Direct precursors to perfluorooctanesulfonate (PFOS): Environment tier II assessment

13 February 2015

CAS Registry Numbers: 29457-72-5, 2795-39-3, 29081-56-9, 56773-42-3, 70225-14-8, 307-35-7.

Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted four years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has three tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

For more detail on this program please visit: www.nicnas.gov.au.

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Acronyms & Abbreviations

Grouping Rationale

This Tier II assessment considers the environmental risks associated with the industrial uses of five salts of perfluorooctanesulfonic acid and perfluorooctane sulfonyl fluoride:

1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt (lithium PFOS)
1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt (potassium PFOS)
1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt (ammonium PFOS)
Ethanaminium, *N*,*N*,*N*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1) (tetraethylammonium PFOS)
1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFOS)
1-Octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (PFOSF)

The chemicals in this group are long chain perfluorinated chemicals containing eight perfluorinated carbons terminated with a sulfonate or sulfonyl fluoride group. The risk assessment of these chemicals has been conducted as a group because all six substances are structurally related compounds each of which has the potential to hydrolyse and/or dissociate into the hazardous perfluorooctanesulfonate anion (PFOS).

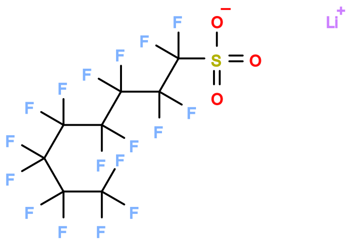
The chemicals in this group have properties which make them useful for a wide range of specialised industrial applications. However, perfluorooctanesulfonic acid, its salts and perfluorooctane sulfonyl fluoride have all been identified as Persistent Organic Pollutants (POPs) under Annex B of the *Stockholm Convention on Persistent Organic Pollutants* (the Stockholm

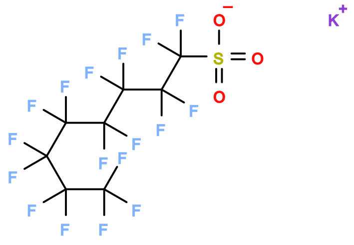
Convention). These substances are also listed on Annex III of the *Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade* (the Rotterdam Convention). These listings on two global conventions on chemicals have led to significant and evolving international restrictions on industrial uses of the chemicals in this group.

The assessment of these chemicals as a group also provides additional relevant information for the risk assessment of more complex derivatives of PFOS which may degrade to this perfluorinated anion in the environment. These more complex derivatives of PFOS have been assessed separately as the Indirect Precursors of Perfluorooctanesulfonate (PFOS) group.

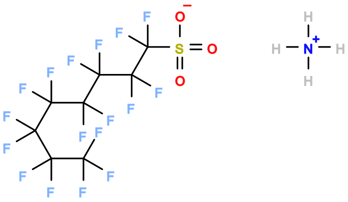
Chemical Identity

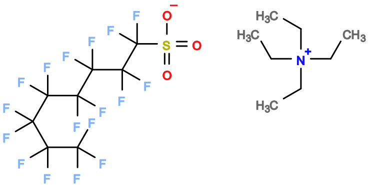
In this assessment, "PFOS" is used to denote the conjugate base anion of perfluorooctanesulfonic acid (i.e. the perfluorooctanesulfonate anion). However, it is noted that this descriptor is commonly used in relation to a range of substances which may easily form the anion in water, such as the parent acid and salts of the acid.

CAS RN	29457-72-5
Chemical Name	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt
Synonyms	lithium PFOS lithium perfluorooctanesulfonate lithium heptadecafluorooctanesulfonate
Structural Formula	
Molecular Formula	$C_8F_{17}LiO_3S$
Molecular Weight (g/mol)	506.06
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].[Li+]

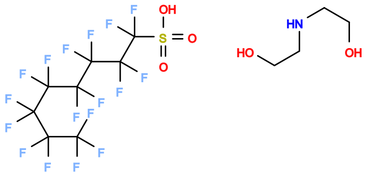
CAS RN	2795-39-3
Chemical Name	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt
Synonyms	potassium PFOS potassium perfluorooctanesulfonate potassium heptadecafluorooctanesulfonate
Structural Formula	
Molecular Formula	$C_8F_{17}KO_3S$
Molecular Weight (g/mol)	538.22
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].[K+]

CAS RN	29081-56-9
Chemical Name	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt
Synonyms	ammonium PFOS ammonium perfluorooctanesulfonate ammonium heptadecafluorooctanesulfonate

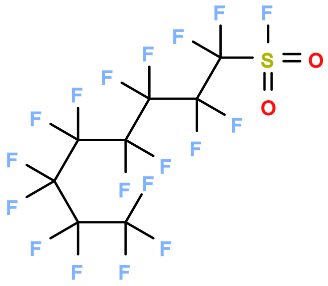
Structural Formula	
Molecular Formula	$C_8H_4F_{17}NO_3S$
Molecular Weight (g/mol)	517.16
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].[NH4+]

CAS RN	56773-42-3
Chemical Name	Ethanaminium, *N*,*N*,*N*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1)
Synonyms	tetraethylammonium PFOS tetraethylammonium perfluorooctanesulfonate tetraethylammonium heptadecafluorooctanesulfonate
Structural Formula	
Molecular Formula	$C_{16}H_{20}F_{17}NO_3S$
Molecular Weight (g/mol)	629.37

SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].C(C)[N+](CC)(CC)CC

CAS RN	70225-14-8
Chemical Name	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1)
Synonyms	diethanolammonium PFOS diethanolammonium perfluorooctanesulfonate diethanolammonium heptadecafluorooctanesulfonate
Structural Formula	
Molecular Formula	$C_{12}H_{12}F_{17}NO_5S$
Molecular Weight (g/mol)	605.27
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)O.C(O)CNCCO

CAS RN	307-35-7
Chemical Name	1-Octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
Synonyms	PFOSF POSF

	perfluorooctanesulfonyl fluoride heptadecafluorooctanesulfonyl fluoride
Structural Formula	
Molecular Formula	$C_8F_{18}O_2S$
Molecular Weight (g/mol)	502.12
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)F

Physical and Chemical Properties

Available physical and chemical property data for PFOSF and potassium PFOS are presented below (Lanners, 2010; OECD, 2002):

Chemical	PFOSF	potassium PFOS
Physical Form	Solid	Solid
Melting Point	> 25°C (exp.)	≥ 400°C (exp.)
Boiling Point	154°C (exp.)	Not measurable
Vapour Pressure	213 Pa at 20°C (exp.)	3.31×10^{-4} Pa at 20°C (exp.)

Water Solubility	0.29 mg/L (calc.)	570 mg/L (exp.)

The parent acid for the salts in this group, perfluorooctanesulfonic acid (CAS RN: 1763-23-1), is a very strong acid in water and is known to be surface-active (Gramstad and Haszeldine, 1957). A comprehensive range of relevant physical and chemical property data have been reported for the potassium salt of this strong acid. The water solubility data available for this salt show that it has moderate to high water solubility in pure water, but that the solubility in aqueous electrolytes (such as natural seawater) is significantly reduced. The octanol-water partition coefficient (K_{OW}) parameter is not considered to provide a reliable indicator of the partitioning behaviour of the surface-active perfluorinated anion in the environment and does not form part of the standard set of chemical property data for these salts (OECD, 2002).

Based on the data available for potassium PFOS, the other salts in this group are all expected to have moderate to high water solubility in pure water, low volatility, and significant surface activity.

The sulfonyl fluoride, PFOSF, is a neutral organic chemical of moderate molecular weight. It is estimated to be only slightly soluble in water. Based on the reported vapour pressure, it is considered to be a highly volatile substance. The hydrolysis of perfluoroalkyl sulfonyl fluorides is relatively slow in water under acid and neutral conditions, and the rate of hydrolysis decreases with increasing carbon chain length (Gramstad and Haszeldine, 1957). A half-life for hydrolysis of PFOSF was not identified. However, the half-life for hydrolysis of the short-chain homologue, perfluorobutanesulfonyl fluoride (CAS RN: 375-72-4), has been reported as 73 hours at pH 7 and 23°C (ECHA, 2015). A measured octanol-water partition coefficient (K_{OW}) value was not identified for PFOSF.

Import, Manufacture and Use

Australia

The five PFOS salts in this group include some of the more commercially important salts of perfluorooctanesulfonic acid used for industrial applications. These salts are often simply referred to as "PFOS" (UNEP, 2006). As the perfluorooctanesulfonate anion does not exist as a separate chemical substance, references to the introduction of "PFOS" in this section can include these commercially important PFOS salts. However, it is noted that quantities of introduced "PFOS" may also include more complex chemical substances which have a perfluorooctanesulfonyl moiety.

Available data indicate that 100 kg of PFOS was imported in bulk in 2013 by one importer. These imported chemicals were reformulated domestically for supply of PFOS-containing industrial products used in Australia. An additional business which imported pre-formulated products containing PFOS was also identified, and is estimated to import approximately 10 kg of these products per year. Further small imports of pre-formulated products containing PFOS were expected (Parliament of Australia, 2014). Recent import data show a decline in quantities of PFOS introduced compared to earlier years (NICNAS, 2013a; Parliament of Australia, 2014).

A survey conducted by NICNAS in 2008 found that the majority of products and mixtures containing PFOS imported into Australia in 2006 and 2007 were imported by the metal plating industry for use as mist suppressants (NICNAS, 2013a). The metal plating applications in Australia for PFOS relate in particular to chrome plating using hexavalent chromium (DSEWPaC, 2011). Other industries which imported products and mixtures containing PFOS in 2008 included the aviation industry where it is used in hydraulic fluid, and the photography and photolithography sectors where it is used as a surfactant (NICNAS, 2013a).

No Australian manufacture or export of PFOS or PFOS related chemicals is known (NICNAS, 2013a; Parliament of Australia, 2014).

It is noted that some of the chemicals in this group may be present in the environment due to historic use, or due to release from articles or the use of chemicals not covered by this assessment.

International

Due to their unique chemical properties, perfluorinated chemicals have been used for a wide range of specialised industrial applications. Nevertheless, use of PFOS containing chemicals has been declining globally. Concerns regarding persistence and bioaccumulation resulted in the largest global manufacturer of PFOS-based chemicals ceasing their production in 2002 (3M, 2014; OECD, 2002).

However, production by various additional companies increased shortly after the phase out by the main manufacturer. Production of PFOSF in China was estimated to have increased to at least 200 tonnes per annum by 2006 (US EPA, 2009b). An additional four countries were also reported to have manufactured PFOS related substances in 2005. Available data suggested a PFOSF production volume of approximately 70 tonnes, with production of tetraethylammonium PFOS and potassium PFOS reported in volumes up to approximately 30 tonnes and 20 tonnes, respectively. Between one and ten tonnes of lithium PFOS, and less than one tonne of ammonium PFOS were also reported to have been produced (OECD, 2006). A subsequent survey in 2008 indicated drastically reduced production of these chemicals. However, the response rate for this survey was very low and the data may not be representative (OECD, 2011).

Developed countries report use of PFOSF as a chemical intermediate, while the salts are used in photo-imaging, in the semiconductor industry, in metal plating (particularly chromium plating) and in fire-fighting foams (ECHA, 2014a; 2014b; UNEP, 2014e; 2014f). A wider range of uses are reported by developing countries, including use for chemically driven oil production, and use in carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, and rubber and plastics (UNEP, 2014e; 2014f).

Tetraethylammonium PFOS is currently registered for use in the European Union at a volume between one and ten tonnes per annum (ECHA, 2014b).

Environmental Regulatory Status

Australia

Amendments made to regulation 11C(1) under the *Industrial Chemicals (Notification and Assessment) Regulations 1990* (Cwlth) in 2014 have resulted in controls being placed on the chemicals in this group (Australian Government Department of Health, 2014). The introduction or export of any chemical in this group is now prohibited unless approval is obtained from the NICNAS Director (Commonwealth of Australia, 1990).

The Australian Government Department of the Environment is currently undertaking a domestic treaty making process to consider ratification of the 2009 amendment to the Stockholm Convention, which includes the listing of perfluorooctanesulfonic acid, its salts and perfluorooctanesulfonyl fluoride (Australian Government Department of the Environment, 2011).

In 2008, a factsheet published by NICNAS recommended that PFOS-based chemicals be restricted to essential uses only, and that importers ensure that alternative chemicals are less toxic and not persistent in the environment (NICNAS, 2013a).

United Nations

All chemicals in this group are captured by the listing of perfluorooctanesulfonic acid, its salts and perfluorooctanesulfonyl fluoride on Annex B of the Stockholm Convention. The listing prohibits production and use of these chemicals for purposes other than those listed as acceptable purposes. Acceptable purposes include industrial use in photo-imaging, in formulation of photo-resist and anti-reflective coatings for semi-conductors, as an etching agent for compound semi-conductors and ceramic filters, in aviation hydraulic fluids, in closed-loop metal plating systems, in fire-fighting foam and in certain medical devices. In addition, a range of specific exemptions for additional uses are also available for a period of time while restrictions are phased in. The listing of these chemicals aims to reduce and ultimately eliminate use as suitable alternatives become available (UNEP, 2009).

Of the 193 member countries of the United Nations, 179 are party to the Stockholm Convention (UNEP, 2014d). Eighteen parties are yet to ratify the 2009 amendment, which includes the listing of perfluorooctanesulfonic acid, its salts and perfluorooctanesulfonyl fluoride. Australia, New Zealand and the USA are among this number (UNEP, 2014b).

In addition, the chemicals in this group are also captured by the listing of perfluorooctane sulfonic acid, perfluorooctanesulfonates, perfluorooctanesulfonamides and perfluorooctanesulfonyls on Annex III of the Rotterdam Convention

(UNEP, 2014c). The Rotterdam Convention aims to facilitate sharing of chemical information to promote shared responsibility for the international trade of certain hazardous chemicals. Of the 193 United Nations member countries, 153 have ratified the Rotterdam Convention, including Australia. The European Union is also a party to the convention (UNEP, 2014a). Listing of the chemicals under the Convention was triggered by the severe restrictions placed on certain members of the group by Canada, the European Union and Japan (UNEP, 2013).

OECD

Perfluorooctanesulfonate and its salts were sponsored for assessment under the Cooperative Chemicals Assessment Programme (CoCAP) by the United Kingdom and the United States of America. The 34th Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology in 2002 endorsed the hazard assessment, which found that PFOS and its salts were candidates for further work (OECD, 2002).

Canada

Perfluorooctanesulfonate and its salts are listed on the Virtual Elimination List under section 65 of the *Canadian Environmental Protection Act 1999* (Government of Canada, 2009). These chemicals must not be released to the environment at quantifiable levels.

Potassium PFOS, ammonium PFOS, tetraethylammonium PFOS and diethanolammonium PFOS are listed on the Canadian Domestic Substances List (DSL). During the Categorization of the DSL, all four chemicals were found to be Persistent (P) and Inherently Toxic to the Environment (iT_E). All were also found to be Bioaccumulative (B), except for tetraethylammonium PFOS, for which the bioaccumulation potential could not be determined (Environment Canada, 2013a). A screening assessment on PFOS, its salts and precursors was subsequently performed in 2006, and the amendment to the Virtual Elimination List was completed in 2009 (Environment Canada, 2006; Government of Canada, 2009). The remaining chemicals in the group, lithium PFOS and PFOSF, are not listed on the Canadian DSL (Environment Canada, 2013b).

European Union

The use of PFOS derivatives, including metal salts and PFOSF, is restricted under Commission Regulation No 850/2004 on Persistent Organic Pollutants (European Commission, 2010). These chemicals may only be used in select applications in electroplating systems, photolithography processes, photographic coatings, chromium plating, and aviation hydraulic fluids. Use is to be phased out as alternate substances or technologies become available.

Tetraethylammonium PFOS and PFOSF are currently registered for use in the European Union under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2014a; 2014b). All other chemicals in the group have been pre-registered, but have not yet undergone the full registration process (ECHA, 2014c).

United States of America

New uses of all chemicals in this group in the United States of America are prohibited without prior approval from the United States Environmental Protection Agency (US EPA) (United States Government, 2002; 2007). The US EPA understands that any existing uses of these chemicals are limited, highly technical uses for which there are no alternatives available, and have low environmental release (US EPA, 2014).

The US EPA published an action plan on long-chain perfluorinated chemicals, covering the chemicals in this group, in 2009. All chemicals were identified as persistent, bioaccumulative and toxic (US EPA, 2009b).

Japan

Perfluorooctanesulfonate and its salts, and PFOSF, have been designated as Class I Specified Chemicals Substances under *The Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc.* (NITE, 2014). Permission must be obtained from the Minister of Economy, Trade and Industry to manufacture, import or use these chemicals in most cases (Government of Japan, 2010).

Class I Specified Chemicals have been identified as persistent and highly bioaccumulative chemicals with risks of long-term toxicity to humans or predator animals at higher trophic levels (NITE, 2014).

Environmental Exposure

It is considered unlikely that PFOSF is used in Australia, as there is no known domestic manufacture of chemicals containing the perfluorooctanesulfonyl moiety. Based on the available information, if the salts in this group are introduced, they are most likely used as mist suppressants in metal plating, particularly chromium plating with hexavalent chromium. Minor use may occur in aviation hydraulic fluids and as surfactants in the photography and photolithography sectors.

Based on standard emission scenarios for industrial electroplating operations, some release of chemical substances used in electroplating to waste water and landfill can be expected (Environment Australia, 1999; OECD, 2004). Available international data suggest that, when used as a mist suppressant in chromium plating, mist suppressants containing PFOS are added to the bath solution and may be discharged to sewage treatment plants (STPs) after on-site waste water treatment. High concentrations of PFOS in STP sludge and effluent have been traced back to chromium plating plants in the USA (US EPA, 2009a). Assuming a similar emission pattern in Australia, and noting that STP sludge may be applied to land as biosolids, emissions of PFOS to environmental surface waters and soil may occur as a result of the use of chemicals in this group in domestic electroplating facilities.

The potassium, ammonium and lithium cations present as counterions in salts of this group are ubiquitous, naturally occurring inorganic species that are essential for many biological functions. The substituted ammonium compounds present as counterions in salts of this group are expected to be readily biodegradable with minimal excess toxicity. The environmental fate and effects of these cations are not further considered in this assessment.

Environmental Fate

Dissolution, Speciation and Partitioning

The salts in this group will dissolve to release the perfluorooctanesulfonic acid anion, which is expected to remain in the water compartment.

Perfluorooctanesulfonic acid is a very strong acid in water and under environmental conditions the acid will exist predominantly as the conjugate base anion (i.e. PFOS) (Brooke, et al., 2004). The salts of this very strong acid will dissociate into their constituent ions in water. The partitioning behaviour of the acid and its salts in the aquatic compartment will be influenced by the surface activity of the perfluorinated anion, which is the dominant species under environment conditions. Based on the comparatively high water solubility of simple PFOS salts, previous studies have concluded that the perfluorooctanesulfonic acid anion should be expected to remain in water if released to this compartment, unless adsorbed to particulate matter or assimilated by organisms. However, it is noted that traditional partitioning assumptions may not be appropriate for this perfluorinated anionic surfactant (OECD, 2002).

The neutral organic member of this group, PFOSF, is less soluble in water than the PFOS salts and highly volatile. Based on these properties, this chemical should be expected to experience enhanced partitioning to the atmosphere, with less partitioning to water.

Degradation

The PFOS component of the chemicals in this group is highly resistant to degradation.

The perfluorooctanesulfonate anion is exceptionally persistent in the environment. Various studies have demonstrated that PFOS is resistant to hydrolysis, aqueous photolysis, and biodegradation. The hydrolysis half life of PFOS has been estimated to be more than 41 years, and there is no indication of direct or indirect photolysis in water (UNEP, 2006). No biodegradation has been observed in ready biodegradability studies conducted according to OECD Test Guideline (TG) 301C (OECD, 2002).

In the environment, PFOSF hydrolyses to release PFOS. The rate of hydrolysis is unknown, but is expected to be slow (Aberlin and Bunton, 1970; Martin, et al., 2010). In the atmosphere, PFOSF has also been found to be resistant to photodegradation and atmospheric hydroxyl radical attack. The chemical has an atmospheric half-life of 3.7 years, with eventual degradation hypothesised to release PFOS (Environment Canada, 2006; UNEP, 2006).

Bioaccumulation

The PFOS component of the chemicals in this group is highly bioaccumulative.

Perfluorinated chemicals have been observed to bioaccumulate by binding to proteins in plasma and liver, rather than the more conventional partitioning to fatty tissue. Studies measuring the concentration of the PFOS in plasma and liver have found bioconcentration factors (BCFs) of 3100 and 2900, respectively, in the fish *Onchorhynchus mykiss*. An additional study found the whole-fish kinetic BCF for the fish *Lepomis macrochirus* to be 2796 (UNEP, 2006). Further, available data also suggest PFOS has a high biomagnification potential. Biomagnification factors (BMFs) based on measured concentrations in wildlife have been estimated to range between 22 and 4000 (UNEP, 2006).

Transport

The PFOS component of the chemicals in this group is a globally distributed pollutant.

As a highly volatile and persistent chemical, PFOSF has properties which indicate strong potential for long-range transport. However, limited data are available to evaluate this.

Numerous studies have identified PFOS in various locations worldwide. The PFOS anion has been measured in marine mammals in remote regions far from anthropogenic emission sources, including Alaska, the Northern Baltic Sea, Arctic and Sable Islands. Additional studies have found PFOS in fish in the Northern Pacific Ocean, and in Antarctica (OECD, 2002). More recent data indicate the presence of PFOS in the Atlantic and Arctic Oceans (Benskin, et al., 2012). The global distribution of PFOS as an environmental contaminant has been difficult to rationalise in terms of conventional long range transport pathways. It has been hypothesised that such distribution may occur through transport in surface water or oceanic currents, transport of volatile PFOS precursors (such as PFOSF), adsorption to particles and/or through living organisms (UNEP, 2006).

Predicted Environmental Concentration (PEC)

A PEC was not calculated for the chemicals in this group, as a significant body of high quality environmental monitoring data for PFOS are available from multiple sites around the world.

A study of six cities in the USA, published in 2001, found STP effluent PFOS concentrations between 0.04-5.29 µg/L and STP sludge concentrations up to 3120 µg/kg (dry weight). In drinking water, PFOS concentrations were found up to 0.06 µg/L, while concentrations in surface waters were found to range up to 0.14 µg/L. Concentrations in sediment were found to be up to 1.13 µg/kg (dry weight). Higher concentrations were found in landfill leachate, with a maximum reported value of 53 µg/L (OECD, 2002). It is noted that the study included four cities with fluorochemical industries, and therefore likely represent a worse-case scenario.

More recently, a review published in 2009 cited data from 2006-8 which suggested surface water concentrations of PFOS in the USA, Japan, Italy, Germany and China were generally less than 0.2 µg/L. However, one study was reported to have found concentrations up to 0.7 µg/L in South Korea, and the United Kingdom Environment Agency was reported to have found concentrations up to 33.9 µg/L at certain targeted sites (Rumsby, et al., 2009). An Australian study of perfluorinated compounds in drinking water published in 2011 reported PFOS concentrations up to 0.02 µg/L, with the perfluorinated anion being detected in half of the 62 samples (Thompson, et al., 2011).

It is noted that many sites globally, including in Australia, have been identified as experiencing high PFOS contamination due to the use of fire fighting foams containing the perfluorinated anion (eg. CRCCARE, 2013; SERDP, 2014). However, fire fighting foam containing PFOS is no longer used for training purposes in Australia, and alternate products are being sought as existing stocks of PFOS based foams are replaced (NICNAS, 2013a).

Environmental Effects

Effects on Aquatic Life

The chemicals in this group will release PFOS in the environment and this is expected to have long-term toxic effects across many organisms.

Toxicity of PFOSF

The following measured median effective concentration (EC50) and median lethal concentration (LC50) values for model organisms across two trophic levels were reported in the REACH Registration Dossier or by Hekster et al. (ECHA, 2014a; Hekster, et al., 2002). No details regarding use of a solubiliser or observation of insoluble matter are provided:

Taxon	Endpoint	Method
Fish	96 h LC50 > 1000 mg/L	Experimental *Pimephales promelas* (Fathead minnow)
Invertebrates	48 h EC50 > 100 mg/L	Experimental *Daphnia magna* (Water flea) OECD TG 202 Nominal concentrations

Toxicity of PFOS salts

The following measured EC50, LC50 and median inhibitory concentration (IC50) values for model organisms across three trophic levels for (a) lithium PFOS and (b) potassium PFOS were reported in the OECD Hazard Assessment of PFOS and its Salts, and the Risk Profile on Perfluorooctane Sulfonate prepared for the Stockholm Convention POPs Review Committee (OECD, 2002; UNEP, 2006). All organisms are freshwater species except for the marine species *Mysidopsis bahia*:

Taxon	Endpoint	Method

Taxon	Endpoint	Method
Fish	(a) 96 h LC50 = 4.7 mg/L	Experimental *Pimephales promelas* (Fathead minnow) Static Nominal concentrations
Invertebrates	(b) 48 h EC50 = 27 mg/L	Experimental *Daphnia magna* (Water flea) OECD TG (1981); static Nominal concentrations
	(b) 96 h LC50 = 3.6 mg/L	Experimental *Mysidopsis bahia* (Mysid shrimp) OPPTS 850.1035; static Measured concentrations
Algae	(b) 96 h IC50 = 48.2 mg/L	Experimental *Pseudokirchneriella subcapitata* (Green algae)

The following no-observed-effect-concentration (NOEC) values for model organisms across three aquatic trophic levels for potassium PFOS were reported in the OECD Hazard Assessment of PFOS and its Salts or the Risk Profile on Perfluorooctane Sulfonate prepared for the Stockholm Convention POPs Review Committee (OECD, 2002; UNEP, 2006). All organisms are freshwater species except the marine species *M. bahia*:

Taxon	Endpoint	Method
Fish	42 d NOEC = 0.3 mg/L	Experimental *Pimephales promelas* (Fathead minnow) OECD TG 210; flow-through Measured concentrations Reduced growth and survival

Taxon	Endpoint	Method
Invertebrates	28 d NOEC = 7 mg/L	Experimental *Daphnia magna* (Water flea) OECD TG (1981); semi-static Nominal concentrations Reproductive toxicity observed
	35 d NOEC = 0.25 mg/L	Experimental *Mysidopsis bahia* (Mysid shrimp) OPPTS 850.1350; flow-through Measured concentrations Reproductive toxicity observed
Algae	96 h NOEC = 5.3 mg/L	Experimental *Pseudokirchneriella subcapitata* (Green algae)

While standard ecotoxicity testing results suggest moderate chronic toxicity, a growing number of non-standard tests have identified high chronic aquatic toxicity as demonstrated by a range of intergenerational effects. Ji et al. (2008) found no significant effects in regards to mortality or condition factors in exposed adult *Oryzias latipes* (Japanese medaka) at PFOS concentrations of 1 mg/L for 14 days. However, cumulative mortality of the offspring after 100 days was significantly increased when the parent had been exposed to 0.01 mg/L PFOS. Mortality increased further when the F_1 generation were also exposed to the perfluorinated anion (Ji, et al., 2008). In a similar study, Du et al. (2009) found significantly higher rates of malformations in the F_1 generation when maternal fish (*Danio rerio*) were exposed to 0.05 mg/L PFOS for 70 days. No deformed larvae survived (Du, et al., 2009). These studies provide emerging evidence to demonstrate high chronic toxic of PFOS in aquatic organisms that are not detected by standard test protocols.

Effects on Sediment-Dwelling Life

The chemicals in this group will release PFOS in the environment and this is expected to have long-term toxic effects in sediment-dwelling organisms.

Toxicity of PFOSF

No suitable data were available to evaluate the effects of PFOSF on sediment-dwelling organisms.

Toxicity of PFOS salts

The toxicity of PFOS to the midge *Chrionomus tentans* has been studied, with a 10 d NOEC of 0.0491 mg/L obtained. Reduced growth and survival rates were observed (UNEP, 2006).

Effects on Terrestrial Life

The chemicals in this group will release PFOS in the environment, which is expected to have long-term toxic effects in terrestrial organisms

Toxicity of PFOS salts

The majority of toxicity testing on terrestrial organisms has been conducted on model organisms to evaluate the toxicity of PFOS in humans. Further information on these studies can be found in the IMAP Tier II Human Health Assessment of Perfluorooctanesulfonic Acid and its Salts (NICNAS, 2015).

Predicted No-Effect Concentration (PNEC)

Use of the chemicals in this group will result in the environmental release of the perfluorooctanesulfonic acid anion, which is highly bioaccumulative and persistent. These two hazard characteristics combined have the potential to result in a range of long term effects on organisms exposed to these chemicals which cannot be readily identified through standard ecotoxicity tests. For such chemicals, it is not currently possible to estimate a safe exposure concentration using standard extrapolation methods based on laboratory screening levels tests. Predicted no-effects concentrations have therefore not been derived for the chemicals in this group.

Categorisation of Environmental Hazard

The categorisation of the environmental hazards of 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt (lithium PFOS); 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt (potassium PFOS); 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt (ammonium PFOS); ethanaminium, *N*,*N*,*N*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1) (tetraethylammonium PFOS); 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFOS); and 1-octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (PFOSF) according to domestic environmental hazard thresholds is presented below (EPHC, 2009; NICNAS, 2013b):

Persistence

Persistent (P). Based on the non-degradability of PFOS, and the expectation that all chemicals in this group will release PFOS in the environment, all chemicals in this group are categorised as Persistent.

Bioaccumulation

Bioaccumulative (B). Based on the bioaccumulation properties of PFOS, and the expectation that all chemicals in this group will release PFOS in the environment, all chemicals in this group are categorised as Bioaccumulative.

Toxicity

Toxic (T). Based on the long-term toxicity of PFOS, and the expectation that all chemicals in this group will release PFOS in the environment, all chemicals in this group are categorised as Toxic.

Summary

1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt; 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt; 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt; ethanaminium, *N*,*N*,*N*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1); and 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1); and 1-octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- are categorised as:

- P
- B
- T

Risk Characterisation

The chemicals in this group have been identified as PBT substances. It is not currently possible to derive a safe environmental exposure level for such chemicals and it is therefore not appropriate to characterise the environmental risks for these chemicals in terms of a risk quotient.

Due to their persistence, PBT chemicals have the potential to become widely dispersed environmental contaminants. Once in the environment, persistent chemicals that are also highly bioaccumulative pose an increased risk of accumulating in exposed organisms and of causing adverse effects. They may also biomagnify through the food chain resulting in very high internal concentrations, especially in top predators. Importantly, it is difficult or impossible to reverse the adverse effects of PBT chemicals once they have been released to the environment. As a result, these chemicals are considered to be of high concern for the environment.

Persistent organic pollutants are chemicals that are very persistent, very bioaccumulative, toxic, and have potential to undergo long-range transport. The Stockholm Convention identifies POPs and aims to reduce or eliminate the environmental release of POP substances. It is noted that all chemicals in this group are listed on Annex B of the Stockholm Convention (UNEP, 2001).

Key Findings

The chemicals in this group have been identified under Annex B of the *Stockholm Convention on Persistent Organic Pollutants* and Annex III of the *Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade* due to their potential to release PFOS to the environment. The PFOS component of the chemicals in this group is recognised globally as an exceptionally persistent, highly bioaccumulative and toxic chemical.

This assessment establishes that 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt (lithium PFOS); 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt (potassium PFOS); 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt (ammonium PFOS); ethanaminium, *N*,*N*,*N*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1) (tetraethylammonium PFOS); and 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFOS); and 1-octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (PFOSF) as PBT substances according to domestic environmental hazard criteria. Therefore, these chemicals are considered to be high concern substances.

The salts in this group are expected to have small scale uses in Australia, with the majority used in chromium plating using hexavalent chromium. Based on international information and standard emission scenarios, release of PFOS to the environment may occur as a result of domestic uses of salts of perfluorooctanesulfonic acid as mist suppressants in industrial electroplating operations. However, domestic use of the chemicals in this group is declining, and is expected to continue to decline as restrictions on use increase in accordance with international treaties and regulatory actions. A Tier III assessment under the IMAP framework may be warranted should there be any changes in the trends in uses and import volumes.

Recommendations

It is recommended that the Australian Government Department of the Environment note the risks posed by industrial use of these chemicals, as outlined in this assessment, under the current domestic treaty-making process which is considering ratification of the 2009 amendment to the *Stockholm Convention on Persistent Organic Pollutants.*

As currently recommended by NICNAS, PFOS based chemicals should be restricted to only essential uses, and importers should ensure alternative chemicals are less toxic and not persistent in the environment.

Environmental Hazard Classification

In addition to the categorisation of environmental hazards according to domestic environmental thresholds presented above, the classification of the environmental hazards of 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt (lithium PFOS); 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt (potassium PFOS); 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt (ammonium PFOS); ethanaminium, *N*,*N*,*N*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1) (tetraethylammonium PFOS); and 1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFOS); and 1-octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (PFOSF) according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS) is presented below (UNECE, 2009):

Hazard	GHS Classification (Code)	Hazard Statement
Acute Aquatic	Category 2 (H401)	Toxic to aquatic life
Chronic Aquatic	Category 1 (H410)	Very toxic to aquatic life with long lasting effects

The classification of the hazards posed by these chemicals has been performed based on the ecotoxicity data presented in this assessment. Acute data demonstrate aquatic toxicity in the range of 1-10 mg/L. Adequate chronic toxicity data were considered to be available for these chemicals, which demonstrate toxicity less than 0.1 mg/L. The chronic categorisation of these chemicals also considered the non-rapid ultimate degradation of these substances and their very high bioaccumulation potential in aquatic ecosystems (UNECE, 2007).

In the environment, PFOSF is expected to hydrolyse to PFOS. The classification of PFOSF should take into consideration the hazardous properties of this transformation product. Therefore, PFOSF has been assigned the same classifications as the salts of perfluorooctanesulfonic acid in this group, based on its potential to cause similarly hazardous environmental effects as other direct precursors to PFOS in the environment.

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