

AUSTRALIA'S APPROACH TO MANAGING PERFLUORINATED CHEMICALS

Satya S*; Healy M, Syed S

National Industrial Chemicals Notification and Assessment Scheme, Department of Health and Ageing, GPO Box 58, Sydney NSW 2001

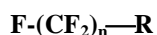
Background

Perfluorinated chemicals (PFCs) or their precursors are present in a variety of industrial, commercial and consumer products in Australia. PFC Precursors are complex chemicals and polymers containing perfluorinated sections that can break down into PFCs of concern. Some of the potential precursors include chemicals known commercially as fluorotelomer alcohols - where a perfluorinated chain is terminated with $-\text{CH}_2-\text{CH}_2-\text{OH}$. The widespread occurrence of certain PFCs in the environment, in certain animal species and in humans, has attracted regulatory concern and/or action globally. Some PFCs are bioaccumulative, in particular those with long perfluorinated carbon chains, and some have been reported to cause toxic effects in laboratory animals. In PFCs of concern all the carbon atoms are fluorinated with the terminal carbon containing a charged carboxylate, sulfonate or phosphonate functional group. Two specific PFCs, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been the subject of significant assessment activities overseas.

By virtue of the strong C-F bonds, PFCs are very stable compounds. They are persistent in the environment, bio-concentrate in wildlife, and are persistent in humans, with most taking years to be cleared from the body. Many chemicals in this group, including PFOS and PFOA, have caused concern because they do not break down in the environment, and build up in wildlife. Indeed PFOA, PFOS and many other PFCs have been found in the blood of many species of birds and animals around the world, including fish, bald eagles and mink. Further investigations of their contamination lead to the conclusion that many of these chemicals arose from the breakdown of larger precursors.

Categories of perfluorinated chemicals

A perfluorinated carbon chain refers to the structure of:



in a chemical substance. The perfluorinated carbon chain could be a portion of the chemical or polymer, which can act as a precursor to a perfluorinated chemical in one of the categories described below.

Perfluoroalkyl sulfonate (PFAS) is a generic term used to describe perfluorinated sulfonate compounds eg. perfluorohexane sulfonic acid (PFHxS). PFOS is a subcategory of PFAS compounds that include compounds of perfluorinated carbon chain length equal to eight eg. perfluorooctane sulfonic acid. PFOS-related substances may be salts of PFOS, e.g. potassium, lithium, ammonium or diethanolamine, or polymers that contain the PFOS as a portion of the entire structure. Perfluorobutane sulfonate (PFBS) is another subcategory of PFAS compounds that include compounds of perfluorinated carbon chain length equal to four e.g. perfluorobutane sulfonic acid.

Perfluorocarboxylic acid (PFCA) is a generic term used to describe any fully fluorinated carbon chain length carboxylic acid eg. PFOA, perfluorohexanoic acid (PFHxA) and potassium perfluorooctanoate. PFOA is a fully fluorinated eight-carbon carboxylic acid, with seven perfluorinated carbon atoms. PFOA-related substances may be salts of PFOA or substances that can degrade to PFOA. PFOA salts, such as ammonium perfluorooctanoate, are used as processing aids in the production of fluoropolymers and fluoroelastomers and in other surfactant uses.

Fluorotelomer is a fluorocarbon based oligomer eg perfluorotelomer iodides, perfluorotelomer alcohols and their derivatives.

Human Health Concerns

PFCs are used in the engineering and chemical, electronics and medical industries because of their surfactant properties (Egeghy and Lorber, 2010). Potential sources of exposure to PFOA and PFOS include direct industrial

releases into air and water, unintentional releases of fire-fighting foam and release from consumer products such as non-stick cookware, water-proof textiles, electronics and oil and stain protective coatings for carpets, apparel and food containers and degradation of telomer based polymers (Giesy et al, 2006). Potential exposure to PFOS and PFOA could occur through air, dust, water and food.

Long-chain PFCs are a concern for children's health. Studies in laboratory animals have demonstrated developmental toxicity, including neonatal mortality (Lau et al, 2007). Children's exposures are greater than adults due to increased intakes of food, water, and air per unit body weight, as well as child-specific exposure pathways such as breast milk consumption, mouthing and ingestion of non-food items, and increased contact with the floor. Biomonitoring studies have found PFCs in cord blood and breast milk (Apelberg et al, 2007).

Developmental and reproductive effects, including reduced birth weight, decreased gestational length, structural defects, delays in postnatal growth and development, increased neonatal mortality, and pregnancy loss in rodents have all been associated with prenatal exposure to PFOS and PFOA. A growing number of human health studies have found associations between prenatal exposure to PFOS or PFOA and a range of adverse birth outcomes, such as low birth weight, decreased head circumference, reduced birth length, and smaller abdominal circumference (Apelberg et al, 2007).

Regulatory Activities in Australia

Australia has taken a range of actions to help minimise the potential impact of PFCs on human health and the environment since 2002. These include monitoring the manufacture, import and use of PFCs in Australia, raising awareness of the chemical industry and the general public through the publication of alerts.

Monitoring and Outreach

NICNAS published 6 alerts (NICNAS, 2002, 2003, 2004, 2007, 2008) that provided regulatory information on PFCA and PFAS (including PFOA and PFOS) and has reviewed the trends in the import quantities and the extent of use of these chemicals since 2002. The most recent survey was conducted in 2008 on PFOS and PFAS. The objective of this survey was to collect import and use data on PFOS and PFAS and related substances for the years 2006 and 2007. This included quantities imported or manufactured in Australia and uses of these products/mixtures. Data were also collected on essential uses of these substances and efforts towards finding safer alternatives. A comparison of the current findings with the results of the previous surveys to observe patterns of change in import and use of PFCs in Australia was also conducted.

Data obtained through this survey (NICNAS, 2009) indicated an overall increase in PFAS and PFOS imports in Australia compared to previous years although there were substantial changes in the type of imports and the use patterns. The use of PFOS in Australia was mainly limited to the aviation, metal plating and photolithography industries where no suitable alternatives are available, and most PFOS stocks were held for emergency use only.

The survey also indicated a move towards telomers and shorter chain length fluorinated sulphonates (mainly C₄ and C₆ chain lengths) or perfluorobutane sulphonates (PFBS) for fire fighting foams. Import of PFOS for applications such as aviation and metal plating and to a small extent for photography and photolithography are likely to continue as there are no viable replacements yet.

PFC Assessments

Existing Chemicals

A number of PFCs are listed on Australia's national inventory and can be used industrially. However, limited toxicological data are available apart from that for the C₈ chemicals (PFOS, PFOA). Data are however being generated for the shorter chain perfluorinated chemicals with the use of these chemicals increasing. NICNAS has assessed data for two short chain perfluorinated chemicals, PFBS and PFHxA currently used in Australia. A comparison of the data with that for PFOA shows that there is a quantitative difference in the hazard potential between the longer and shorter chain chemicals. A hazard assessment of the potassium salt of PBFS conducted (NICNAS, 2005) indicated that in Australia, the major use of PFBS-based chemicals is in the high performance industrial chemical category. Based on the current use pattern, potential public exposure to PFBS is expected to be

through the degradation of certain fluoropolymers to PFBS in the environment. The assessment found that PFBS is not bioaccumulative or toxic to aquatic organisms and has low health hazards. However, being a persistent chemical, its levels may build up and be distributed widely in the environment over time.

NICNAS is in the process of conducting an assessment of health and environmental studies of perfluorohexanoic acid (PFHxA). The outcome of the assessment will assist in refining the default assumptions in the NICNAS position paper described below.

New Chemicals

NICNAS has developed specific data requirements for assessing the risks of PFCs that are not listed on the national inventory ('new chemicals') (NICNAS, 2006). If these data are not available, NICNAS has identified the default position that will be used. If these data are not available, then NICNAS's assessment of a new PFAS chemical will utilise the OECD hazard assessment of PFOS (OECD, 2002), and the hazard assessment of a new PFCA based chemical will utilise the US EPA hazard assessment of PFOA (USEPA, 2005).

NICNAS has also identified the additional data requirements in those cases where an introducer believes that the default position should not apply for a specific chemical and sets out the mechanism for changing these default assumptions, which requires the submission of toxicological data on the relevant degradation product, followed by assessment by NICNAS.

International Activities

The concerns with PFCs have been recognised internationally with a number of regulatory and non-regulatory activities underway. A key activity is the listing of PFOS in the Stockholm Convention (POPs, 2009). The Stockholm Convention on Persistent Organic Pollutants (POPs) is a global treaty that aims to protect human health and the environment from the effects of persistent organic pollutants (POPs). The Convention found that PFOS met the screening criteria for POPs and in 2009 PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOSF) were listed in the Convention subjecting it to restrictions on production and use. The Australian Government is undertaking a treaty making process, informed by stakeholder consultation, prior to making a decision on whether to ratify the listing of PFOS in the Convention. The treaty making process will assess the impact of any regulatory action on PFOS and its salts.

The OECD has been monitoring the manufacture, use and in some cases the emission arising from PFCs since 2004. The goal of the surveys was to gather information that would assist OECD and member and non-member countries in assessing potential contributions of PFOS, PFAS, PFOA and longer chain length PFCAs to environmental loadings. The surveys in 2004 and 2006 monitored the use and manufacture of PFOS and PFCA compounds. The 2006 survey indicated a decrease in the quantities of PFOS and PFOA-related substances manufactured and used globally. The survey indicated that PFBS-based substances (C4) were the main PFAS compounds used and that these are replacing PFOS/PFOA related substances. The production volume of PFBS based compounds was increased markedly since the 2004 survey (OECD, 2005, 2006).

A revised approach was adopted for the third survey (OECD, 2011) to ensure achievement of the underlying goal. The survey monitored the production and use of PFCs and their release to the environment (air, water and land) during the manufacturing process and during formulation of products. The survey showed that the number of PFCA and PFOA related chemicals, manufactured and/or present in products was larger than the PFAS and PFOS groups of chemicals, and very small quantities of PFC were released to air or water systems compared to landfill.

Australia by alerting industry of the health and environmental hazards of PFCs, since 2002, and recommending that industry move away from the use of PFOS and PFOA has been able to reduce the imports into Australia of PFOS and PFOA. Where imports have occurred these are for use in applications where no safer alternatives are available. Early assessment of the short chain PFBS clearly provided advice that PFBS has limited health and environment toxicity and is a safe substitute for PFOS. A number of countries such as the European Union, United States, Japan and Canada have also implemented activities to minimise risks from PFCs.

References

- Andersen, M.E., Butenhoff, J.L., Chang, S.C., Farrar, D.G., Kennedy, G.L., Lau, C., Olsen, G.W., Seed, J., Wallace, K.B., 2008. Perfluoroalkyl acids and related chemistries – toxicokinetics and modes of action. *Toxicol. Sci.* 102, 3–14.
- Apelberg BJ, Witter FR, Herbstman JB, Calafat AM, Halden RU, Needham LL, Goldman LR. (2007). Cord serum concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in relation to weight and size at birth. *Environ Health Perspect*, 115: 1670-1676.
- Egghy, P. and Lorber, M (2011) An assessment of the exposure of Americans to perfluorooctane sulfonate: A comparison of estimated intake with values inferred from NHANES data. *Journal of Exposure Science and Environmental Epidemiology* (2011) 21, 150–168.
- Giesy, J.P., Mabury, S.A., Martin, J.W., Kannan, K., Jones, P.D., Newsted, J.L., and Coady K.S. Perfluorinated compounds in the Great Lakes. *Hdb Env Chem* 2006: 5(Part N); 391-438
- Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J., (2007) Perfluoroalkyl acids: a review of monitoring and toxicological findings. *Toxicol. Sci.* 99, 366–394.
- NICNAS Alert No.1 Perfluorooctanyl sulfonate (PFOS), July 2002, http://www.nicnas.gov.au/Publications/NICNAS_Alerts/Alert_1_PFOS_PDF.pdf
- NICNAS Alert No.2 Perfluorooctanyl sulfonate (PFOS) April 2003, http://www.nicnas.gov.au/Publications/NICNAS_Alerts/Alert_2_PFOS_PDF.pdf
- NICNAS Alert No 4 Perfluorooctanoic Acid (PFOA) and its derivatives, November 2004, http://www.nicnas.gov.au/Publications/NICNAS_Alerts/Alert_4_PFOA_PDF.pdf
- NICNAS Alert No.5 Perfluorooctane sulfonate (PFOS) and Perfluoroalkyl sulfonate (PFAS), February 2007, http://www.nicnas.gov.au/Publications/NICNAS_Alerts/EC_Alert5.pdf
- NICNAS Alert No 6 Perfluorooctanoic Acid (PFOA) & Perfluorocarboxylic acid (PFCA), February 2007 http://www.nicnas.gov.au/Publications/NICNAS_Alerts/EC_Alert6.pdf
- NICNAS Alert No. 8 Perfluorooctane sulfonate (PFOS) and Perfluoroalkyl sulfonate (PFAS) December 2008, http://www.nicnas.gov.au/Publications/NICNAS_Alerts/EC_Alert8.pdf
- NICNAS (2005) Existing chemical hazard assessment report: Potassium perfluorobutane sulfonate. Sydney, National Industrial Chemicals Notification and Assessment Scheme.
- NICNAS (2006) Position paper regarding data requirements for notification of new chemical substances containing a perfluorinated carbon chain. Sydney, National Industrial Chemicals Notification and Assessment Scheme.
- NICNAS – Current status of Perfluorooctane sulfonate (PFOS) and Perfluoroalkyl sulfonate (PFAS) in Australia, April 2009, http://www.nicnas.gov.au/Publications/NICNAS_Alerts/PFOS_Survey_Report_Final.pdf
- OECD, 2002 Hazard Assessment of Perfluorooctane sulphonate (PFOS) and its salts ENV/JM/RD(2002)17/FINAL <http://www.oecd.org/dataoecd/23/18/2382880.pdf>
- OECD Survey “Production and Use Information on Perfluorooctane Sulfonate (PFOS), Perfluoroalkyl Sulfonate (PFAS), Perfluorooctanoic Acid (PFOA), related Substances and Products/Mixtures containing these Substances” 2005 ENV/JM/MONO(2005)1 [http://www.olis.oecd.org/olis/2005doc.nsf/LinkTo/env-jm-mono\(2005\)1](http://www.olis.oecd.org/olis/2005doc.nsf/LinkTo/env-jm-mono(2005)1).
- OECD Survey “Production and Use of PFOS, PFAS, PFOA, PFCA and their Related Substances and Products/Mixtures Containing these Substances” 2006 ENV/JM/MONO(2006)36 [http://appl1.oecd.org/olis/2006doc.nsf/linkto/env-jm-mono\(2006\)36](http://appl1.oecd.org/olis/2006doc.nsf/linkto/env-jm-mono(2006)36)
- OECD PFCs: Outcome of the 2009 survey on the production, use and release of PFOS, PFAS, PFOA PFCA, their related substances and products/mixtures containing these substances, ENV/JM/MONO(2011)1, [http://www.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/jm/mono\(2011\)1&doclanguage=en](http://www.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/jm/mono(2011)1&doclanguage=en)

POPs (2009). Stockholm Convention on Persistent Organic Pollutants, In: Fourth Meeting of the Conference of the Parties, Geneva, 4–8 May 2009. <<http://chm.pops.int>>.

US EPA, 2005 Draft Risk Assessment of the Potential Human Health Effects Associated with Exposure to Perfluorooctanoic Acid (PFOA) and its Salts, Office of Pollution Prevention and Toxics Risk Assessment Division.