose-response observations precluded such an estimate at present.

Currently, the mode(s) of action by which PFOS or PFOA may cause adverse biological effects have 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 the postulated indirect mechanisms of action could lead to changes in DNA replication or cell division and thus increase cancer risk. Such processes may also play a role in non-cancer adverse effects. Suggested mechanisms include: electrostatic binding to

biopolymers (especially proteins) with resultant alterations in conformation and activity, changes in metabolism due to displacement of substances normally bound to serum albumin or other proteins, binding to and activation of receptors which cause activation or suppression of gene transcription, or interference with intercellular communication.

The US EPA data evaluation showed that foetal development was particularly sensitive to the adverse effects of both PFOS and PFOA, therefore information from animal toxicology studies on these aspects was used to derive the Health Advisory levels for drinking water. For both PFOS and PFOA the HA level is 70 parts per trillion (0.070 µg/L), with an assumption that water accounts for 20% of total exposure. Given that the two contaminants may occur together, and their effects are similar, it is recommended that the combined concentration in drinking water should not exceed 0.070 µg/L. These lifetime HA levels are considered protective for other health effects and other exposed population groups. Given that adverse developmental effects may arise from exposures during critical windows in the development process, these levels are also regarded as applicable to short term exposures during pregnancy and lactation.

Both PFOS and PFOA were added to the US EPA Candidate Contaminant List 3 in 2009, and information on concentrations of PFOS, PFOA and four other perfluorinated chemicals was collected under the Third Unregulated Contaminant Monitoring Rule. This testing program covered all US public water systems supplying more than 10,000 people, as well as 800 smaller public water systems. The program was completed in December 2015, and not all test results have yet been reported and collated. As of April 2016, data from 4864 water systems showed that 46 (0.9%) exceeded the new HA level for PFOS and 13 (0.3%) exceeded the HA for PFOA. As many water supply systems draw water from more than one source, the percentage of individual water sources that exceed the HA level is likely to be considerably lower. The results have not yet been assessed to determine how many systems exceed the new HA level if concentrations of both chemicals are summed.

Evaluation of evidence on water treatment methods has indicated that nanofiltration and reverse osmosis filtration appear to be the most effective technologies for removal of both long and short chain PFASs from drinking water supplies, although the performance of nanofiltration has been verified only in small scale applications (4). Granular activated carbon (GAC) and anion exchange techniques are capable of removing long chain compounds but less effective for shorter PFASs. 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 PFASs levels.

The actions taken in the US to reduce the production and use of long chain PFASs appear to have been effective in reducing human exposure. Tests performed as part of periodic National Health and Nutrition Examination Surveys have shown that levels of PFOS and PFOA in the US population have declined since these measures were implemented. The geometric mean concentration of PFOS in human serum decreased from 30.4 µg/L to 6.31 µg/L and the 95th percentile concentration decreased from 75.7 µg/L to 21.7 µg/L between 1999 and 2010. For PFOA, the geometric mean concentration decreased from 5.2 to 2.1 µg/L, and the 95th percentile concentration decreased from 11.9 to 5.7 µg/L.

In Australia, the importation and use of PFOS and PFOA have declined markedly since 2000, and use of long chain compounds has been restricted in line with international practices. Tests of pooled sera from Australian blood donors show 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. Environmental contamination by perfluorinated chemicals has had a relatively low profile in Australia, however the issue has risen to public prominence in recent years following revelations of water pollution in several states. 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, Victoria was permanently closed following the discovery of extensive PFOS contamination at the site. Later in 2015, contamination from the Williamstown 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 not only to avoid drinking or preparing food with bore water, but also not to eat eggs from chickens, or drink milk from cows or goats kept in the area.

These instances of contamination from past use of firefighting foams using PFASs resulted in an Australian Senate Inquiry into contamination of Australia's Defence force facilities and other Commonwealth, state and territory sites with firefighting foam. Historical documents presented at the inquiry revealed that in 2003 an internal Defence report warned that inadequate management practices for firefighting foams containing PFOS and PFOA were likely to result in environmental contamination. The risk of contaminants spreading from Defence land to neighbouring properties and water bodies was also noted. The Senate Inquiry delivered two reports that made a number of recommendations including that the Commonwealth government should voluntarily acquire properties at two sites that have already been demonstrated to be affected by PFOS/PFOA contamination, and compensate commercial fishermen affected by closure of fisheries. These recommendations have not been accepted, although the Commonwealth government has agreed to recommendations on provision of water services to affected properties, increased support for mental health and counselling services, and establishment of a joint task force with the NSW government to coordinate responses to the Williamstown contamination. The Commonwealth response to second Senate report (which dealt with the contamination Oakey) has not yet been announced. The Australian Department of Defence is currently conducting detailed environmental investigations of PFOS/PFOA contamination at five sites in four states, and preliminary sampling programs are being carried out at 13 other sites.

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. To address the need for nationally consistent guidance, a workshop was convened in April 2016 under the auspices of the Environmental Health Standing Committee of the Australian Health Protection Principal Committee to review international approaches to deriving guidance and regulatory limits for these compounds. Information from seven countries was assessed, including draft versions of the new US EPA Health Advisories. The conference participants concluded that the 2008 European Food Safety Authority's (EFSA) derivation of Tolerable Daily Intake (TDI) values for PFOS and PFOA was considered to be an appropriate interim national guidance for use in site investigations in Australia (5). The resultant interim health reference values are given in the table below:

Toxicity reference value	PFOS	PFOA
Tolerable Daily Intake ($\mu\text{g}/\text{kg}/\text{d}$)	0.15	1.5
Drinking Water Quality Guideline ($\mu\text{g}/\text{L}$)	0.5	5
Recreational Water Quality Guideline ($\mu\text{g}/\text{L}$)	5	50

The values for PFOS are also applicable to perfluorohexane sulfonate, another chemical commonly used with PFOS in firefighting foams. When both chemicals are present their concentrations should be summed. The enHealth Council also recommended that Food Standards Australia New Zealand (FSANZ) undertake an assessment of the available toxicity data on PFOS, PFOA and PFHxS and publish relevant reference values in the Australia New Zealand Food Standards Code. FSANZ values will immediately replace interim toxicity reference values recommended above by enHealth.

(1) <https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos>

(2) These substances have previously been referred to as PFCs (per- and polyfluorinated chemicals), but this nomenclature is now being phased out as it may cause confusion with another group of chemicals, namely the perfluorocarbons (commonly recognised as greenhouse gases), which are a separate group with different chemical properties.

(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 the 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) Treatment Mitigation Strategies for Poly- and Perfluorinated Chemicals - Report 4322. Water Research Foundation (2016). <http://www.waterrf.org>

(5) enHealth Statement: Interim national guidance on human health reference values for per- and poly-fluoroalkyl substances for use in site investigations in Australia. June 2016.

<http://www.health.nsw.gov.au/environment/factsheets/Documents/pfas-interim-health-values-ahppc.pdf>

Update On Flint Water Crisis

Criminal charges have been laid against three people and a civil lawsuit have been brought against two engineering companies as a result of the Flint water crisis. The charges follow an investigation by the Michigan Attorney General into the events which resulted in exposure of residents of the town of Flint to high levels of lead in their drinking water over a period of 17 months (1). The elevated lead levels were caused by failure to implement control measures to prevent corrosion of lead service pipes when the water source was changed in early 2014.

Two supervisors from the Michigan Department of Environmental Quality were charged on 20 April over their role in the decision not to implement corrosion control, and in relation to purposefully misleading the US Environmental Protection Agency into believing that a corrosion control system was being used for the Flint water supply, when in fact no such control existed. One supervisor was also charged over improperly manipulating the collection of water samples and removing test results from samples to be included in federal reports. An administrator at the Flint water treatment plant was charged with tampering with evidence by falsifying reports to state environmental officials, and wilful neglect of duty. The various charges carry maximum jail sentences ranging from 5 to 20 years imprisonment, and up to \$45,000 in fines. It has been reported that the Flint Water administrator