NATIONAL TOXICS NETWORK PRELIMINARY SUBMISSION; 15 September 2015

Summary

“Given the inherent properties of PFOS, together with demonstrated or potential environmental concentrations that may exceed the effect levels for certain higher trophic level biota such as piscivorous birds and mammals; and given the widespread occurrence of PFOS in biota, including in remote areas; and given that PFOS precursors may contribute to the overall presence of PFOS in the environment, it is concluded that PFOS is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted.”

PERFLUOROOCTANE SULFONATE RISK PROFILE
Adopted by the Persistent Organic Pollutants Review Committee at its second meeting November 2006

There are large groups of manufactured fluorinated chemicals that are widely used in a variety of consumer goods from non-stick kitchenware to waterproof clothing, as well as many industrial applications. Produced commercially since the 1950s, two groups of perfluorinated compounds (PFCs), the perfluoroalkyl sulfonates (PFSAs) and the perfluorocarboxylic acids (PFCAs) have raised alarm bells. In particular, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been shown to be toxic and very persistent, posing a global contamination problem.

The most well known PFOA is the Teflon chemical used in non-stick coatings. It is a very toxic chemical, which has been nominated for listing on the United Nation’s Stockholm Convention on Persistent Organic Pollutants, a convention that seeks to eliminate some of the world’s most dangerous chemicals. Its sister chemical, PFOS, was also well known in 3M’s Scotchguard products. It’s an extremely persistent
industrial chemical that does not break down. PFOS is already listed on the Stockholm Convention as a persistent organic pollutant or POP. PFOS is toxic and travels the world in water and air currents, contaminating ecosystems and their inhabitants.

Australian citizens have both PFOS and PFOA in their blood, urine and breast milk. These chemicals are not manufactured in Australia but are found in many imported products and in current stockpiles of old, but still used, fire-fighting foams. The use of these fire-fighting foams has led to extensive contamination of groundwater and soil with PFOS and PFOA affecting rural and regional communities across Australia.

Currently there are investigations into environmental contamination with PFOS and PFOA in Victoria at the Fiskville Country Fire Authority’s (CFA) training college in Victoria, at the Williamstown Air Base, NSW and the Army Aviation Centre near the rural town of Oakey, in Queensland.¹

**How toxic are perfluorinated compounds?**

Everyone is exposed to mixtures of perfluorinated chemicals through exposure to dust, indoor and outdoor air, food, water and PFC products. PFCs including PFOS and PFOA are found in human blood, urine, breast-milk and babies umbilical cord blood. Due to their long half-life in human beings (PFOS 5.4 years and PFOA 3.8 years approx), there is an increased risk that the exposure will cause adverse effects.

Mixtures of PFCs have been shown to interfere with the functioning of hormones. Research has demonstrated that at least five PFCs are endocrine disrupting compounds (EDC) and can affect sex hormones like the estrogen and androgen receptor. In some cases, the mixture effect of exposure to multiple PFCs is more than just additive and researchers emphasised the importance of considering the combined action of PFCs when assessing health risks.² Unfortunately, other than


PFOA and PFOS, there is little information on the toxicology and health impacts of the suite of fluorochemicals people are exposed to.\(^3\)

Based on the data of 3,974 adults sampled in the US National Health and Nutrition Examination Survey (NHANES), researchers concluded that higher concentrations of serum PFOA and PFOS are associated with current thyroid disease in the general adult population.\(^4\)

In laboratory animals, PFOS has caused testicular and pancreatic tumours, reproductive and developmental impacts, neurotoxicity and immunotoxicity,\(^5\) as well as affecting the liver.\(^6\) PFOA is a reproductive toxin causing increased mortality in rat pups. It is also a developmental toxicant with prenatal exposure to PFOA causing significant delays in mammary developmental in the female offspring.\(^7\) The US EPA review concluded that PFOA poses a risk for childbearing women; the estimated exposure range for humans, based on rat studies, having already overlapped with what the US EPA deem as unacceptable for toxic substances.\(^8\) In Europe, PFOA is classified as reproductive toxin and is required to be labelled, "May damage the unborn child".

Both PFOA and PFOS suppress immune responses in adult mice\(^9\) and exposed humans. Elevated levels of PFOA and PFOS have also been associated with significant changes in clinical markers of immune and inflammatory responses.\(^10\)

There is mounting evidence to suggest that immune suppression occurs at serum


\(^4\) Proposal to list pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-related compounds in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants


\(^6\) Preliminary Risk Assessment of the developmental toxicity associated with exposure to Perfluorooctanoic acid and its salts. PERFLUOROOCTANOIC ACID AND ITS SALTS, U.S. Environmental Protection Agency Office of Pollution Prevention and Toxics Risk Assessment Division, April 10, 2003


\(^8\) Preliminary Risk Assessment of the developmental toxicity associated with exposure to Perfluorooctanoic acid and its salts. U.S. Environmental Protection Agency Office of Pollution Prevention and Toxics Risk Assessment Division, April 10, 2003


\(^10\) Ibid
concentrations below, within, or just above the reported range for highly exposed humans and wildlife. For PFOS, some human and wildlife species have serum concentrations that exceed the threshold for PFOS-induced immune effects, suggesting a potential risk for altered disease resistance. Thus, the risk of immune effects for humans and wildlife exposed to PFCs cannot be discounted, especially when bioaccumulation and exposure to multiple PFCs are considered. 11

PFOA has been shown to affect the expression12 of genes13, while other researchers have demonstrated that PFOA has ‘genotoxic’ effects14 on human liver cells.15 Genotoxic chemicals damage the genetic information within a cell, which can cause mutations and lead to cancer. These chemicals may have no safe level of exposure. The US EPA’s expert committee recommended that PFOA be considered ‘likely to be carcinogenic to humans.’ 16

Following the class action between DuPont (a manufacturer of Teflon which contains PFOA) and US residents in the vicinity of a major contamination incident, the jointly established C8 Science Panel concluded that PFOA can cause kidney cancer, testicular cancer, ulcerative colitis, thyroid disease, pregnancy induced hypertension and medically diagnosed high cholesterol in humans.17

To assess health risks from environmental contamination with PFCs, all PFCs should be included in monitoring and their human exposure assessed. More research studies on toxicity, bioaccumulation, carry-over rates and exposure pathways for the other approximately 1000 PFAS are needed in addition to the gaps of PFOS exposure pathways. 18

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11 Ibid
12 Gene expression is the process by which inheritable information from a gene is translated and made into a functional gene product in the cell
14 Genotoxicity describes the property of chemical agents that damages the genetic information within a cell causing mutations, which may lead to cancer. While genotoxicity is often confused with mutagenicity, all mutagens are genotoxic, however, not all genotoxic substances are mutagenic.
Perfluorinated compounds in the Australian population

People and animals are exposed to PFCs via food, drinking water, direct contact with products and exposure from indoor and ambient air. PFCs remain in the human body for many years, accumulating primarily in the blood, kidneys and liver. Most Australians have concentration of perfluorochemicals (eg PFOS and PFOA) in their bodies.

The UN PFOS risk profile reports, “Pooled serum samples from 3802 Australian residents, collected 2002-2003 and divided in relation to age, gender and region, were analysed for perfluoroalkylsulfonates, perfluoroalkylcarboxylates and PFOSA. PFOS and PFOSA were quantified in all pooled serum samples with a total range of 12.7-29.5 ng/ml (mean 17.2 ng/ml) and 0.36-2.4 ng/ml (mean 0.81 ng/ml), respectively.”

Concentrations of both PFOS and PFOA have been decreasing in Australian adults\textsuperscript{19}, most likely due to the decline in global use since 2002. PFOS in 2008/09 ranged from 5.3–19.2 ng/ml to 4.4–17.4 ng/ml in 2010/11. PFOA was the next highest concentration at 2.8–7.3 ng/ml (2008/09) and 3.1–6.5 ng/ml (2010/11). All other measured PFCs were detected at concentrations <1 ng/ml with the exception of perfluorohexane sulfonate, which in 2010-11 was detected at 1.4–5.4 ng/ml.\textsuperscript{20}

When compared to monitoring results from elsewhere, concentrations of PFOS and PFOA in the Australian population in 2010-2011 are similar or higher than our overseas counterparts. Concentrations in Australian women of child-bearing age are almost twice that found in pregnant women from Germany and PFOS and PFOA concentrations are 1.5 and twice those found in adults from the USA.\textsuperscript{21}


\textsuperscript{20} Toms et al. 2014.

\textsuperscript{21} Ibid.
Perfluorinated compounds in Australian fire fighters

A 2014 study found that 149 Queensland fire fighters had multiple PFCs detected in their serum. The three most prevalent and detected in all samples were PFOS, perfluorohexanesulfonic acid (PFHxS) and PFOA. Their serum levels of PFOS were approximately six to ten times higher than those found in the general population in Australia. The median/mean level in fire fighters was 66/74 ng/mL compared to 12 ng/mL (mean) and 6.8 (median) ng/mL in the general population in Australia. The serum levels of other PFCs like PFHxS in fire fighters were approximately 10 to 15 times higher compared to the general population levels in Australia. Even ten years after the phase out of 3M AFFF Industrial Fire Fighting Foam, PFOS serum levels remained above 100 ng/mL and 200 ng/mL in 27% and 3% of the participating fire fighters, respectively. 22

Is there a ‘safe’ level for perfluorinated compounds?

In 2006, the Biomonitoring Commission of the German Federal Environmental Agency established preliminary reference values for PFOA and PFOS in plasma of children and adults. They recommended a maximum permissible serum level for PFOA of 10 μg/l for all groups. For PFOS, it recommended 10 μg/l for children at school beginner age, 15 μg/l for adult females and 25 μg/l for adult males.23 24

Recent research suggests that PFOS concentrations at current population levels may already be causing adverse health impacts,25 26 which indicates that even these values may be too high. A recent study27 argues that the mean serum levels of PFOS of 14.1 ng/ml are associated with impacts on DNA methylation, suggesting

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27 Ibid.
that PFOS may be epigenetically active.\textsuperscript{28} Methylation modifies the function of the DNA, typically acting to suppress gene transcription, which in turn may be associated with the development of cancer.\textsuperscript{29}

In 2014, the US EPA released a draft \textsuperscript{30} of its proposed new reference dose for PFOS of 0.00003 milligrams/kilogram/per day based on developmental toxicity and adverse liver effects. This would be an estimate of how much a person can safely consume daily over a lifetime.

The proposed reference dose for PFOA is 0.00002 mg/kg/day due to adverse changes in the liver linked to developmental effects and adverse changes in the kidney. That proposed reference dose would translate to a legal limit for PFOA of 0.1 ppb in drinking water. While a significant reduction on current advisory level of 0.4ppb, it is dismissed by some researchers as not protective enough of human health, based on new research. These proposed changes to the reference dose have been criticised by state regulators for EPA’s failure to consider infant and neonatal exposure levels to two perfluorochemicals (PFCs).\textsuperscript{31}

The US state of New Jersey has set their own advisory level for PFOA in drinking water of 0.04 ppb – ten times more protective than EPA’s advisory level but still well above Grandjean and Clapp 2015 recommended 0.001 ppb (based on a serum concentration of 0.1 ng/mL).\textsuperscript{32}

As PFOS and PFOA have no means of break down, being passed from one generation to the next via breast milk and \textit{in utero}, and have in some cases demonstrated changes in gene expression at very low levels, it is possible that like lead and mercury, there may be no safe level of exposure to PFOS and /or PFOA.

\textsuperscript{28} Epigenetics refers to heritable changes in gene expression (active versus inactive genes) that does not involve changes to the underlying DNA sequence (source: http://www.whatisepigenetics.com/fundamentals/)
\textsuperscript{30} http://drinkingwateradvisor.com/2014/03/12/reference-dose-rfd-proposed-for-pfoa-pfos/
Perfluorinated compounds in the environment

PFCs are released into the air and water from waste sites, manufacturing facilities, sewerage treatment works and fire-fighting operations. They migrate out of consumer products like all weather clothing, carpets and camping gear into the air, household dust, food, soil, as well as ground and surface water.

PFCs are extremely persistent in the environment and travel the globe via air and water currents. In the air, volatile PFCs (eg polyfluorinated fluorotelomer alcohol (FTOH) and sulfonates) are transported thousands of kilometres and others are carried by suspended particulate matter, which is eventually washed out and deposited in rain and snow. PFCs are also found in water, soil and wildlife and now contaminate every ecosystem in the world from the remote Arctic to the tropics. In recent sampling of snow in remote locations and water from mountain lakes, PFCs were present in nearly all the samples. Including short chain PFCs, which industry is increasingly using, arguing that they are less harmful than long chain PFCs like PFOS. Unfortunately, like many of the PFCs, there is a dearth of information on toxic effects of short chain PFCs, however, their detection in remote places is of concern.

PFOS has shown no evidence of degradation in the environment and the results of various degradation tests and field monitoring data support the conclusion that no biodegradation of PFOA occurs either. Additionally PFOA-related substances can degrade to PFOA under environmentally relevant conditions. PFOS and PFOA bioaccumulate in fish, birds and mammals with concentrations increasing further up the food chain.

The use of PFCs, particularly in fire-fighting foams has been linked to environmental contamination of groundwater in Germany, Sweden and the US. In 2006 in

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34 Ibid.
36 Proposal to list pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-related compounds in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants
Sauerland, Germany PFOS contamination of water, pasture, forage and animal products occurred from industrially contaminated biosolids applied to land, while in 2007 there was broad scale contamination of groundwater with PFOS from fire fighting foams in Düsseldorf, Germany. In 2013, surface, ground and tap water was found to be contaminated with PFOS in Italy, downstream from a PFAS production plant. In November 2015, US company, Dupont will face the first trial in litigation from 3,500 residents near one of its plants in West Virginia who have accused the company of contaminating their drinking water with PFOA, resulting in sickness including cancer.

Since biodegradation and adsorption is not known to occur in the aquifers and soils, PFOS and PFOA are transported at nearly the same rate as groundwater, with the concentrations decreasing only with distance from the source due to diffusion and dispersion.

The 2015 Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs) signed by scientists and environmental health specialists from across the globe called for urgent action noting: “PFASs are highly persistent, as they contain perfluorinated chains that only degrade very slowly, if at all, under environmental conditions.”

**International regulatory responses**

In 2000, the Organisation for Economic Cooperation and Development (OECD) undertook a hazard assessment on PFOS and its salts, concluding that the persistence of PFOS in the environment, its toxicity and bioaccumulation potential indicated cause for concern for the environment and human health.

In 2002, under pressure from the United States Environmental Protection Agency (US EPA), the major manufacturer of PFOS and its precursors, 3M, ceased

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production. Canada prohibited the manufacture, use, sale, offer for sale and import of PFOS and related substances and in 2006, the European Union (EU) adopted a resolution restricting the marketing and use of PFOS and related substances. The US EPA severely restricted the use of PFOS and other perfluoroalkyl substances (PFASs) to uses where no safer alternative is available.

In 2010, PFOS was formally listed on the Stockholm Convention on Persistent Organic Pollutants, a convention for some of the world’s most dangerous chemicals. Listing on Annex B permitted some limited ongoing uses. Work by the conventions scientific and technical committee continues to phase out the remaining uses and in May 2015, the Stockholm Convention’s conference of parties removed six of those permitted uses. Australia has not ratified the listing of PFOS.

In October 2015, PFOA was nominated for listing on the United Nation’s Stockholm Convention on Persistent Organic Pollutants. DuPont had agreed to phase out production of PFOA by 2015.

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41 The resolution set the maximum concentrations of 0.1% by mass for PFOS-containing semifinished products or articles, 0.005% by mass for PFOS preparations, and 1 μg/m² PFOS for textiles or other coated materials. http://www.nicnas.gov.au/communications/publications/information-sheets/existing-chemical-info-sheets/pfc-derivatives-and-chemicals-on-which-they-are-based-alert-factsheet