Direct Precursors to Perfluorocyclohexane Sulfonate and Related Perfluoroalkylcyclohexane Sulfonates: Human health tier II assessment

05 February 2016

Chemicals in this assessment

Chemical Name in the Inventory	CAS Number
Cyclohexanesulfonic acid, undecafluoro-, potassium salt	3107-18-4
Cyclohexanesulfonic acid, decafluoro(pentafluoroethyl)-, potassium salt	67584-42-3
Cyclohexanesulfonic acid, nonafluorobis(trifluoromethyl)-, potassium salt	68156-01-4
Cyclohexanesulfonic acid, decafluoro(trifluoromethyl)-, potassium salt	68156-07-0

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**

Disclaimer

ACRONYMS & ABBREVIATIONS

Grouping Rationale

This Tier II assessment considers the human health risks associated with the industrial uses of potassium salts of four perfluorinated cycloalkyl sulfonic acids:

- Cyclohexanesulfonic acid, undecafluoro-, potassium salt (potassium perfluorocyclohexane sulfonate)
- Cyclohexanesulfonic acid, decafluoro(trifluoromethyl)-, potassium salt (potassium perfluoromethylcyclohexane sulfonate)
- Cyclohexanesulfonic acid, nonafluorobis(trifluoromethyl)-, potassium salt (potassium perfluoro-dimethylcyclohexane sulfonate)
- Cyclohexanesulfonic acid, decafluoro(pentafluoroethyl)-, potassium salt (potassium perfluoro-ethylcyclohexane sulfonate)

The organic anions of all four salts contain a perfluorocyclohexane ring with an attached sulfonate group. The four salts differ principally in the number and type of perfluoroalkyl substituents attached to the perfluorocyclohexane ring. All four substances are expected to dissociate in water to release potassium cations and the perfluorocyclohexane sulfonate anion or one of three substituted perfluoroalkylcyclohexane sulfonate anions.

The perfluorinated cyclohexylsulfonate anions of the salts in this group have six, seven or eight perfluorinated carbon atoms in their structure. The parent acids of the salts considered in this assessment are related to a larger group of industrially important perfluorinated alkane sulfonic acids with linear or branched perfluoroalkyl chain compounds. This group includes perfluoroalkylsulfonic acids with six or more perfluorinated carbons in a chain which are known to be of high human health and

environmental concern. An important member of this group of high concern chain compounds is the C8 acid, perfluorooctanesulfonic acid, which dissociates into the perfluorooctanesulfonate anion (PFOS).

Perfluorooctanesulfonic acid and certain PFOS-related substances are 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 under 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 of these chemicals have led to significant and evolving international restrictions on industrial uses of PFOS-related substances. Further information on PFOS-related substances can be found in the IMAP Human Health (NICNAS, 2015a) and Environment (NICNAS, 2015b) Tier II Assessments of the Direct Precursors to Perfluorooctanesulfonate (PFOS) group.

It is currently unclear what influence the cyclic arrangement of the perfluorinated carbon atoms in these chemicals has on their human health hazard characteristics relative to the comparable linear or branched perfluoroalkyl chain compounds, such as PFOS. This assessment will therefore evaluate the available exposure and hazard data for perfluorinated cyclohexylsulfonates and consider whether it is currently possible to characterise the human health risks for these substances.

Import, Manufacture and Use

Australian

No specific Australian use, import, or manufacturing information has been identified, except for potassium perfluoro-ethylcyclohexane sulfonate (CAS No 68156-42-3) and potassium perfluoro-dimethylcyclohexane sulfonate (CAS No 68156-01-4). Based on the most recent data collected by NICNAS, about 50 tonnes of aviation hydraulic fluids containing these chemicals were imported into Australia in 2007 (NICNAS, 2013).

In addition, perfluoroalkyl sulfonates in general, 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, 2013).

The chemicals in this group are not manufactured in Australia (NICNAS, 2013). 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 C4 perfluoroalkylsulfonic acid, perfluorobutanesulfonic acid (CAS No 375-73-5).

International

The chemicals in this group have been used:

- as erosion inhibitors in specialised phosphate ester hydraulic fluids used in the aviation industry (RPA & BRE, 2004; Jarnberg et al., 2007; UNEP, 2011; UNEP, 2013);
- as active ingredients in the second generation wetting agents/fume suppressants (Paulson et al., 2004); and
- in etchant solutions for integrated circuit manufacture (Posner et al., 2009).

The chemicals have been commercially available from the 3M Company as a mixture under the tradename FC-98 (3M Canada Company, 1997; De Silva, et al., 2011; UNEP, 2011). However, the production of potassium perfluoro-ethylcyclohexane sulfonate (CAS No 67584-42-3) has been ceased by 3M (UNEP, 2011; UNEP, 2013). FC-98 has been a component in Chemguard S-103A used to formulate premium Aqueous Film-Forming Foam (AFFF) agents meeting the US Military specification and in Chemguard S106A used in wetting and levelling agents.

According to the patent literature, the perfluorocyclohexyl sulfonate salts in this group can also have other potential industrial uses including as components in printer inks (Wei-Ping, 2002), in codeposition of metal and fluorocarbon resin particles (Brown, 1972), and in thermal dye bleach construction (Randall, 1994).

The chemical potassium perfluoro-ethylcyclohexane sulfonate (CAS No 67584-42-3) also has non-industrial uses as insecticide (Posner et al., 2009).

In addition, a structurally similar chemical, potassium perfluoro-4-ethylcyclohexane sulfonate (CAS No 335-24-0) has uses in photoresist compositions (Cameron, 2000), as a nonfoaming surfactant for metal electrowinning (Posner et al., 2009) and as a component of fire-resistant hydraulic fluids in aircrafts (Switzerland, 2009).

Restrictions

Australian

No known restrictions have been identified.

International

United States of America

Use of the chemicals in this group is subject to a Significant New Use Rule (SNUR). Under the SNUR, approval must be sought from the United States Environmental Protection Agency (US EPA) for specified new uses of these chemicals (US EPA, 2007; US EPA, 2013).

Existing Worker Health and Safety Controls

Hazard Classification

The chemicals are not listed on the Hazardous Substances Information System (HSIS) (Safe Work Australia).

Exposure Standards

Australian

No specific exposure standards are available.

International

No specific exposure standards are available.

Health Hazard Information

The human health hazards of these chemicals are not known. However, these chemicals belong to a larger group of industrially important perfluorinated alkane sulfonic acids (including PFOS) which are known to be of high human health and environmental concern (see ***Grouping Rationale***). It is currently unclear what influence the cyclic arrangement of the perfluorinated carbon atoms in these species has on their human health hazard characteristics relative to the comparable linear or branched perfluoroalkyl chain compounds, such as PFOS.

The potassium cation present as a counterion in these four salts is a ubiquitous, naturally occurring inorganic species that is essential for many biological functions. The human health effects of this cation are not further considered in this assessment.

Risk Characterisation

Critical Health Effects

The human health hazards of these chemicals are not known. However, these chemicals belong to a larger group of industrially important perfluorinated alkane sulfonic acids (including PFOS) which are known to be of high human health and environmental concern (see ***Grouping Rationale***).

Public Risk Characterisation

Use in consumer products

Given the Australian and international uses identified for these chemicals, it is unlikely that the public will be exposed. Hence, the public risk from these chemicals is not considered to be unreasonable.

Secondary exposure via the environment

Public exposure to these chemicals could occur through secondary exposure via the environment.

Based on the globally integrated nature of the aviation industry, it is assumed that the substances in this group will be present in the hydraulic fluids of aircraft operating in Australia. Hence, it is considered possible that perfluorocyclohexyl sulfonates are potentially being emitted into the domestic environment. Recent monitoring studies conducted internationally have identified perfluoromethyl- and perfluoroethylcyclohexane sulfonates in the environment (De Silva, et al., 2011; Houde, et al., 2013; Lescord, et al., 2015; Letcher, et al., 2015). It is uncertain if these measured environmental concentrations are indicative of ongoing release of perfluorinated cyclohexylsulfonates used in aircraft hydraulic fluids, or whether they may also represent emissions from other industrial uses (current or historical) and/or the degradation of unidentified precursors to perfluorinated cyclohexylsulfonates.

Occupational Risk Characterisation

Based on the available use information, the chemicals or their products are not manufactured in Australia. The chemicals are not likely to be used in significant quantities in Australia with the most likely use, if any, in aircraft hydraulic fluids. Further assessment of the chemicals in this group may be necessary to inform the risk to workers if information becomes available indicating that these chemicals are introduced into Australia in significant quantities.

Long-term occupational exposure to these chemicals could occur while using the formulated products. However, epidemiological studies in workers exposed to PFOS, the most well studied member of the perfluorinated alkane sulfonic acids, have not provided clear evidence of effects in humans (NICNASa). Therefore, the chemicals are not considered to pose an unreasonable risk to the health of workers.

NICNAS Recommendation

Currently it is recommended that industry seek alternatives to perfluorinated alkane sulfonic acids (PFSA) related to PFOS and chemicals that can degrade to PFSA, and ultimately aim to phase out their use.

The chemicals in this group are recommended for Tier III assessment to determine: whether the chemicals are used in Australia; availability of toxicological information for these chemicals to enable their hazard characterisation; and whether risk management controls, including measures to encourage the use of safer chemistry, are required.

Regulatory Control

Advice for industry

Control measures

Control measures to minimise the risk from exposure to the chemicals should be implemented in accordance with the hierarchy of controls. Approaches to minimise risk include substitution, isolation and engineering controls. Measures required to eliminate, or minimise risk arising from storing, handling and using a hazardous chemical depend on the physical form and the manner in which the chemicals are used. Examples of control measures that could minimise the risk include, but are not limited to:

- using closed systems or isolating operations;
- using local exhaust ventilation to prevent the chemicals from entering the breathing zone of any worker;
- health monitoring for any worker who is at risk of exposure to the chemicals, if valid techniques are available to monitor the effect on the worker's health;
- air monitoring to ensure control measures in place are working effectively and continue to do so;
- minimising manual processes and work tasks through automating processes;5
- work procedures that minimise splashes and spills;
- regularly cleaning equipment and work areas; and
- using protective equipment that is designed, constructed, and operated to ensure that the worker does not come into contact with the chemicals.

Guidance on managing risks from hazardous chemicals are provided in the *Managing risks of hazardous chemicals in the workplace—Code of practice* available on the Safe Work Australia website.

Personal protective equipment should not solely be relied upon to control risk and should only be used when all other reasonably practicable control measures do not eliminate or sufficiently minimise risk. Guidance in selecting personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

Obligations under workplace health and safety legislation

Information in this report should be taken into account to help meet obligations under workplace health and safety legislation as adopted by the relevant state or territory. This includes, but is not limited to:

- ensuring that hazardous chemicals are correctly classified and labelled;
- ensuring that (material) safety data sheets ((M)SDS) containing accurate information about the hazards (relating to both health hazards and physicochemical (physical) hazards) of the chemicals are prepared; and
- managing risks arising from storing, handling and using a hazardous chemical.

Your work health and safety regulator should be contacted for information on the work health and safety laws in your jurisdiction.

Information on how to prepare an (M)SDS and how to label containers of hazardous chemicals are provided in relevant codes of practice such as the *Preparation of safety data sheets for hazardous chemicals—Code of practice* and *Labelling of workplace hazardous chemicals—Code of practice*, respectively. These codes of practice are available from the Safe Work Australia website.

A review of the physical hazards of these chemicals has not been undertaken as part of this assessment.

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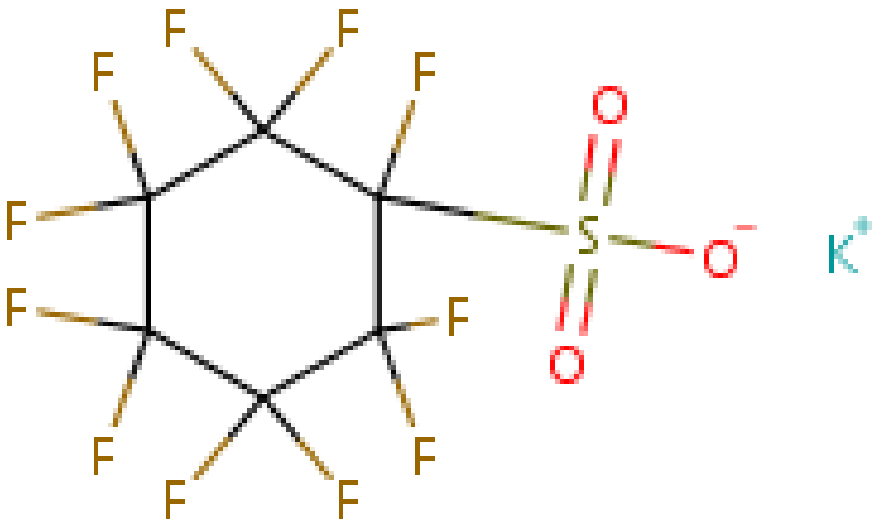
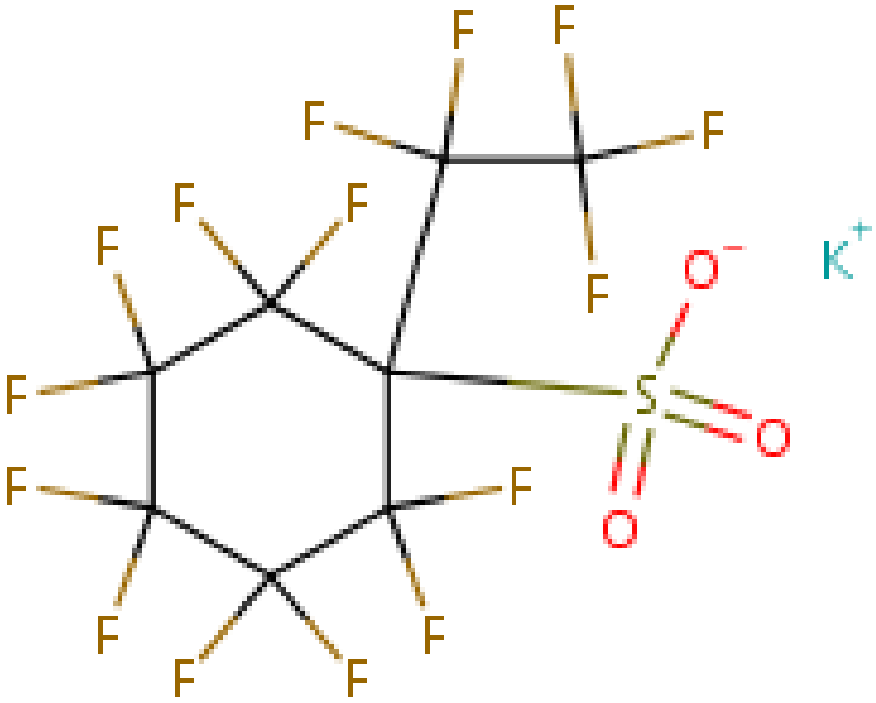
Last Update 05 February 2016

Chemical Identities

Chemical Name in the Inventory and Synonyms	**Cyclohexanesulfonic acid, undecafluoro-, potassium salt** potassium perfluorocyclohexane sulfonate PFCHS
CAS Number	3107-18-4
Structural Formula	
Molecular Formula	C6HF11O3S.K
Molecular Weight	

Chemical Name in the Inventory and Synonyms	**Cyclohexanesulfonic acid, decafluoro(pentafluoroethyl)-, potassium salt** pentafluoro-ethyldecafluorocyclohexanesulfonic acid, potassium salt potassium perfluoro-ethylcyclohexane sulfonate PFECHS

CAS Number	67584-42-3
Structural Formula	
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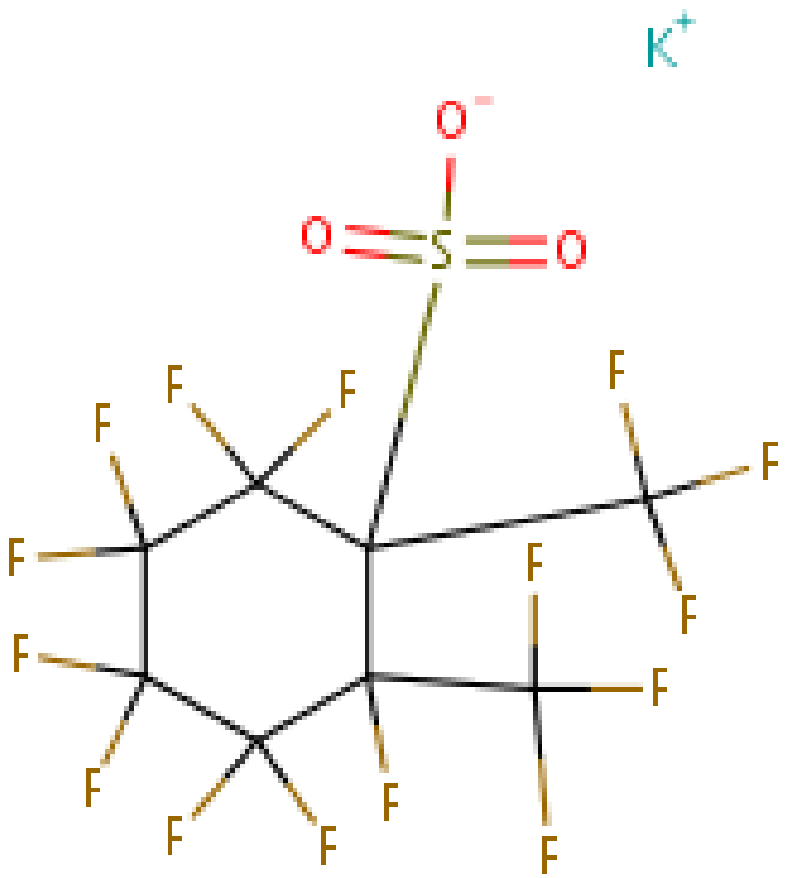
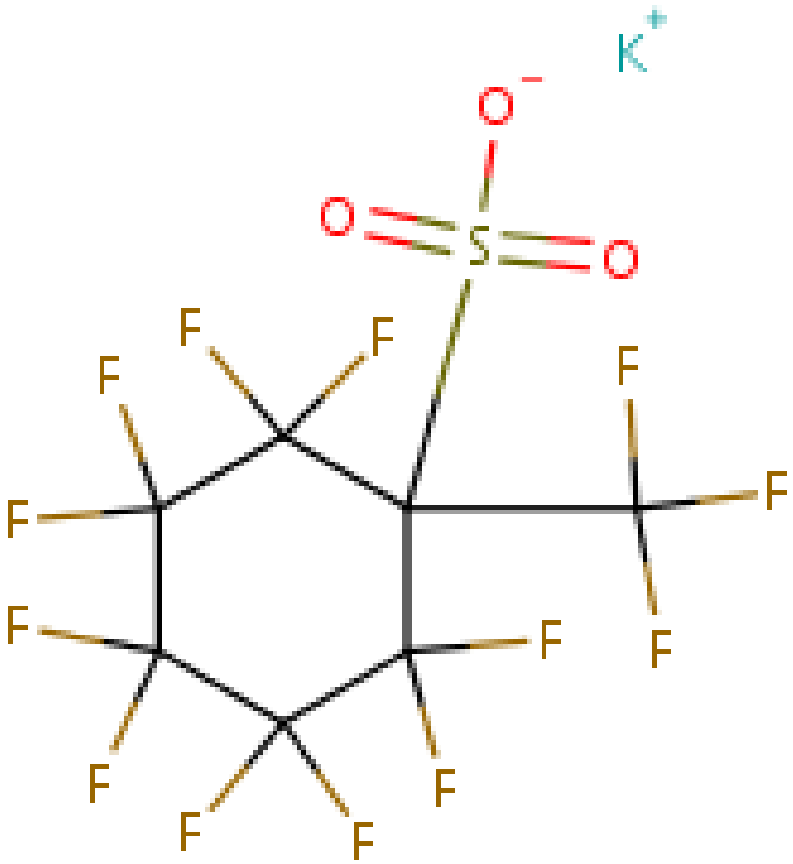
Molecular Weight	

Chemical Name in the Inventory and Synonyms	**Cyclohexanesulfonic acid, nonafluorobis(trifluoromethyl)-, potassium salt** nonafluorodi(trifluoromethyl)cyclohexanesulfonic acid, potassium salt potassium perfluoro-dimethylcyclohexane sulfonate
CAS Number	68156-01-4
Structural Formula	

	
Molecular Formula	C8HF15O3S.K
Molecular Weight	

Chemical Name in the Inventory and Synonyms	**Cyclohexanesulfonic acid, decafluoro(trifluoromethyl)-, potassium salt** decafluoro(trifluoromethyl)cyclohexanesulfonic acid, potassium salt potassium perfluoro-methylcyclohexane sulfonate PFMeCHS
CAS Number	68156-07-0
Structural Formula	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Molecular Weight	

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