

6:2 Fluorotelomer sulfonamide surfactants: Environment tier II assessment

12 December 2019

CAS Registry Numbers: 34455-29-3, 94088-80-9 and 65256-46-4



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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 two closely related fluorinated surfactants (or fluorosurfactants). Both chemicals are polyfluoroalkyl substances (PFAS) which have a terminal perfluoroalkyl linear chain segment containing six carbon atoms which is linked to a sulfonamide group through an ethylene unit. Chemicals which have this polyfluoroalkyl chain as a substituent are commonly described as '6:2 fluorotelomer' substances. This terminology is used to indicate the number and arrangement of fully fluorinated and non-fluorinated carbon atoms in a linear polyfluoroalkyl chain (Buck, et al., 2011). It also indicates that these chemicals are made by a process which involves telomerisation, as discussed in the next section.

This group assessment also includes a chemical product that has been allocated its own CAS RN (listed on AICS). The product contains one of the fluorinated surfactants as an ingredient. The conclusions that apply to the fluorosurfactant ingredient will also apply to the chemical product. The two 6:2 fluorotelomer sulfonamide surfactants in this group are expected to ultimately degrade in the environment into short-chain perfluoroalkyl carboxylic acids (PFCA), including perfluorohexanoic acid (PFHxA). The environmental fate and effects of short-chain PFCAs have been assessed under the IMAP Framework (NICNAS, 2015a). Based on the findings of this assessment, short chain PFCAs are considered to be extremely persistent and mobile environmental contaminants. However, they are not currently considered to pose a bioaccumulation or toxicity hazard and they are, therefore, considered to be of lower overall concern than homologous long-chain PFCAs, including perfluorooctanoic acid (PFOA).

Both chemicals in this group have industrial uses as surfactants in aqueous film forming foams (AFFF), a special class of firefighting foams used to extinguish fires fuelled by flammable liquids and gases such as hydrocarbons. This use pattern has the potential to result in significantly more concentrated emissions to the environment than is typical for the other indirect precursors to short-chain PFCAs on the Inventory. These two chemicals have, therefore, been assessed separately from other indirect precursors to short-chain PFCAs under the IMAP Framework.

The purpose of this separate assessment is to consider the currently available information regarding the environmental transformation of these two chemicals and to establish whether it is possible to determine: (a) the likely rate of biodegradation of these two chemicals into their terminal PFCA degradants; (b) whether persistent and/or bioaccumulative intermediate degradants are formed following the release of these chemicals to the environment; and (c) whether current risk management measures applicable to the use of fluorosurfactants in AFFFs are sufficient for the chemicals in this group.

The separate IMAP Environment Tier II assessments of direct and indirect precursors to short-chain PFCAs have both been used as reference assessments (NICNAS, 2015a, b). These assessments should be consulted by those interested in the impacts of cumulative emissions of short-chain PFCAs on the environment.

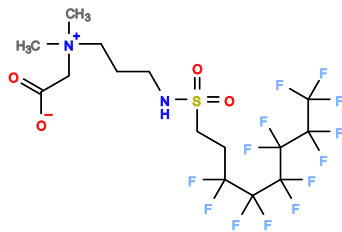
Chemical Identity

The two chemicals in this group are closely similar, except for the structure of their polar head-groups. The first chemical in this group (CAS RN 34455-29-3; 6:2 FTSAB) is an inner salt (or betaine) in which the polar head-group has an ionised carboxymethyl unit bonded to a quaternary nitrogen atom. This intramolecular arrangement of an anionic carboxymethyl function adjacent to a cationic nitrogen centre affords an amphoteric surfactant wherein the polar head-group has no net charge, except when the terminal carboxylate group is protonated under acid conditions. This chemical is the fluorosurfactant ingredient in the chemical product identified as Forafac 1157 (CAS RN 65256-46-4). The other chemical (CAS RN 94088-80-9; 6:2 FTSAQ) is a quaternary ammonium salt in which the carboxymethyl unit of the betaine has been replaced by a non-ionic methyl substituent. This polyfluorinated organic cation is a cationic surfactant.

Both chemicals belong to a larger group of PFASs that are collectively described as 'fluorotelomer-based' surfactants (Buck, et al., 2011). All of the chemicals in this larger group of specialty industrial chemicals are derived from a limited range of fluorotelomer intermediates. The manufacturing processes used to make these intermediates relies on the controlled addition of a perfluorinated olefin to a perfluoroalkyl iodide, followed by termination of the reaction by addition of ethylene (CAS RN 74-85-1), in a process called telomerisation. The length of the perfluoroalkyl chain in the fluorotelomer intermediates and their derivatives is dependent on the carbon chain lengths of both reactants and the number of olefins that are added to the starting perfluoroalkyl iodides during telomerisation. For example, the six perfluorinated carbon atoms in a 6:2 fluorotelomer chain are obtained by the addition of two molecules of the perfluorinated olefin, tetrafluoroethylene (CAS RN 116-14-3), to pentafluoroethyl iodide (CAS RN 354-64-3) (Lehmler, 2005).

Historically, fluorotelomers were manufactured with a range of carbon atom chain lengths, which included chemicals with eight or more perfluorinated carbon atoms. Fluorotelomers with eight or more perfluorinated carbon atoms are potential precursors to long-chain PFCAs, including PFOA, and there are now regulatory controls on their production and use (NICNAS, 2015c). Since 2005, the major global manufacturers of fluorotelomers have modified their processes to first reduce and then finally eliminate the production of fluorotelomers containing eight or more perfluorinated carbon atoms (US EPA, 2019a). These changes have also included introducing new processes to minimise or eliminate PFCA impurities from technical materials placed onto the market (DuPont, 2010). Consequently, when these chemicals are manufactured according to contemporary standards the commercially available technical materials would be expected to contain very low levels of long-chain PFCAs or their potential precursors. However, the presence of long-chain PFCAs or their potential precursors in chemical products such as AFFFs remains a potential concern which will be considered in this assessment.

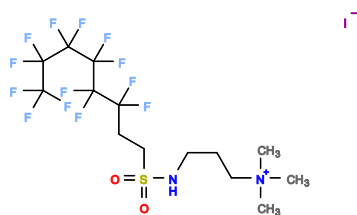
CAS RN	34455-29-3
Chemical Name	1-Propanaminium, <i>N</i> -(carboxymethyl)- <i>N,N</i> -dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, hydroxide, inner salt
Synonyms	6:2 fluorotelomer sulfonamide alkyl betaine (6:2 FTSAB)
Structural Formula	



Molecular Formula	C ₁₅ H ₁₉ F ₁₃ N ₂ O ₄ S
Molecular Weight (g/mol)	570.37
SMILES	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCS(=O)(=O)NCCC[N+](C)(C)CC(=O)[O-]

CAS RN	94088-80-9
Chemical Name	1-Propanaminium, <i>N,N,N</i> -trimethyl-3-[[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, iodide
Synonyms	6:2 fluorotelomer sulfonamide propyltrimethylammonium iodide (6:2 FTSAQ)

Structural Formula



Molecular Formula	C ₁₄ H ₂₀ F ₁₃ N ₂ O ₂ S.I
Molecular Weight (g/mol)	654.27
SMILES	C[N+](C)(C)CCCNS(=O)(=O)CCC(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F.[I-]

The Inventory listing for Forafac 1157 is known to refer to a chemical product which contains 6:2 FTSAB (CAS RN 34455-29-3) at a concentration of 27 wt% in a solvent consisting of a mixture of ethanol and water (RSC Information Services, 1995; UNEP, 2012). This product is a fluorosurfactant concentrate for use in AFFF formulations. For the purposes of this assessment, discussion and conclusions relating to 6:2 FTSAB are considered to apply to this product, and it will not be separately assessed.

CAS RN	65256-46-4
Chemical Name	Forafac 1157

Physical and Chemical Properties

Physical and chemical property data for 6:2 fluorotelomer sulfonamide alkyl betaine (6:2 FTSAB) were reported in the dossier for this chemical that was submitted under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation in the European Union (REACH, 2018):

Chemical	6:2 FTSAB
Physical Form	solid
Melting Point	≥ 150°C (exp.)
Vapour Pressure	0.017 Pa at 25°C (exp.)
Ionisable in the Environment?	yes

The terminal perfluorohexyl chain segment common to both chemicals in this group has both hydrophobic and lipophobic characteristics. This combination of characteristics confers unusual properties on these and other fluorosurfactants, including high surface activity (Lehmle, 2005). Surfactants lower the surface tension of the solvent in which they are dissolved and surface activity is often characterised by measuring this reduction in surface tension. The surface tension of a solution of 6:2 FTSAB in water has been measured and was found to be 17.0 millinewtons per metre (mN/m) at 20°C (REACH, 2018). This is a very low value for the surface tension of water and indicates that 6:2 FTSAB has high surface activity. No surface tension measurements were identified for 6:2 FTSAQ, but the structural similarity of this fluorinated quaternary ammonium cation to 6:2 FTSAB, and the identified use of both chemicals as fluorosurfactants indicates that they are likely to have comparable surface activity.

Import, Manufacture and Use

Australia

6:2 FTSAB has reported use as a surfactant in fire suppressant products.

Forafac 1157, identified by CAS RN 65256-46-4, was previously introduced to Australia, but has now been discontinued. This product contained 6:2 FTSAB as an active ingredient.

No specific Australian use, import, or manufacturing information was identified for 6:2 FTSAQ.

Fluorotelomer-based surfactants are one of the active components in AFFF products. AFFFs are a type of Class B firefighting foam which are used to extinguish fires fuelled by a range of flammable liquids including oils, gasoline, solvents and alcohols (ITRC, 2018). When mixed with water, AFFFs produce an aqueous film which spreads across the surface of a flammable liquid fire. This film both extinguishes the flame and prevents reignition (burnback) by forming a vapour barrier between the fuel and oxygen in the atmosphere (Baduel, et al., 2015; ITRC, 2018). AFFFs are primarily used in the petroleum and chemical industry, in the aviation industry, and in the military, where large quantities of flammable liquids are regularly stored and used.

According to a recent overview of AFFFs which was prepared by the Interstate Technology Research Council (ITRC) in the United States of America (USA), AFFFs can be categorised into legacy PFOS (perfluorooctanesulfonate)-based AFFF, legacy fluorotelomer AFFF containing short-chain and long-chain PFASs, and modern fluorotelomer AFFF containing only short-chain PFASs (ITRC, 2018). Although modern AFFFs are only intended to contain short-chain PFASs, according to the ITRC they may still contain trace amounts (parts per billion (ppb) levels) of PFOA and PFOA precursors as impurities (ITRC, 2018).

Currently available information indicates that AFFFs used in Australia contain fluorotelomer-based surfactants and, hence, may contain chemicals in this group. The Australian Government Department of Defence is currently using fluorotelomer-based AFFFs which do not contain PFOS and PFOA as active components and these are only used in emergency situations or in controlled environments to test equipment (Australian Government Department of Defence, 2019). Airservices Australia has not used PFAS-based firefighting foams since 2010 at any of the 24 civilian airports where they are responsible for Aviation Rescue Fire Fighting Services (ARFFS) (Airservices Australia, 2018).

International

Based on available international data, the two 6:2 fluorotelomer sulfonamides in this group are principally used as fluorosurfactants in AFFF products.

6:2 FTSAB and chemicals with similar structures are reported to be components of firefighting foams and commercial surfactant concentrates used in the USA and Canada (Buck, et al., 2011; D'Agostino and Mabury, 2014; Jensen, et al., 2008; Place and Field, 2012; SFT, 2007). 6:2 Fluorotelomer sulfonamide alkylamines, which are analogous to 6:2 FTSAQ, were also identified in a number of AFFF formulations and commercial fluorinated surfactants used in the USA and Canada (Buck, et al., 2011; D'Agostino and Mabury, 2014 ; Jensen, et al., 2008; Place and Field, 2012; SFT, 2007).

6:2 FTSAB is manufactured and/or imported in the European Economic Area in volumes of 100–1000 tonnes per year (ECHA, 2018). In addition to use in firefighting foams, the chemical has reported uses in other products such as inks and toners, paper chemicals and dyes, polymers, semiconductors and textile treatment products and dyes, polishes and waxes and washing and cleaning products (ECHA, 2018). 6:2 FTSAB was also registered as a flame retardant and extinguishing agent in Nordic countries (Nordic Council of Ministers, 2016).

Environmental Regulatory Status

Australia

NICNAS has developed an action plan and data requirements to assess and manage chemicals with a perfluorinated chain of four or more carbons which may degrade to perfluorinated carboxylic acids, perfluoroalkyl sulfonates and similar chemicals. The primary assumption outlined in this action plan is that chemicals with a perfluorinated carbon chain terminated with an alkyl or aryl group will degrade to form a mix of perfluorocarboxylic acids, with both the original perfluorinated chain length and one less perfluorinated carbon atom (NICNAS, 2019a). Data for other perfluorinated chemicals suggest that the major product of environmental biodegradation will be perfluorocarboxylic acids with one less perfluorinated carbon atom (NICNAS, 2015c). Under the NICNAS action plan, hazard information for PFOA is used to estimate the hazard of perfluorocarboxylic acid (PFCA) degradation products (with four or more perfluorinated carbons) unless sufficient toxicological data are available to demonstrate a lower toxicity profile.

NICNAS has recommended that PFOS and related PFAS chemicals be restricted to only essential uses (NICNAS, 2019b). For firefighting, it is recommended that Class B foams based on these chemicals should only be used where there are no suitable and less hazardous alternatives, and they should not be used for training purposes to minimise dispersal in the environment (NICNAS, 2019c). It is also recommended that PFOS not be replaced by PFOA as an alternative and industry should ensure that the alternative chemicals used are less toxic and not persistent in the environment (NICNAS, 2019b).

NICNAS has data requirements for notification of new industrial chemicals and polymers that require PFAS impurities and/or residual monomers to be characterised (NICNAS, 2019a). Generally, impurities and residual monomers containing perfluorinated chains will need to be characterised at greater than or equal to 100 parts per million (ppm); however, where a new chemical or polymer has a food contact application, impurities and residual monomers should be characterised at greater than or equal to 1 ppm (NICNAS, 2019a).

The National Chemicals Working Group of the Heads of EPAs Australia and New Zealand (HEPA) has developed the *PFAS National Environmental Management Plan* (PFAS NEMP) which provides governments with a risk-based framework for the environmental regulation of PFAS-contaminated materials and sites (HEPA, 2018).

Some state governments in Australia have introduced regulations regarding the management of PFAS containing firefighting foams, which could impact the use, release, and disposal of chemicals in this group in these states. In South Australia, the Environmental Protection Agency prohibited potentially hazardous fluorinated firefighting foams on 30 January 2018 (EPA South Australia, 2018). This prohibition covers any firefighting foam containing a fluorinated organic compound or compounds, which would include the chemicals in this group.

The Queensland Government Department of Environment and Heritage Protection (now the Department of the Environment and Science) has introduced a policy for the environmental management of firefighting foams (Queensland Government, 2016). In Queensland, foams containing short-chain fluorotelomers (i.e., fluorotelomers with a perfluorohexyl (C6) or shorter perfluoroalkyl chain) can be used in situations when they are the only viable option, after firefighting effectiveness, short and long-term health, safety and environmental risks and property protection characteristics have all been appropriately considered. However, end-users must be aware of the foam composition and it must be 'C6 purity compliant'. For the purposes of this policy, C6 purity compliant means it must not have greater than 50 mg/kg of total impurities in the concentrate for any compounds where the *perfluorinated* part of the carbon chain is longer than 6 carbon atoms (e.g. PFOA and PFOA precursors), but excluding PFOS which has a separate impurity limit of 10 mg/kg. In addition, there must be no releases to the environment and all releases must be fully contained on site, and all wastes must be disposed of as regulated waste to a facility authorised to accept such wastes (Queensland Government, 2016).

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, 2013).

The OECD has been leading an international collaboration on the scientific assessment of, and surveys of, perfluorinated chemicals (OECD, 2018). Since July 2000, Australia has been actively involved in this work through NICNAS.

Canada

6:2 FTSAB is listed on the Canadian Domestic Substances List (DSL) (Environment and Climate Change Canada, 2018). It was categorised as P, but not B and not iT_E during the Categorization of the DSL (Environment and Climate Change Canada, 2019). 6:2 FTSAQ is not listed on the DSL (Environment and Climate Change Canada, 2018).

European Union

6:2 FTSAB is registered for use in the EU under the REACH legislation (ECHA, 2018). 6:2 FTSAQ is pre-registered under the REACH legislation (ECHA, 2017).

United States of America

6:2 FTSAB is listed on the Toxic Substances Control Act (TSCA) Inventory and has 'active' status which indicates that it has recently been manufactured, imported or processed by industry in the USA (US EPA, 2019b).

In January 2006, the United States Environmental Protection Agency (US EPA) launched a global PFOA stewardship program. The eight major companies that manufacture fluoropolymers and telomers committed to reduce facility emissions of all PFOA, PFOA precursors and related chemicals by 95% by no later than 2015 (compared to 2000 baseline). All participating companies have stated that they have met the goals of the program, and most have stopped manufacturing and importing long-chain PFASs and have now transitioned to alternative chemicals (US EPA, 2019a).

Environmental Exposure

The use of these chemicals in firefighting foams is expected to present the greatest potential for environmental exposure. Releases of these chemicals to the environment can result from the use of AFFFs during firefighting emergency response, and during firefighting training exercises and system and equipment testing.

PFOS used historically in legacy firefighting foams in training exercises and firefighting in Australia is estimated to have a final environmental fate of 65% in surface water, 10% in groundwater, 14% in land and soil and 11% in landfill (Australian Government Department of Environment and Energy, 2017). The direct environmental release of these foams has resulted in localised contamination at many sites of AFFF use (Airservices Australia, 2018; Australian Government Department of Defence, 2003, 2019; Australian Government Department of Environment and Energy, 2017 ; NSW EPA, 2018).

Direct environmental release of the chemicals in this group in firefighting foams is therefore of high concern. A field study has shown high concentrations of chemicals in this group and their degradation products in the environment after fluorotelomer-based AFFFs have been deployed during emergency responses in Canada (Mejia-Avenidaño, et al., 2017). However, historical use and controls of PFAS-containing firefighting foams that have led to widespread contamination may not be reflective of current industry standards and practice.

AFFFs currently in use are stored and used in locations with high possibilities of fire involving flammable hydrocarbons and other liquids. These sites include airports, oil and gas industries, and chemical manufacturers. AFFFs may also be used in offshore applications, such as on ships and oil rigs, where the very high safety risk in the event of fire necessitates stringent fire safety measures (Australian Government Department of Defence, 2003; Offshore Technology Reports, 2015). AFFFs may be deployed using portable firefighting equipment, firefighting vehicles, or fire suppression systems. Typically, AFFFs are stored as a concentrate which is mixed with water using a proportioning system when deployed (Australian Government Department of Defence, 2003).

During emergency response use of AFFFs, rapid extinguishing of the fire and regard for firefighter and public safety is generally of primary concern, and may preclude measures to limit environmental exposure. AFFF exposure in these scenarios may also be accompanied by significant amounts of flammable liquids. Emergency use of these foams in fixed fire suppression systems installed at sites of significant flammable liquid use or storage frequently have preinstalled containment measures that are designed to reduce or prevent environmental release. Most of the immediate environmental release is expected to be to the soil compartment, with subsequent exposure to aqueous compartments dependent on proximity of surface waters and depth of the water table (HEPA, 2018).

A relatively larger total volume of firefighting foams is expected to be used in training and system and equipment testing as opposed to use in emergency response, and therefore these uses are expected to present a greater total potential for environmental release (Australian Government Department of Defence, 2003; Baduel, et al., 2015; FFFC, 2016; FPAA, 2017). A common training ground for Class B firefighting training involves a concrete slab with a mock-up structure or vehicle, which is doused with flammable liquid and ignited (Baduel, et al., 2015). Fixed fire suppression systems using AFFFs are periodically tested, generally on an annual basis (Australian Government Department of Defence, 2018a). Environmental exposure may occur though incomplete containment of discharged foam, which may contain PFAS chemicals at concentrations of mg/L (Baduel, et al., 2015; Weiner, et al., 2013). Fire training infrastructure that has been exposed to PFAS on a regular basis can also be important

sources of long-term release of PFAS through rainfall run off (Baduel, et al., 2015). Again, the immediate release is likely to be to the soil compartment, with the likelihood of subsequent exposure to aqueous bodies dependent on site-specific considerations.

A number of best practice management guidelines and policies for the use of PFAS-containing Class B firefighting foams from Australian industry and government bodies include a range of measures expected to greatly reduce environmental emissions of these chemicals. These measures generally include but are not limited to: the use of surrogate liquids in place of PFAS-containing foams in training and system and equipment testing, implementation of proper containment and disposal of foams and firewater, and the use of alternative Class B fluorosurfactant-free foams in firefighting applications where capability requirements and performance standards are met (Australian Government Department of Defence, 2018b; FPA, 2017; Queensland Government, 2016).

Environmental Fate

Partitioning

Both chemicals in this group are expected to significantly sorb to soil and sediment. There, they may serve as a long-term reservoir for their more mobile terminal degradants.

Both 6:2 FTSAB and a very close structural analogue of 6:2 FTSAQ showed high sorption strength to soils with varying characteristics in batch sorption experiments using a commercially available AFFF (Barzen-Hanson, et al., 2017a). In a Canadian field study, 6:2 FTSAB and chemicals with similar structures were detected in soil compartments and sediments collected at an AFFF-impacted site (Mejia-Avenidaño, et al., 2017; Munoz, et al., 2017).

6:2 FTSAB was also one of the predominant PFASs found in surface soil of a firefighting training site used for more than three decades (Dauchy, et al., 2019). The same study showed that 6:2 FTSAB can reach a water table 20 m below the surface indicating that the parent chemicals in this group may leach into groundwater.

An investigation of an Australian AFFF-impacted site found that the soil and drainage system sediment contained a variety of perfluoroalkyl acid (PFAA) precursor compounds, which were generally not found in surface and groundwater at the same site (Casson and Chiang, 2018). The most abundant PFAS chemicals found in surface and groundwater were the terminal PFAA degradants, confirming further that PFAA precursors have significantly partitioned to the solid phase with subsequent transformation to more mobile short-chain PFAAs.

The short-chain PFCA terminal degradation products of the chemical in this group, which are further discussed below, are expected to show high mobility in the environment and readily leach from soil to surface water and groundwater. However, the presence of other AFFFs components (solvents, hydrocarbon surfactants and additives), unburned fuel, site-specific soil chemistry, hydrodynamic and climate conditions will significantly affect partitioning behaviour and transport of parent chemicals and their degradation products at sites impacted by AFFFs (Guelfo and Higgins, 2013).

Degradation

Both chemicals in this group are expected to biodegrade slowly in the environment and ultimately form short-chain PFCAs as the terminal degradants.

6:2 FTSAB underwent photolysis in water to produce a number of degradants, including 6:2 fluorotelomer sulfonic acid (6:2 FTSA; CAS RN 27619-97-2) and short-chain PFCAs (Trouborst, 2016). This pathway may be a dissipation pathway for the chemical in sunlit surface waters depleted in dissolved organic carbon. However, this is not expected to be a major degradation pathway for the chemicals in this group.

6:2 FTSAB was shown to undergo microbial degradation to short-chain PFCAs by both microbial consortia in wastewater treatment plant sludge and by isolated pure culture through similar pathways (D'Agostino and Mabury, 2017; Shaw, et al., 2019). 6:2 FTSA was not found in significant amounts among the quantifiable degradation products. This indicates that, unlike some other sulfur-containing 6:2 fluorotelomer compounds, the environmental biodegradation of the chemicals in this group is not likely to be a major source of 6:2 FTSA. Some of the quantifiable intermediates included 6:2 fluorotelomer sulfonamide and 6:2 fluorotelomer alcohol (6:2 FTOH), 6:2 fluorotelomer unsaturated carboxylic acid, 6:2 fluorotelomer carboxylic acid (FTCA), 5:3 FTCA, 5:2 fluorotelomer ketone and short-chain PFCAs including perfluorohexanoic acid (PFHxA), perfluoropentanoic acid

(PFPeA), and perfluorobutanoic acid (PFBA) (D'Agostino and Mabury, 2017; Shaw, et al., 2019). The presence of these intermediate and terminal degradants in incubation studies is consistent with the established microbial degradation pathways for fluorotelomer compounds and indicates that the chemicals in this group will degrade primarily to short-chain PFCAs (D'Agostino and Mabury, 2017; NICNAS, 2015b; Shaw, et al., 2019).

The microbial degradation rates of chemicals in this group and yields of degradation products are influenced by environmental conditions such as microbial activity, nutrient status, pH, redox conditions, hydrodynamic and climate conditions. For example, an isolated strain degraded 70.4% of 6:2 FTSAB in 7 days under sulfur-limiting conditions. In contrast, slow biodegradation of 6:2 FTSAB and 6:2 FTSAA occurred over 109 days with microbial consortia under aerobic conditions. Both chemicals degraded slowly but the exact rates are not known due to incomplete mass recoveries and significant loss of parent chemicals in the experimental setup (D'Agostino and Mabury, 2017). Intermediate degradation products such as 6:2 fluorotelomer sulfonamide were shown to persist for several months in the incubation study with wastewater treatment sludge (D'Agostino and Mabury, 2017).

Field studies conducted at AFFF-impacted areas in Canada indicate that the chemicals in this group are expected to degrade to PFCAs in soil. PFASs including 6:2 FTSAB were measured in soils following the use of 33 000 L of AFFF concentrate in response to a fire at a train derailment in the town of Lac-Mégantic (Mejia-Avendaño, et al., 2017). In comparison to soil collected immediately after the accident, soil collected two years after the accident showed an increase in the proportion of PFCAs and a decrease in the proportion of precursor PFAS including 6:2 FTSAB, which was concluded to be due predominantly to biotransformation.

Bioaccumulation

The chemicals in this group and their degradation products are not expected to significantly bioaccumulate or biomagnify in aquatic food webs based on the currently available information.

A bioconcentration study was conducted according to OECD Test Guideline (TG) 305 using carp with nominal concentrations of 5 and 50 µg/L of 6:2 FTSAB (REACH, 2018). While this study did not determine a steady-state BCF, the results indicated relatively low bioaccumulation potential for this chemical in fish.

Short-term laboratory studies (48–96 hours) showed that 6:2 FTSAB was metabolised by both blue mussel (*Mytilus edulis*) and turbot (*Scophthalmus maximus*) (Moe, et al., 2012). In these studies the 6:2 fluorotelomer sulfonamide moiety was retained in most of the identified metabolites (Moe, et al., 2012).

Field studies have provided evidence of biotransformation of long chain 8:2 and 10:2 FTSAB homologues in benthic fish collected from AFFF-impacted freshwater lake and river in Canada (Munoz, et al., 2017). In this study the concentrations of fluorotelomer sulfonamide betaines were shown to decrease in fish over one year with detection of intermediate biotransformation products including fluorotelomer sulfonamides and fluorotelomer carboxylic acids (Munoz, et al., 2017).

The short-chain PFCA terminal degradants of the chemicals in this group are not expected to be bioaccumulative based on the currently available evidence (NICNAS, 2015a).

Transport

Parent Chemicals

The parent chemicals in this group are not expected to undergo long-range transport.

The parent chemicals in this group are expected to have low volatility and they will partition to solid phases in the environment based on their ionic and surface-active properties which will limit their potential for long range transport. However, they do have the potential to migrate from AFFF-impacted sites by transport in surface water run-off into waterways and by leaching through the soil horizon into groundwater.

Degradation products

The degradation products of the chemicals in this group are expected to undergo long-range transport.

Volatile microbial degradation products of the chemicals in this group such as 6:2 FTOH may partition to the atmosphere (D'Agostino and Mabury, 2017; Shaw, et al., 2019). In the atmosphere, oxidation by chlorine or hydroxyl radicals is expected to contribute to the formation of short-chain PFCAs (NICNAS, 2015b). The global distribution of these persistent environmental contaminants is generally attributed to atmospheric transport of acids, transport of anions in surface waters or ocean currents, and/or transport of volatile precursors such as FTOH (NICNAS, 2015b).

Predicted Environmental Concentration (PEC)

PECs were not calculated for the chemicals in this group as any environmental contamination is site-specific and strongly influenced by the circumstances of the AFFF use and the characteristics of the local environment. No Australian monitoring data have been identified for the parent chemicals in this assessment.

Interpretation of domestic and international environmental monitoring results at AFFF-impacted sites is challenging due to the limited available information about historic use and chemical composition of the AFFF formulations used. This information is often not available as PFAS identities in AFFF formulations and concentrates are typically proprietary. Also, most monitoring studies only quantify a small sub-set of priority PFASs because quantification methods are not available for all of the very large number of possible PFAS contaminants that may be present at these sites. In some cases, a measure of total PFAS contamination is reported which is based on the total oxidisable precursor assays (TOPA) (Casson and Chiang, 2018; HEPA, 2018). No environmental studies of AFFF-impacted sites in Australia that directly monitored either of the chemicals in this group were identified for this assessment. The individually quantified PFAS contaminants were generally long-chain and short-chain PFCAs, perfluoroalkylsulfonates and fluorotelomer sulfonates (Baduel, et al., 2015; Casson and Chiang, 2018).

Available international data indicates that 6:2 fluorotelomer-based derivatives including chemicals in this group have been detected in surface water, groundwater, soil, sediment and biota near sites of AFFF use at military facilities, civilian airports, and accident sites (Barzen-Hanson, et al., 2017b; Dauchy, et al., 2019; Mejia-Avenidaño, et al., 2017; Moe, et al., 2012; Munoz, et al., 2017). While the chemicals in this group are expected to largely partition to soils, 6:2 FTSAB has also been measured in groundwater at a concentration in the range of 4267–5350 nanograms per litre (ng/L) at an AFFF-impacted site 28 years after the explosion of an oil storage depot in France (Dauchy, et al., 2017). The chemical has also been detected in deep soil layers and in groundwater near potential aquifer entry points at a firefighting training site used for more the 30 years (Dauchy, et al., 2019).

Environmental Effects

Effects on Aquatic Life

The following measured effective concentration (EC50) values for aquatic organisms across two trophic levels were reported for 6:2 FTSAB (CAS RN 34455-29-3) in the REACH Registration Dossier (REACH, 2018):

Taxon	Endpoint	Method
Invertebrates	48 h EC50 = 144 mg/L	Experimental <i>Daphnia magna</i> (Water flea) OECD TG 202 Static

Taxon	Endpoint	Method
Algae	72 h EC50 = 3.26 mg/L 72 h NOEC = 0.087 mg/L	Experimental <i>Pseudokirchneriella subcapitata</i> (Green algae) OECD TG 201 Static

No aquatic toxicity data were identified for 6:2 FTSAQ. However, this chemical is expected to be more acutely toxic to aquatic life than 6:2 FTSAB considering the generally greater aquatic toxicity of cationic surfactants compared with analogous alkyl betaines (Madsen, et al., 2001).

The chemicals in this group are expected to ultimately degrade to the extremely persistent short-chain perfluorocarboxylic acids, the effects of which are summarised in the IMAP Environment Tier II assessments of direct and indirect precursors to short-chain PFCAs (NICNAS, 2015a, b). Based on data for PFHxA and PFBA, all short-chain perfluorocarboxylic acids, including PFPeA, were categorised as not Toxic (Not T) according to domestic environmental hazard criteria.

Categorisation of Environmental Hazard

The categorisation of the environmental hazards of 6:2 FTSAB, 6:2 FTSAQ and Forafac 1157 according to domestic environmental hazard thresholds is presented below (EPHC, 2009):

Persistence

Persistent (P). The chemicals in this group are expected to slowly degrade to short-chain PFCAs. These terminal degradants are extremely persistent in the environment. The chemicals in this group are, therefore, categorised as Persistent.

Bioaccumulation

Not Bioaccumulative (Not B). A study conducted according to OECD TG 305 indicated that 6:2 FTSAB has low bioconcentration potential in fish and there is evidence of metabolism of these chemicals in fish and mussels. The short-chain PFCA terminal degradants of the chemicals in this group have previously been categorised as Not B. The chemicals in this group are therefore categorised as Not Bioaccumulative.

Toxicity

Toxic (T). Based on measured chronic aquatic toxicity endpoint value less than 0.1 mg/L for 6:2 FTSAB, both chemicals in this group are categorised as Toxic.

Summary

1-Propanaminium, *N*-(carboxymethyl)-*N,N*-dimethyl-3-[[[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, hydroxide, inner salt (6:2 FTSAB) and 1-Propanaminium, *N,N,N*-trimethyl-3-[[[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, iodide (6:2 FTSAQ), and Forafac 1157 are categorised as:

- P
- Not B

- T

The expected terminal degradants PFHxA, PFPeA and PFBA have previously been categorised as Persistent, not Bioaccumulative and not Toxic (P, Not B, Not T) (NICNAS, 2015a).

Risk Characterisation

The two 6:2 fluorotelomer sulfonamide surfactants in this group are known to be used in firefighting foams. This use pattern may involve the direct and concentrated emissions of these chemicals into the environment. Based on detailed environmental evaluations of past uses of firefighting foams containing related fluorosurfactants, it is known that these concentrated emissions can lead to contamination of the local and surrounding environment with extremely persistent and mobile long-chain and short-chain perfluorocarboxylic acids.

The risk resulting from the release of long-chain PFAS associated with use of 6:2 fluorotelomer-based chemicals have largely been addressed by international and domestic regulations, policy and guidelines. As a result, recently manufactured chemicals in this group are expected to contain low levels of long-chain PFCAs or their potential precursors. However, there is no nationally standardised maximum allowable concentration for long-chain PFAS chemicals in AFFFs in Australia.

Direct environmental exposure of the chemicals in this group is possible through AFFF use in emergency response, accidental release, and use in training and system and equipment testing. Historical use in the absence of adequate control measures has resulted in environmental contamination of chemicals used in legacy AFFFs. This has led to the development of improved management practices by federal, state or industry bodies, which are assumed to greatly reduce the environmental exposure associated with these uses. However, there are as yet no nationally standardised best management practices for use of AFFFs containing chemicals in this group.

In situations where use of chemicals in this group is essential in firefighting foams and direct release is unavoidable, there will be both short and long-term environmental risks resulting from concentrated release in the immediate vicinity of the deployment of the AFFFs. A number of factors including soil chemistry, proximity to surface and/or groundwater, and presence of other chemicals will define the extent of the influence of the released chemicals and their degradants on the environment. The parent chemicals in this group are expected to accumulate mainly in soil and sediment, and become a long-term source of mobile and extremely persistent short-chain PFCAs. The contamination of water bodies with these PFAS chemicals may lead to secondary exposure to humans through bore water and surface water use (NICNAS, 2016).

The primary long-term risk posed to the environment by the chemicals in this group is assumed to result from the cumulative localised and dispersive release of their short-chain PFCA terminal degradants. Due to their extreme persistence, short-chain PFCA levels in the environment may continue to increase over time. The scale and time frame of such an increase and its relevance to characterising the long term environmental risk profile of these PFCAs is unknown.

Key Findings

Based on available domestic and international data, chemicals in this group have current industrial uses in fire-fighting foams. Modern manufacturing methods for chemicals in this group are expected to result in very low levels of long-chain PFAS in accordance with international and domestic regulations and policies designed to eliminate long-chain PFAS from commerce. However, there are no nationally consistent guidelines for use of firefighting foams containing long-chain PFAS impurities. Environmental exposure of products containing such impurities will contribute to the cumulative impacts of long-chain PFAS contamination of the environment.

Historic use patterns of firefighting foams suggest that there is high potential for direct release of these chemicals to the environment. These historic use patterns may not represent current practices. A number of best practice management guidelines have been adopted by governments and industry bodies which include measures expected to reduce the environmental release of the chemicals in this group through their use in firefighting foams.

Airservices Australia no longer uses fluorosurfactants in firefighting foams at civilian airports, and this is expected to reduce the risk of any additional contamination of these major facilities with PFASs as a result of their use in AFFFs for aviation rescue firefighting. Regulations on the use of fluorinated firefighting foams are in place in South Australia and Queensland and this is also expected to greatly reduce the environmental release of these chemicals through their use in firefighting foams in these states.

However, there is not a consistent national approach regarding risk management measures for the use of fluorosurfactants in AFFFs.

The chemicals in this group are expected to degrade slowly in the environment to short-chain PFCAs including PFHxA. No intermediate degradation products of greater concern than the terminal degradants were identified. Terminal short-chain PFCAs are extremely persistent and mobile environmental contaminants whose long-term environmental risk profile is currently unknown.

Recommendations

Introducers and users of the chemicals in this group should be aware of and comply with the federal, state and territory regulations and policies and industry recommendations regarding their use in AFFFs. Adherence to these regulations and practices where relevant will minimise the risks to the environment from the use of these chemicals in AFFFs.

Introducers of the chemicals should specify the quantity of long-chain PFAS impurities present in firefighting foam formulations to environmental regulators and end-users to ensure that effective best management practices are implemented prior to an emergency and during their use.

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-propanaminium, *N*-(carboxymethyl)-*N,N*-dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, hydroxide, inner salt (6:2 FTSAB) and of Forafac 1157 according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS) are 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 acute and chronic aquatic hazards posed by 6:2 FTSAB was performed based on the measured ecotoxicity data presented in this assessment and lack of rapid degradability (UNECE, 2009). The classification of the acute and chronic aquatic hazards posed by Forafac 1157 was performed according to the method for classifying mixtures under the GHS, wherein 6:2 FTSAB is considered to be the relevant ingredient for classification purposes and noting that it comprises 27% of the mixture.

Insufficient data are presented in this assessment to classify the aquatic hazards of 6:2 fluorotelomer sulfonamide propyltrimethylammonium iodide (FTSAQ) in this group under the GHS (UNECE, 2009).

It is noted that the PFHxA degradant that can be formed from both of the chemicals in this group has been classified as Acute Aquatic Category 3 (H402: Harmful to aquatic life) under the GHS.

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