Indirect precursors of perfluorobutanesulfonate (PFBS): Environment tier II assessment

13 February 2015

CAS Registry Number: 34454-97-2, 34449-89-3, 34455-00-0, 68957-59-5, 53518-00-6, 67939-95-1, 67584-51-4, 67939-89-3, 17329-79-2, 68298-79-3, 68310-18-9, 68568-54-7, 68900-97-0.

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

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Acronyms & Abbreviations

Grouping Rationale

This Tier II assessment considers the environmental risks associated with the industrial uses of 12 perfluorobutanesulfonamide derivatives and one perfluorobutanesulfonic ester.

The chemicals in this group are structurally related compounds in that they all contain a chain of four perfluorinated carbons linked to a terminal sulfonamide or sulfonic ester group.

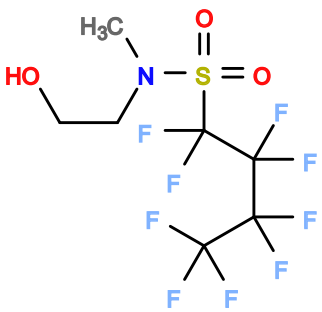
The assessment of this group has been conducted in accordance with the NICNAS Action Plan for Assessment and Management of Chemicals which may degrade to Perfluorinated Carboxylic Acids, Perfluoroalkylsulfonates and similar chemicals (the Action Plan). The primary assumption outlined in the Action Plan is that chemicals with a perfluorinated chain terminated by a sulfonyl group will degrade to the perfluoroalkylsulfonate. On this basis the chemicals in this group are each considered to have the potential to degrade into the environmentally persistent perfluorobutanesulfonate anion (PFBS). More information on the plan can be found in Appendix G of the NICNAS Handbook for Notifiers.

Chemicals based on PFBS were introduced as alternatives to the longer chain perfluoroalkyl sulfonates (PFAS) (containing carbon chain lengths of 6 or higher) including substances which may be a source of the hazardous perfluorooctanesulfonate anion (PFOS) in the environment (UNEP, 2013). Perfluorooctanesulfonic acid and certain PFOS-related substances have recently been identified as Persistent Organic Pollutants under Annex B of the *Stockholm Convention on Persistent Organic Pollutants*. 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*. Further information on PFOS can be found in the Environment Tier II Assessment of the Direct Precursors to Perfluorooctanesulfonate (PFOS) group (see NICNAS, 2015a).

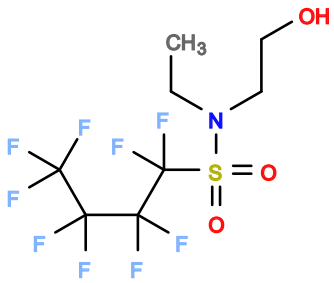
The degradation of PFBS is very slow compared with its rate of formation from degradation of the precursors and PFBS will be the final degradant from multiple precursors. Therefore, the amount of PFBS in the environment (general or local) is expected to be higher than that of any of the precursors. It will therefore be assumed for the purposes of this assessment that the primary risk posed by the chemicals in this group results from the release of PFBS to the environment. The IMAP-Environment Tier II assessment of Perfluorobutanesulfonic Acid and its Direct Precursors (see NICNAS, 2015b) has been used as a reference assessment.

Chemical Identity

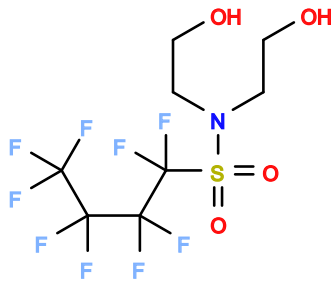
In this assessment, "PFBS" is used to denote the conjugate base anion of perfluorobutanesulfonic acid (i.e. the perfluorobutanesulfonate anion). However, it is noted that this descriptor is commonly used in relation to a range of substances which may easily form the anion in water, such as the parent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

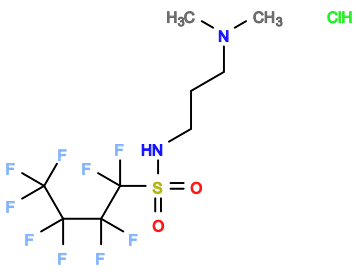
CAS RN	34454-97-2
Chemical Name	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-
Synonyms	*N*-MeFBSE alcohol *N*-Methylperfluorobutanesulfonamidoethyl alcohol
Structural Formula	
Molecular Formula	$C_7H_8F_9NO_3S$
Molecular Weight (g/mol)	357.19
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(C)CCO

CAS RN	34449-89-3

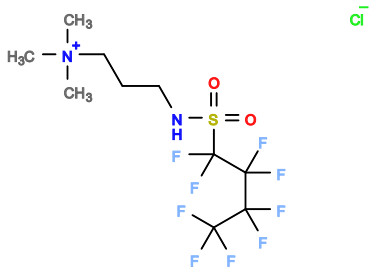
Chemical Name	1-Butanesulfonamide, *N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-
Synonyms	*N*-EtFBSE alcohol *N*-Ethylperfluorobutanesulfonamidoethyl alcohol
Structural Formula	
Molecular Formula	$C_8H_{10}F_9NO_3S$
Molecular Weight (g/mol)	371.22
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CCO)CC

CAS RN	34455-00-0
Chemical Name	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*,*N*-bis(2-hydroxyethyl)-
Synonyms	*N*-EtFBSE diol *N*,*N*-Bis(hydroxyethyl)perfluorobutanesulfonamide
Structural Formula	

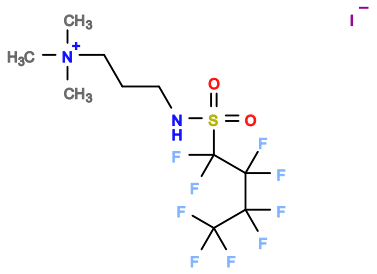
	
Molecular Formula	$C_8H_{10}F_9NO_4S$
Molecular Weight (g/mol)	387.22
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CCO)CCO

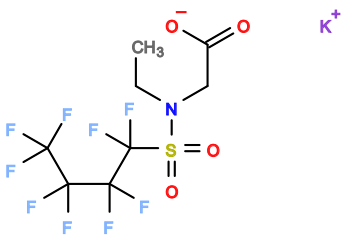
CAS RN	68957-59-5
Chemical Name	1-Butanesulfonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,4-nonafluoro-, monohydrochloride
Synonyms	*N*-(3-(dimethyl)aminopropyl)perfluorobutanesulfonamide monohydrochloride
Structural Formula	
Molecular Formula	$C_9H_{14}ClF_9N_2O_2S$
Molecular Weight (g/mol)	420.72

SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)NCCCN(C)C.Cl

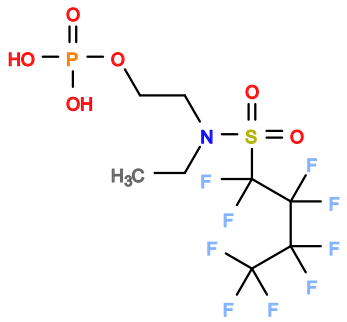
CAS RN	53518-00-6
Chemical Name	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(nonafluorobutyl)sulfonyl]amino]-, chloride
Synonyms	*N*-(3-(trimethyl)aminopropyl)perfluorobutanesulfonamide chloride
Structural Formula	
Molecular Formula	$C_{10}H_{16}ClF_9N_2O_2S$
Molecular Weight (g/mol)	434.75
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)NCCC[N+](C)(C)C.[Cl-]

CAS RN	67939-95-1
Chemical Name	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(nonafluorobutyl)sulfonyl]amino]-, iodide
Synonyms	*N*-(3-(trimethyl)aminopropyl)perfluorobutanesulfonamide iodide
Structural Formula	

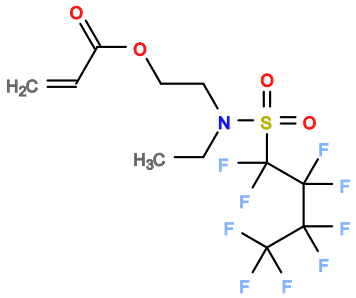
	
Molecular Formula	$C_{10}H_{16}F_9IN_2O_2S$
Molecular Weight (g/mol)	526.20
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)NCCC[N+](C)(C)C.[I-]

CAS RN	67584-51-4
Chemical Name	Glycine, *N*-ethyl-*N*-[(nonafluorobutyl)sulfonyl]-, potassium salt
Synonyms	potassium *N*-EtFBSA acetate potassium *N*-ethylperfluorobutanesulfonamide acetate
Structural Formula	
Molecular Formula	$C_8H_7F_9KNO_4S$
Molecular Weight (g/mol)	423.29

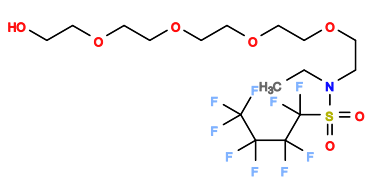
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CC(=O)[O-])CC.[K+]

CAS RN	67939-89-3
Chemical Name	Ethanol, 2-[ethyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]-, dihydrogen phosphate (ester)
Synonyms	*N*-EtFBSE phosphate *N*-Ethylperfluorobutanesulfonamidoethyl phosphate
Structural Formula	
Molecular Formula	$C_8H_{11}F_9NO_6PS$
Molecular Weight (g/mol)	451.20
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CCOP(=O)(O)O)CC

CAS RN	17329-79-2
Chemical Name	2-Propenoic acid, 2-[ethyl[(nonafluorobutyl)sulfonyl]amino]ethyl ester
Synonyms	*N*-EtFBSE acrylate *N*-Ethylperfluorobutanesulfonamidoethyl acrylate

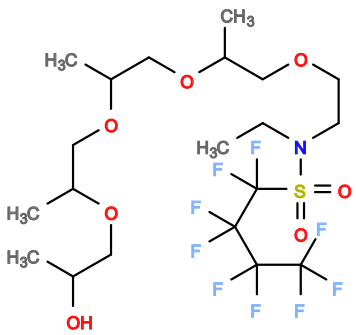
Structural Formula	
Molecular Formula	$C_{11}H_{12}F_9NO_4S$
Molecular Weight (g/mol)	425.27
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CCOC(=O)C=C)CC

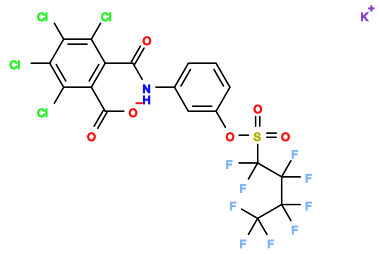
The substance represented by CAS RN 68298-79-3 is a mixture of discrete organic chemicals. Representative chemical structure information is provided below. However, it should be noted that this substance is expected to include chemicals with polyethylene glycol chains of varying lengths.

CAS RN	68298-79-3
Chemical Name	Poly(oxy-1,2-ethanediyl), .alpha.-[2-[ethyl[(nonafluorobutyl)sulfonyl]amino]ethyl]-.omega.-hydroxy-
Synonyms	PEG *N*-EtFBSE Polyethylene glycol *N*-ethylperfluorobutanesulfonamide
Representative Structural Formula	
Representative Molecular Formula	$C_{16}H_{26}F_9NO_7S$

Representative Molecular Weight (g/mol)	547.43
Representative SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CCOCCOCCOCCOCCO)CC

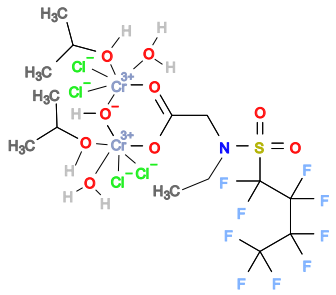
The substance represented by CAS RN 68310-18-9 is a mixture of discrete organic chemicals. Representative chemical structure information is provided below. However, it should be noted that this substance is expected to include chemicals with polypropylene glycol chains of varying lengths.

CAS RN	68310-18-9
Chemical Name	Poly[oxy(methyl-1,2-ethanediyl)], .alpha.-[2-[ethyl[(nonafluorobutyl)sulfonyl]amino]ethyl]-.omega.-hydroxy-
Synonyms	PPG *N*-EtFBSE Polypropylene glycol *N*-ethylperfluorobutanesulfonamide
Representative Structural Formula	
Representative Molecular Formula	$C_{20}H_{34}F_9NO_7S$
Representative Molecular Weight (g/mol)	603.54
Representative SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CCOCC(C)OCC(C)OCC(C)OCC(C)O)CC

CAS RN	68568-54-7
Chemical Name	Benzoic acid, 2,3,4,5-tetrachloro-6-[[[3-[[(nonafluorobutyl)sulfonyl]oxy]phenyl]amino]carbonyl]-, monopotassium salt
Synonyms	Potassium 2,3,4,5-tetrachloro-6-[[[3-[[perfluorobutanesulfonyl]oxy]phenyl]amino]carbonyl] benzoate
Structural Formula	
Molecular Formula	$C_{18}H_5Cl_4F_9KNO_6S$
Molecular Weight (g/mol)	715.20
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)Oc1cc(NC(=O)c2c(C(=O)[O-])c(Cl)c(Cl)c(Cl)c2Cl)ccc1.[K+]

The substance represented by CAS RN 68900-97-0 is a dinuclear coordination complex of chromium. The chromium ions in this complex are present in the 3+ oxidation state.

CAS RN	68900-97-0
Chemical Name	Chromium, diaquatetrachloro[.mu.-[*N*-ethyl-*N*-[(nonafluorobutyl)sulfonyl]glycinato-O1:O1']]-.mu.-hydroxybis[2-propanol]di-
Synonyms	*N*-EtFBSE acetate chromium complex *N*-Ethylperfluorobutanesulfonylethyl acetate chromium complex

Structural Formula	
Molecular Formula	$C_{14}H_{28}Cl_4Cr_2F_9NO_9S$
Molecular Weight (g/mol)	803.23
SMILES	C(F)(F)(C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)N(CC1O[Cr+++]([OH]C(C)C)([OH2])([Cl-])([Cl-])[OH-][Cr+++]([OH2])([OH]C(C)C)([Cl-])([Cl-])O=1)CC

Physical and Chemical Properties

No experimental physical and chemical property data were located for the chemicals in this group.

The substances in this group include low to moderate molecular weight neutral organic chemicals, organic salts, and a coordination complex. The salts and the chromium coordination complex are expected to be involatile, whereas the relatively low molecular weight neutral organic substances may be volatile. For example, the analogue chemical *N*-MeFBSE acrylate (CAS RN 67584-55-8) is known to be volatile based on a reported vapour pressure of 0.25 Pa (ECHA, 2015).

The measured water solubility value available for *N*-MeFBSE acrylate (2.0 mg/L) indicates that some chemicals in this group may only be slightly soluble in water (ECHA, 2015). When considered alongside the volatility of this analogue chemical, these data also suggest that *N*-EtFBSE acrylate is moderately volatile from water (estimated Henry's Law constant = 52 Pa m^3/mol for *N*-MeFBSE acrylate) (US EPA, 2008).

Import, Manufacture and Use

Australia

The 3M company is the primary producer of substances based on PFBS technology internationally (Poulsen, et al., 2005; UNEP, 2013). Based on available information, only one of these chemicals is currently used in one specific application (specialised printing ink) at very low volumes (less than 1 kg per annum).

Information collected by NICNAS in 2005 indicated that no PFBS derivatives were manufactured in Australia (NICNAS, 2005).

International

The use of PFBS derivatives as an alternative to the use of PFOS has been identified for the following uses (Poulsen, et al., 2005; UNEP, 2013):

- impregnation of textiles, leather and carpets;
- industrial and commercial cleaning products;
- surface coatings, paints and varnishes;
- oil production and mining;
- semiconductor industry; and
- electroplating.

These uses are considered potentially relevant to the chemicals in this group.

Use data available for Nordic countries indicate that *N*-MeFBSE alcohol, potassium *N*-EtFBSA acetate and the quaternary ammonium iodide salt (CAS RN 67939-95-1) were in use in Denmark in 2012. Potassium *N*-EtFBSA was reported to be used in surface treatments and as a cleaning agent. Additionally, PEG *N*-EtFBSE was used in Denmark in 2011. Other chemicals in this group were used in preceding years (Nordic Council of Ministers, 2014).

Environmental Regulatory Status

Australia

The use of the chemicals in this group is not subject to any specific national environmental regulations.

United Nations

No chemicals in this group are currently identified as a Persistent Organic Pollutant (UNEP, 2001), ozone depleting substance (UNEP, 1987), or hazardous substance for the purpose of international trade (UNEP & FAO, 1998).

OECD

None of the chemicals in this group have been sponsored for assessment under the Cooperative Chemicals Assessment Programme (OECD, 2013).

Canada

All chemicals in this group, except *N*-EtFBSE acrylate, *N*-EtFBSE diol, *N*-EtFBSE phosphate and PPG *N*-EtFBSE, are listed on the Canadian Domestic Substances List (DSL). During the Categorization of the DSL, all listed chemicals in this group were found to be Persistent (P). In addition, the tetrachlorophthalic acid derivative (CAS RN 68568-54-7) was found to be Bioaccumulative (B), and the chromium complex (CAS RN 68900-97-0) was found to be Inherently Toxic to the Environment (iT_E) (Environment Canada, 2013a). The chromium complex was prioritised for further assessment, but this has not yet been conducted (Environment Canada, 2013b).

European Union

All chemicals in this group, except PPG *N*-EtFBSE, have been pre-registered under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2014a). No chemicals in this group have undergone the full

registration process for use in the European Union under the REACH legislation (ECHA, 2014b).

United States of America

The United States Environmental Protection Agency (US EPA) published an action plan for long-chain perfluorinated chemicals in 2009 (US EPA, 2009). However, the action plan does not include the chemicals in this group (US EPA, 2013).

Environmental Exposure

The available domestic use information for chemicals in this group indicates that they are not being introduced as industrial chemicals in significant volumes. Therefore, direct release of these chemicals to the environment in Australia as a result of current industrial uses is considered unlikely. These substances may be released to the environment from disposal of imported articles treated with chemicals in this group. However, this exposure route is beyond the scope of this assessment.

The environmental degradant of primary concern for the chemicals in this group is PFBS. This perfluorinated anion is purely of anthropogenic origin and is both exceptionally resistant to degradation and mobile in the environment. However, unlike its long-chain homologue, the perfluorooctanesulfonate anion, PFBS is not currently identified as a highly bioaccumulative substance (NICNAS, 2015b).

The perfluorobutanesulfonate anion is present in the Australian environment based on domestic monitoring information. For example, PFBS has recently been detected in the Parramatta River (main tributary of Sydney Harbour) and in the Brisbane River (following major flooding) at concentrations up to 30 nanograms per litre (ng/L) (NICNAS, 2015b).

There are multiple potential sources of PFBS in the environment including past industrial use of other perfluorochemicals contaminated with this substance, use in articles, or from the use of derivatives of PFBS which degrade to this substance in the environment. Due to the use of PFBS-based chemicals as alternatives to PFOS-based chemicals, and the potential for these replacement chemicals to release PFBS, the concentrations of PFBS in the environment are expected to increase over time.

Environmental Effects

No ecotoxicity data were located for the parent chemicals in this group.

The currently available ecotoxicity data for PFBS were summarised in the IMAP-Environment Tier II assessment of Perfluorobutanesulfonic Acid and its Direct Precursors. Data currently available for PFBS indicate low acute (median lethal/effective concentration values > 372 mg/L) and chronic (no-observed-effect concentration (NOEC) values > 502 mg/L) toxicity to aquatic organisms, and low toxicity to birds (NOEC = 900 mg/kg) (NICNAS, 2015b).

It is noted that the chemicals in this group contain a range of functional groups and moieties which are correlated with acute toxic effects in aquatic organisms. However, these possible effects have not been considered in this assessment, as the primary risk posed by the chemicals in this group is assumed to result from the cumulative release of PFBS into the environment.

Predicted No-Effect Concentration (PNEC)

A PNEC was not calculated for the chemicals in this group as these substances are not expected to be released to the environment as a result of current industrial use.

Categorisation of Environmental Hazard

Insufficient data are presented in this assessment to categorise the chemicals in this group according to domestic environmental hazard thresholds (EPHC, 2009).

It is noted that direct precursors to PFBS are categorised as Persistent, but Not Bioaccumulative and Not Toxic (NICNAS, 2015b).

Risk Characterisation

Risk quotients (RQs) have not been calculated for these chemicals. The substances in this group do not appear to have any significant current uses as industrial chemicals in Australia.

However, it is noted that PFBS, which is the recalcitrant degradant assumed to be formed from each of the chemicals in this group, is highly persistent and environmental levels may continue to increase over time due to indirect release pathways. The scale and time frame of such an increase, and its relevance to characterising the long term environmental risk profile of PFBS, currently remain unknown.

Key Findings

The chemicals in this group are not expected to have significant current industrial use in Australia. Only one chemical is known to be used as an industrial chemical in Australia. This chemical is introduced in very low volumes for one specific application.

The principal risk posed by the chemicals in this group if emitted to the environment has been assumed to result from the cumulative releases of PFBS. This perfluorinated organic anion is highly persistent and mobile and, as a result, has the potential to become globally distributed. Nevertheless, currently available data indicate that PFBS is not expected to be highly bioaccumulative or toxic to aquatic organisms.

The chemicals in this group have not been categorised according to domestic environmental hazard criteria. This finding does not indicate a lack of potential hazard for some parent chemicals in this group, but rather a lack of suitable data to characterise these hazards for each individual chemical.

Recommendations

The chemicals in this group are not prioritised for further assessment under the IMAP Framework.

However, further assessment may be necessary if information becomes available indicating that these chemicals are introduced into Australia in significant quantities, or if hazard data become available indicating adverse effects on the environment from either the parent chemicals or the common PFBS degradant.

Environmental Hazard Classification

Insufficient data are presented in this assessment to classify the aquatic hazards of chemicals in this group according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS) (UNECE, 2009).

It is noted that simple salts of PFBS are not classified for aquatic hazards under the GHS based on the currently available hazard data (NICNAS, 2015b).

References

ECHA (2014a). *Pre-registered substances*. European Chemicals Agency, Helsinki, Finland. Accessed 1 May 2014 at http://echa.europa.eu.

ECHA (2014b). *Registered Substances*. European Chemicals Agency, Helsinki, Finland. Accessed 9 May 2014 at http://echa.europa.eu.

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Last update 13 February 2014

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