Direct precursors to perfluoroheptanesulfonate (PFHpS), perfluorohexanesulfonate (PFHxS) and perfluoropentanesulfonate (PFPeS): Environment tier II assessment

03 July 2015

CAS Registry Numbers: 60270-55-5, 68259-07-4, 70225-15-9, 3871-99-6, 68259-08-5, 70225-16-0, 423-50-7, 3872-25-1, 68259-09-6.

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 nine related perfluorinated chemicals. The chemicals in this group include salts (and an acid fluoride derivative) of long-chain perfluoroalkyl sulfonic acids containing seven or six perfluorinated carbons, and salts of an intermediate chain length acid with five perfluorinated carbons.

All of the chemicals in this group are expected to hydrolyse and/or dissociate into the perfluoroheptanesulfonate anion (PFHpS), the perfluorohexanesulfonate anion (PFHxS) or the perfluoropentanesulfonate anion (PFPeS), respectively, in the aquatic environment.

The perfluorinated anions released by the chemicals in this group have chain lengths which complete the series between the homologous C_4 perfluorobutanesulfonate anion (PFBS) and the C_8 perfluorooctanesulfonate anion (PFOS). Data currently available for simple salts of PFBS indicate that although this short-chain anion is exceptionally persistent in the environment, it is not bioaccumulative or toxic (NICNAS, 2015a). However, the long-chain PFOS anion is persistent, bioaccumulative, and toxic, and substances which release this anion are considered to pose a significant hazard both to human health and the environment (NICNAS, 2015d; 2015e).

Perfluorooctanesulfonic acid, its salts and perfluorooctane sulfonyl fluoride have recently 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 perfluoroalkyl sulfonates containing eight perfluorinated carbons. Further information on PFOS can be found in the IMAP Environment Tier II Assessment of the Direct Precursors to Perfluorooctanesulfonate (PFOS) group (see NICNAS, 2015d).

Under the NICNAS action plan for assessing and managing chemicals that could degrade to perfluorinated carboxylic acids, perfluoroalkyl sulfonates and similar chemicals, hazard information for PFOS is used to estimate the hazard of perfluoroalkyl sulfonate degradation products (with four or more perfluorinated carbons), unless sufficient toxicological data are available to demonstrate a lower toxicity profile. More information on the plan can be found in Appendix G of the NICNAS Handbook for Notifiers on the NICNAS website (NICNAS, 2015f).

This assessment will evaluate:

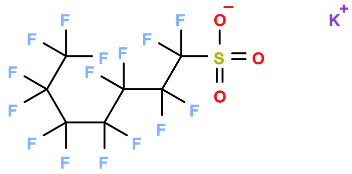
a) the properties of the chemicals in this group and compare them with both PFOS and short-chain homologues; and

b) whether there are sufficient data to use in place of the default assumptions of the action plan.

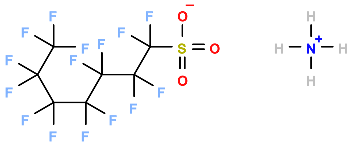
The assessment of these chemicals as a group also provides additional relevant information for the risk assessment of more complex derivatives of PFHpS, PFHxS and PFPeS which may degrade to these perfluoroalkyl sulfonates in the environment. These more complex derivatives have been assessed separately as the Indirect Precursors to Perfluoroalkyl Sulfonates group (NICNAS, 2015g).

Chemical Identity

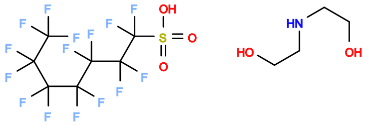
In this assessment, “PFHpS” is used to denote the conjugate base anion of perfluoroheptanesulfonic acid (i.e. the perfluoroheptanesulfonate anion), “PFHxS” is used to denote the conjugate base anion of perfluorohexanesulfonic acid (i.e. the perfluorohexanesulfonate anion), and “PFPeS” is used to denote the conjugate base anion of perfluoropentanesulfonic acid (i.e. the perfluoropentanesulfonate anion) (Buck, et al., 2011).

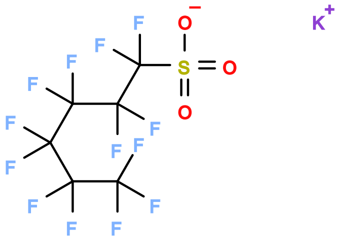
CAS RN	60270-55-5
Chemical Name	1-Heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, potassium salt
Synonyms	potassium PFHpS potassium perfluoroheptanesulfonate potassium pentadecafluoroheptanesulfonate
Structural Formula	
Molecular Formula	$C_7F_{15}KO_3S$

Molecular Weight (g/mol)	488.21
SMILES	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+]

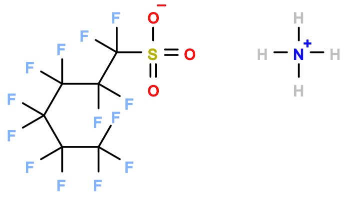
CAS RN	68259-07-4
Chemical Name	1-Heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, ammonium salt
Synonyms	ammonium PFHpS ammonium perfluoroheptanesulfonate ammonium pentadecafluoroheptanesulfonate
Structural Formula	
Molecular Formula	$C_7H_4F_{15}NO_3S$
Molecular Weight (g/mol)	467.15
SMILES	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	70225-15-9
Chemical Name	1-Heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1)

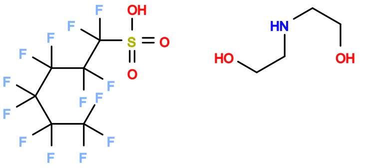
Synonyms	diethanolammonium PFHpS diethanolammonium perfluoroheptanesulfonate diethanolammonium pentadecafluoroheptanesulfonate
Structural Formula	
Molecular Formula	$C_{11}H_{12}F_{15}NO_5S$
Molecular Weight (g/mol)	555.26
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)O.C(O)CNCCO

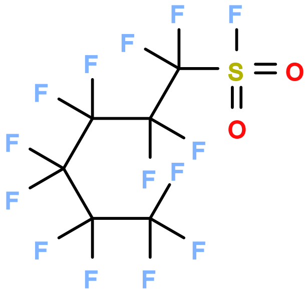
CAS RN	3871-99-6
Chemical Name	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, potassium salt
Synonyms	potassium PFHxS potassium perfluorohexanesulfonate
Structural Formula	
Molecular Formula	$C_6F_{13}KO_3S$

Molecular Weight (g/mol)	438.20
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].[K+]

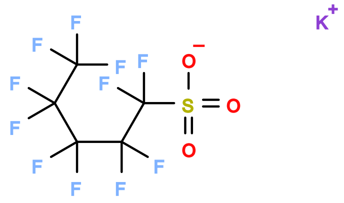
CAS RN	68259-08-5
Chemical Name	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, ammonium salt
Synonyms	ammonium PFHxS ammonium perfluorohexanesulfonate
Structural Formula	
Molecular Formula	$C_6H_4F_{13}NO_3S$
Molecular Weight (g/mol)	417.15
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].[NH4+]

CAS RN	70225-16-0
Chemical Name	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1)

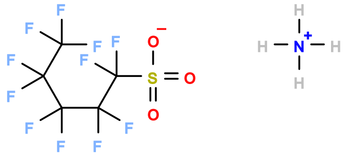
Synonyms	diethanolammonium PFHxS diethanolammonium perfluorohexanesulfonate
Structural Formula	
Molecular Formula	$C_{10}H_{12}F_{13}NO_5S$
Molecular Weight (g/mol)	505.25
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)O.C(O)CNCCO

CAS RN	423-50-7
Chemical Name	1-Hexanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-
Synonyms	PFHxSF PHxSF perfluorohexanesulfonyl fluoride
Structural Formula	
Molecular Formula	$C_6F_{14}O_2S$

Molecular Weight (g/mol)	402.11
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)F

CAS RN	3872-25-1
Chemical Name	1-Pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, potassium salt
Synonyms	potassium PFPeS potassium perfluoropentanesulfonate
Structural Formula	
Molecular Formula	$C_5F_{11}KO_3S$
Molecular Weight (g/mol)	388.20
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].[K+]

CAS RN	68259-09-6
Chemical Name	1-Pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, ammonium salt

Synonyms	ammonium PFPeS ammonium perfluoropentanesulfonate
Structural Formula	
Molecular Formula	$C_5H_4F_{11}NO_3S$
Molecular Weight (g/mol)	367.14
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)[O-].[NH4+]

Physical and Chemical Properties

No measured physical and chemical property data were identified for the chemicals in this group. The measured data available for the properties of the two salts, potassium perfluorobutanesulfonate (potassium PFBS) and potassium perfluorooctanesulfonate (potassium PFOS), are presented below to define the range of values expected for simple salts of perfluoroalkyl sulfonic acids in this group (NICNAS, 2015a; 2015d). Based on these data, the salts in this group are all expected to be solids with moderate solubility in pure water and low volatility:

Chemical	potassium PFBS	potassium PFOS
Physical Form	Solid	Solid
Melting Point	270°C (exp.)	≥ 400°C (exp.)
Vapour Pressure	< 1.22×10^{-5} Pa (exp.)	3.31×10^{-4} Pa (exp.)
Water Solubility	52.6-56.6 mg/L (exp.)	570 mg/L (exp.)

The parent acids for the salts in this group are expected to be very strong acids in water, and to be surface active (NICNAS, 2015a; 2015d). The octanol-water partition coefficient (K_{OW}) parameter is not considered to provide a reliable indicator of the partitioning behaviour of surface-active perfluorinated anions in the environment, and does not form part of the standard set of chemical property data for these chemicals (OECD, 2002).

The available data for homologous sulfonyl fluorides suggest that PFHxSF will be only slightly soluble in water. However, the chemical is expected to highly volatile. The measured values for the vapour pressure of the C_4 and C_8 perfluoroalkyl sulfonyl fluorides are reported to be 16 665 and 213 Pa, respectively (NICNAS, 2015a; 2015d). 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). 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 (NICNAS, 2015a).

Import, Manufacture and Use

Australia

No specific Australian use, import, or manufacturing information has been identified. However, general information on the use of perfluoroalkyl sulfonates has been reported. The most recent data collected by NICNAS indicate that perfluoroalkyl sulfonates are predominantly used in Australia in mist suppressants for the metal plating industry and in fire fighting foams. Approximately 60 tonnes of fire fighting foams containing perfluoroalkyl sulfonates at concentrations up to 5% were held in Australia in 2007. Other uses included carpet treatments, curatives, industrial coatings and printing inks (NICNAS, 2013a).

In 2004, it was reported that 1.6 tonnes of perfluoroalkyl sulfonates and related chemicals were imported into Australia. By 2007, the imported quantity of these chemicals had increased to 13.6 tonnes. It was reported that the majority of these imports were of chemicals based on the C_4 homologue, perfluorobutanesulfonic acid. The chemicals in this group are not manufactured in Australia (NICNAS, 2013a).

It is noted that the chemicals in this group may be present in the environment due to historic use, release from pre-treated articles, or the use of other chemicals not in this group (which may degrade to these chemicals or contain these chemicals as contaminants). However, release from these uses is beyond the scope of this assessment.

International

Salts of PFHpS, PFHxS and PFPeS have previously been reported to have use as components of etchants for electroplating, in antireflective coatings for photolithography, in photoresists, in carpet treatments and in fire-fighting foams (Beesoon, et al., 2012; Liu and Chang, 2014; OECD, 2011; Olsen, et al., 2005; UNEP, 2007). However, concerns regarding the persistence and bioaccumulation hazards of long-chain perfluoroalkyl sulfonates resulted in the largest manufacturer of these chemicals ceasing their production in 2002 (Buck, et al., 2011). This is expected to have significantly reduced the global supply of most chemicals in this group.

However, subsequent to the cessation in production by the major manufacturer, the diethanolammonium salt of PFHxS was reported to be used as a component of etchants for electroplating (UNEP, 2007). Limited data are available to evaluate the degree to which the remaining salts in this group are used for the above listed purposes. Nevertheless, it is noted that use of the three potassium salts in this group was reported in 2012 in Denmark (Nordic Council of Ministers, 2015).

The sulfonyl fluoride is expected to be used as a chemical intermediate in the production of other fluorochemicals. Manufacture of the chemical was reported in 2008 (OECD, 2011).

Environmental Regulatory Status

Australia

In 2008, a factsheet published by NICNAS recommended that PFOS-based and related PFAS-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

The chemicals in this group are not currently identified as Persistent Organic Pollutants (UNEP, 2001), ozone depleting substances (UNEP, 1987), or hazardous substances for the purpose of international trade (UNEP & FAO, 1998).

OECD

The chemicals in this group have not been sponsored for assessment under the Cooperative Chemicals Assessment Programme (CoCAP) (OECD, 2013a).

The OECD has been leading an international collaboration on the scientific assessment of, and surveys of, perfluorinated chemicals. Since July 2000, Australia has been actively involved in this work through NICNAS.

Canada

Substances having perfluoroheptyl derivatives with the formula C_7F_{15} as a structural element, except those derivatives with the formula C_7F_{15}-X, where X = F, Cl, Br are listed under Schedule 1 (the Toxic Substances List) of the *Canadian Environmental Protection Act 1999* (Government of Canada, 1999). A proposal to prohibit the import, manufacture and use of these chemicals has been released, and is expected to be finalised by January 2016 (Environment Canada, 2012).

All chemicals in this group, apart from PFHxSF, are listed on the Canadian Domestic Substances List (DSL). During the Categorization of the DSL, ammonium PFHpS and diethanolammonium PFHpS were identified as Persistent (P), Bioaccumulative (B) and Inherently Toxic to the Environment (iT_E). All remaining salts in the group were also found to be P. Ammonium PFHxS was found to be B and Not iT_E, while potassium PFHpS and diethanolammonium PFHxS were found to be Not B but iT_E. The three remaining chemicals were found to be Not B and Not iT_E (Environment Canada, 2013a).

Four chemicals in this group (potassium PFHpS, ammonium PFHpS, diethanolammonium PFHpS and diethanolammonium PFHxS) were prioritised for further assessment. The subsequent screening assessment found that these chemicals were not entering the environment in a manner which posed a danger to the environment (Environment Canada, 2015).

European Union

Substances having linear or branched perfluoroheptyl derivatives with the formula C_7F_{15} as a structural element, including its salts except those derivatives with the formula C_7F_{15}-X, where X = F, Cl, Br are subjected to a current restriction proposal to ban the manufacture, use and placing on the market as substances on their own, as constituents of other substances, in a mixture or in articles (ECHA, 2015c).

All chemicals in this group have been pre-registered, but have not yet undergone the full registration process, under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2015a; 2015b).

United States of America

New uses of the 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 published an action plan on long-chain perfluorinated chemicals, covering perfluoroheptanesulfonic acid, perfluorohexanesulfonic acid, and their salts and precursors, in 2009. All chemicals were identified as persistent, bioaccumulative and toxic (US EPA, 2009).

Environmental Exposure

Based on the available domestic and international information, previous uses of the chemicals in this group are considered to have been potentially diverse, including use in fire-fighting foams and carpet treatments. However, use of the chemicals in this group is expected to have been largely phased out due to international concerns regarding the persistence and bioaccumulation hazards of long-chain perfluoroalkyl sulfonates (Buck, et al., 2011). Any current industrial uses are expected to be specialist and low volume in nature. Therefore, direct release of the chemicals to the environment as a result of current industrial uses is considered unlikely, as these chemicals are not expected to have significant use in Australia.

The chemicals in this group are considered more likely to be released to the environment from the use and disposal of other perfluorinated chemicals, which may contain the chemicals in this group as impurities or degrade to them in the environment. However, this exposure route is beyond the scope of this assessment. Indirect releases of the chemicals in this group as a result of environmental degradation of other industrial perfluorinated chemicals listed on the Inventory have been considered in the Indirect Precursors to Perfluoroalkyl Sulfonates group (NICNAS, 2015g).

The potassium and ammonium cations present as counterions in salts of this group are ubiquitous, naturally occurring inorganic species that are essential for many biological functions. The diethanolammonium cations 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 perfluoroalkyl sulfonate anions, which are expected to remain in the water compartment.

Perfluoroalkyl sulfonic acids are very strong acids in water and under environmental conditions these acids will exist predominantly as the conjugate base anion (NICNAS, 2015d). The salts of these strong acids will dissociate into their constituent ions in water. The partitioning behaviour of the acids and their salts in the aquatic compartment will be influenced by the surface activity of the perfluorinated anions. Previous studies have indicated that perfluoroalkyl sulfonate anions with less than nine perfluorinated carbons should be expected to remain in water if released to this compartment, unless adsorbed to particulate matter or assimilated by organisms (NICNAS, 2015a; 2015d). However, it is noted that traditional partitioning assumptions may not be appropriate for these chemicals (OECD, 2002).

The sulfonyl fluoride is expected to be less soluble in water than the salts, and to be 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 chemicals in this group are expected to be highly resistant to degradation.

Multiple studies conducted on a range of perfluorinated substances, including the C_4 and C_8 homologues of the chemicals in this group, have found no evidence of potential for biodegradation, hydrolysis or aqueous photolysis under environmental conditions (NICNAS, 2015a; 2015b; 2015d).

In the environment, PFHxSF is expected to hydrolyse to release PFHxS. The rate of hydrolysis is unknown. Based on data available for the C_8 homologue (NICNAS, 2015d), PFHxSF is also expected to be resistant to atmospheric degradation.

Bioaccumulation

The perfluoroheptanesulfonate and perfluorohexanesulfonate anions are bioaccumulative. The bioaccumulation potential of the perfluoropentanesulfonate anion is uncertain.

Perfluorinated chemicals have been observed to bioaccumulate by binding to proteins in plasma and liver, rather than the more conventional partitioning to fatty tissue (Ng and Hungerbühler, 2014). The C_8 homologue of the chemicals in this group has been found to be highly bioaccumulative when taking into account accumulation in protein-rich tissues, but also based on high biomagnification factors measured in wildlife (NICNAS, 2015d). However, information currently available for the C_4 homologue, PFBS, indicates that this short-chain perfluorinated anion does not pose a bioaccumulation hazard (NICNAS, 2015a).

Studies considering fish muscle have found PFHxS to have low to moderate bioaccumulation potential in fish. For example, concentrations published following a field study conducted in China allow calculation of whole body bioaccumulation factors (BAF) between 157 and 1784 L/kg for various species of fish (Fang, et al., 2014). However, when considering liver concentrations, PFHxS has been found to have high biomagnification potential. Biomagnification factors (BMF) between 6 and 8.5 have been obtained for liver concentrations of PFHxS from various prey-predator relationships in the Barents Sea (Haukås, et al., 2007). This is consistent with studies that find PFHxS to have a longer bio-elimination half life than PFOS in some terrestrial mammals (Lau, et al., 2007; OECD, 2013b). Therefore, this chemical is considered to be bioaccumulative.

No bioaccumulation data were identified for PFHpS or PFPeS. It has previously been reported that the bioaccumulation potential of perfluoroalkyl sulfonates increases with chain length (Martin, et al., 2003a; Martin, et al., 2003b; Ng and Hungerbühler, 2014). Therefore, as PFHpS has a chain length between the two bioaccumulative immediate homologues, PFHxS and PFOS, this long-chain perfluorinated anion is also expected to be bioaccumulative.

The C_5 homologue, PFPeS, is intermediate in chain length between PFBS, which is not currently considered to pose a bioaccumulation hazard, and PFHxS, which is bioaccumulative. It is currently not possible to determine which of these two immediate homologues best represents the likely bioaccumulation potential of PFPeS. Nevertheless, it is noted that one study has found estimated concentrations of PFPeS in the liver of young seals to be up to ten times higher than those of PFBS in the late 1990s. While work conducted in the early 2000s failed to detect PFBS, PFPeS was detected in all samples. In more recent times, as production of PFBS has increased, estimated concentrations of PFPeS have continued to exceed PFBS by a factor of three (Ahrens, et al., 2009). Based on these data, it is concluded that PFPeS may be bioaccumulative, although the magnitude of the bioaccumulation hazard is currently uncertain.

Transport

Perfluorohexanesulfonate is a globally distributed environmental contaminant. The remaining chemicals in this group have potential to become globally distributed pollutants.

Numerous studies have identified various perfluoroalkyl sulfonates in locations worldwide. Perfluorobutanesulfonate has been detected in the Greenland Sea, while PFOS has been found in Alaska, the Northern Baltic Sea, the Arctic and Antarctica (NICNAS, 2015a; 2015d). The global distribution of perfluoroalkyl sulfonates as environmental contaminants 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 precursors, adsorption to particles and/or through living organisms (UNEP, 2006).

Monitoring data available for PFHxS indicate that it is also a globally distributed pollutant, with this perfluorinated anion being detected in the liver of Arctic polar bears, in the Atlantic Ocean, and in Antarctic fur seals (Benskin, et al., 2012; Greaves, et al., 2012; Schiavone, et al., 2009; Smithwick, et al., 2005; Zhao, et al., 2012). Limited data are available for PFHpS, but it has been identified in Arctic foxes (Aas, et al., 2014).

No monitoring data were identified for PFPeS to provide evidence for long-range transport. Nevertheless, perfluoroalkyl sulfonates with shorter chains are expected to have increased potential to undergo long-range transport through surface water and ocean currents (NICNAS, 2015a). Based on monitoring data available for the similarly persistent and highly mobile C_4 homologue, PFPeS is also considered to have potential to become a globally distributed pollutant.

Predicted Environmental Concentration (PEC)

The chemicals in this group are not expected to have significant current industrial use in Australia and PEC values have therefore not been calculated.

Nevertheless, the chemicals in this group may be present in the environment due to past industrial use of other perfluorochemicals contaminated with these substances, use in articles, or from the use of perfluorinated chemicals which degrade to these substances in the environment. In Australia, PFHxS has been detected in 100% of water samples taken from the Parramatta River (main tributary of Sydney Harbour), with a mean concentration of 3.7 nanograms per litre (ng/L) (Thompson, et al., 2011b). The chemical has been detected in Australian drinking water at concentrations up to 13 ng/L (Thompson, et al., 2011a). Sampling of the Brisbane River catchment following a major flooding event in 2011 also found PFHxS present in water at Somerset Dam, Jindalee, Oxley Creek, West End, Bulimba and Moreton Bay. The chemical was detected in all samples obtained at these sites in concentrations ranging between 0.09 and 17 ng/L (Gallen, et al., 2014).

No Australian monitoring data were identified for PFPeS or PFHpS. In addition, limited monitoring data are available internationally for these chemicals. However, PFHpS has recently been identified in effluent from sewage treatment plants in Spain at a mean concentration of 2.91 ng/L. The chemical was also found in sludge at a mean concentration of 1.98 nanograms per gram (ng/g) (Campo, et al., 2014).

Environmental Effects

The potential long-term toxicity of these chemicals is uncertain.

No measured aquatic toxicity data were available for the chemicals in this group. In addition, limited mammalian toxicity data are available. One study conducted in rats has found PFHxS to have low reproductive and developmental toxicity (Butenhoff, et al., 2009; NICNAS, 2015c). However, the relevance of this single study to toxicity in aquatic organisms is unclear.

The findings available for other perfluorinated acids indicate that the primary toxicity concern for these substances is chronic, intergenerational toxicity. Fish toxicity data available for the C_8 homologue, PFOS, indicate potential for increased mortality in offspring when the parent generation are exposed to concentrations as low as 0.01 milligrams per litre (mg/L) (NICNAS, 2015d). However, other studies indicate that the toxicity of perfluoroalkyl sulfonates decreases with chain length (Hagenaars, et al., 2011; Ulhaq, et al., 2013). Consistent with this trend, data currently available for the C_4 homologue, PFBS, do not indicate a potential for high chronic toxicity (NICNAS, 2015a).

Although the toxicity of the perfluoroalkyl sulfonate anions in this group is expected to decrease with perfluorinated chain length, there are insufficient data to reliably interpolate the chronic ecotoxicity of the chemicals in this group from the effects of short and long-chain homologues. Therefore, the chronic ecotoxicity of the chemicals in this group is currently uncertain.

Predicted No-Effect Concentration (PNEC)

Use of the chemicals in this group will result in the environmental release of the PFPeS, PFHxS and PFHpS anions, which are persistent and either bioaccumulative, or potentially bioaccumulative. 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-heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, potassium salt (potassium PFHpS); 1-heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, ammonium salt (ammonium PFHpS); 1-heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, compounds with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFHpS); 1-hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, potassium salt (potassium PFHxS); 1-hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, ammonium salt (ammonium PFHxS); 1-hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFHxS); 1-hexanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro- (PFHxSF); 1-pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, potassium salt (potassium PFPeS); and 1-pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, ammonium salt (ammonium PFPeS) according to domestic environmental hazard thresholds is presented below (EPHC, 2009; NICNAS, 2013b):

Persistence

Persistent (P). Based on the non-degradability of other perfluoroalkyl sulfonates, including PFBS and PFOS, all chemicals in this group are categorised as Persistent.

Bioaccumulation

Potassium PFPeS and ammonium PFPeS

Uncertain (Uncertain B). There is currently insufficient information to conclude whether the bioaccumulation potential of PFPeS is comparable to highly bioaccumulative long-chain homologues or to less bioaccumulative short-chain perfluoroalkyl sulfonates. The bioaccumulation potential of these chemicals is therefore categorised as Uncertain.

All remaining chemicals

Bioaccumulative (B). Based on the available bioaccumulation and biomagnification factors for PFHxS and PFOS, all chemicals in this group, except for potassium PFPeS and ammonium PFPeS, are categorised as Bioaccumulative.

Toxicity

Uncertain (Uncertain T). The primary toxicity concern for the chemicals in this group is chronic toxicity. There is currently insufficient information to conclude whether the long-term aquatic toxicity of the chemicals in this group is comparable to toxic long-chain homologues or to less toxic short-chain perfluoroalkyl sulfonates. The toxicity of these chemicals is therefore categorised as Uncertain.

Summary

Potassium PFPeS and ammonium PFPeS are categorised as:

- P
- Uncertain B
- Uncertain T

Potassium PFHpS, ammonium PFHpS, diethanolammonium PFHpS, potassium PFHxS, ammonium PFHxS, diethanolammonium PFHxS and PFHxSF are categorised as:

- P
- B
- Uncertain T

Risk Characterisation

Risk quotients (RQs) have not been calculated for these chemicals.

Seven chemicals in this group have been identified as persistent and bioaccumulative substances. Chemicals which are persistent and bioaccumulative remain in the environment and accumulate in biota over an extended period of time, even if new emissions of the chemicals cease. These characteristics can result in very high internal concentrations in exposed organisms, which may cause long-term toxic effects that are not readily identified through standard testing protocols. Chemicals with these hazard characteristics are therefore considered to be of concern for the environment.

The bioaccumulation potential of the two C_5 perfluoroalkyl sulfonate chemicals in this group is uncertain. However, their close structural similarity to the bioaccumulative longer chain homologues and biomonitoring results which have consistently identified the perfluoropentanesulfonate anion in biota, indicate that these two chemicals should also be considered of concern for the environment.

Key Findings

The chemicals in this group are not expected to have significant current industrial use in Australia. However, if released to the environment, the chemicals in this group are expected to release surface-active perfluoroalkyl sulfonate anions. These perfluorinated anions are, or have potential to become, globally distributed pollutants. Further, these anions have been demonstrated to be, or may be, bioaccumulative. The persistence and bioaccumulation of perfluoroalkyl sulfonate anions increases the potential for chronic toxicity. However, no suitable chronic toxicity data are currently available for the chemicals in this group. Nevertheless, it is noted that the C_8 homologue, PFOS, can cause chronic intergenerational toxicity in fish.

All chemicals in this group have been categorised as persistent (P) according to domestic environmental hazard criteria. Most chemicals in this group have also been categorised as bioaccumulative (B), although for some chemicals insufficient data were available to determine a categorisation for this hazard characteristic. Insufficient data were available for all chemicals in this group to determine a reliable categorisation for toxicity.

In the absence of data which demonstrate a lower toxicity profile for C_5 to C_7 perfluoroalkyl sulfonate anions compared to PFOS, the chemicals in this group should be assumed to be of equivalent concern to direct precursors to PFOS in accordance with the action plan.

Recommendations

The chemicals in this group have been assessed as having the potential to give rise to adverse outcomes for the environment. These chemicals are currently listed on the Australian Inventory of Chemical Substances (the Inventory), and are available to be introduced into Australia without the requirement for assessment by NICNAS. Other chemicals with reduced potential for adverse outcomes are becoming available but, given the properties of these chemicals, their assessment as new chemicals under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the ICNA Act) is still required to fully characterise the human health and the environmental risks associated with their use.

It is recommended that NICNAS consult with industry and other stakeholders to consider strategies, including regulatory mechanisms available under the ICNA Act, to encourage the use of safer chemistry.

The Action Plan

Insufficient data are available to demonstrate a lower toxicity profile for the chemicals in this group compared with direct precursors to PFOS. It is therefore recommended that the action plan currently contained in Appendix G of the Handbook for Notifiers should continue to be applied to the assessment of chemicals which degrade to PFHpS, PFHxS and PFPeS (NICNAS, 2015f).

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-heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, potassium salt (potassium PFHpS); 1-heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, ammonium salt (ammonium PFHpS); 1-heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, compounds with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFHpS); 1-hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, potassium salt (potassium PFHxS); 1-hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, ammonium salt (ammonium PFHxS); 1-hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compound with 2,2′-iminobis[ethanol] (1:1) (diethanolammonium PFHxS); 1-hexanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro- (PFHxSF); 1-pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, potassium salt (potassium PFPeS); and 1-pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, ammonium salt (ammonium PFPeS) 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
Chronic Aquatic	Category 4 (H413)	May cause long lasting harmful effects to aquatic life

There are insufficient data available to categorise the acute aquatic hazards of the chemicals in this group. The long-term aquatic hazard of the chemicals in this group was classified as Chronic Category 4 ("safety net" classification), as the available evidence indicates that all perfluoroalkyl sulfonate anion components of these chemicals are highly persistent and are bioaccumulative, or there are significant concerns that they may be bioaccumulative, in aquatic ecosystems (UNECE, 2007).

In the environment, PFHxSF is expected to hydrolyse to PFHxS. The classification of PFHxSF should take into consideration the hazardous properties of this transformation product. Therefore, PFHxSF has been assigned the same classification as the salts of perfluorohexanesulfonic acid in this group.

Should additional data become available to suggest an alternate hazard classification is warranted for any of the chemicals in this group, these classifications may be revised as appropriate.

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