Carbamic acid, [2-(sulfothio)ethyl]-, C-(.gamma.-.omega.-perfluoro-C6-9-alkyl) esters, monosodium salts: Environment tier II assessment

29 June 2018

CAS Registry Number: 95370-51-7.

Preface

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

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

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

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

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage

One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

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

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

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

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

Disclaimer

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Acronyms & Abbreviations

Rationale

This Tier II assessment considers the environmental risks associated with the industrial uses of a UVCB substance comprising sodium salts of polyfluorinated organic acids based on fluorotelomer alcohols. The organic anions in this mixture contain a terminal perfluorinated carbon atom chain segment containing four to seven carbon atoms. The perfluoroalkyl chain segment is linked to a carbamate group through a non-fluorinated ethylene unit.

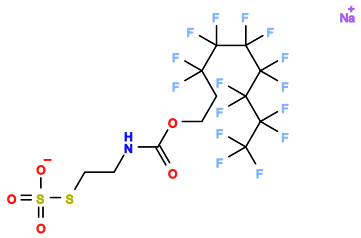
NICNAS has developed an action plan to assess and manage chemicals with a perfluorinated chain of four or more carbons which may degrade to perfluorinated carboxylic acids (PFCAs), perfluoroalkyl sulfonates and similar chemicals. Under the action plan, chemicals with a perfluorinated chain followed by an alkyl or aryl group are assumed to degrade to a mixture of PFCAs with both the original perfluorinated chain length, and with one fewer perfluorinated carbon atom. Data for other perfluorinated chemicals suggest that the major product of environmental biodegradation will be PFCAs with one less perfluorinated carbon atom (NICNAS, 2018c).

The most significant environmental biotransformation product for this substance is expected to be perfluoroheptanoic acid (PFHpA; CAS RN 375-85-9), which contains six fully fluorinated carbon atoms. The IMAP Environment Tier II assessment of PFHpA concluded that this PFCA is extremely persistent in the environment and has uncertain bioaccumulation potential and toxicity (NICNAS, 2015a). No data were available to demonstrate that PFHpA is less hazardous to the environment than the hazardous homologue, perfluorooctanoic acid (PFOA; CAS RN 335-67-1), which is a Persistent (P), Bioaccumulative (B) and Toxic (T) chemical (NICNAS, 2015b). Therefore, under the action plan, PFHpA is considered to be of equivalent concern to PFOA.

The degradation of PFHpA is very slow compared with the rate of formation from degradation of its precursor chemicals. It will therefore be assumed for the purposes of this assessment that the primary risk posed by this substance will be the release of PFHpA to the environment. The IMAP Environment Tier II assessment for perfluoroheptanoic acid (PFHpA) and its direct precursors (NICNAS, 2015a) has been used as a reference assessment.

Chemical Identity

The substance represented by CAS RN 95370-51-7 is in the category of unknown or variable composition, complex reaction products or biological materials (UVCB). This UVCB is a mixture of sodium salts of *S*-alkyl esters of thiosulphuric acid. The parent organic acids for these salts are derived from linear (perfluoroalkyl)ethyl alcohols, or n:2 fluorotelomer alcohols (n:2 FTOH) (Waldmann, 1975). The parent acid with the longest polyfluoroalkyl chain is derived from an FTOH with a terminal perfluoroalkyl chain segment containing seven carbon atoms (7:2 FTOH; CAS RN 755-02-2). Representative chemical identity information is provided below for the sodium salt of the thiosulphuric acid ester derived from 7:2 FTOH:

CAS RN	95370-51-7
Chemical Name	Carbamic acid, [2-(sulfothio)ethyl]-, C-(.gamma.-.omega.-perfluoro-C6-9-alkyl) esters, monosodium salts
Representative Structural Formula	
Molecular Formula	$C_{12}H_9F_{15}NNaO_5S_2$
Molecular Weight (g/mol)	619.30
SMILES	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCOC(=O)NCCSS(=O)(=O)[O-].[Na+]

Physical and Chemical Properties

No physical or chemical property data for this substance were identified for this assessment.

The organic anion components of this substance are expected to be surface active based on their potential application as emulsifiers in the aqueous emulsion or dispersion polymerisation of fluorinated acrylate monomers (Waldmann, 1975).

Import, Manufacture and Use

Australia

Information collected by NICNAS in 2006 indicated this substance was not manufactured, imported or used in Australia at that time (NICNAS, 2018b).

The organic acid components of this substance may be present in the environment due to historic use of the substance or through their release from articles treated with the substance. However, emissions to the environment from these sources is beyond the scope of this assessment.

International

No specific information on international uses of this substance were identified.

According to the patent literature, sodium salts of *S*-alkyl esters of thiosulphuric acid with chemical structures that include the definition of this substance can be used as anionic emulsifiers in the synthesis of side-chain fluorinated acrylate polymers. Aqueous dispersions of these fluoropolymers together with the anionic emulsifiers are used to impart oil repellent (oleophobic) finishes on porous materials such as textiles. They are also reported to be effective at imparting oleophobic properties to porous non-textile substrates such as wood, paper, leather, paving tiles, natural stone, and concrete (Waldmann, 1975).

Environmental Regulatory Status

Australia

The use of this substance is not subject to any specific national environmental regulations.

United Nations

The *S*-alkyl ester of thiosulphuric acid derived from 7:2 FTOH has a linear perfluoroheptyl moiety as a structural element. According to the Persistent Organic Pollutant Review Committee of the *Stockholm Convention on Persistent Organic Pollutants*, substances which contain a linear or branched perfluoroheptyl moiety directly attached to another carbon atom can degrade to PFOA and are categorised as “PFOA-related compounds” (UNEP, 2017). The polyfluorinated organic salt derived from 7:2 FTOH and the UVCB substance evaluated in this assessment (CAS RN 95370-51-7) are both PFOA-related compounds according to this definition.

The Committee has recommended that PFOA, its salts and PFOA-related compounds be listed under Annex A (Elimination) or Annex B (Restriction) of the Convention with specific time-limited exemptions for specialised uses in the manufacture of semiconductors, photographic films, and certain textiles for use in the protection of workers from exposure to dangerous liquids (UNEP, 2017). If this recommendation is accepted, use of these chemicals may be severely restricted globally, in advance of their eventual elimination from production and use (UNEP, 2001).

This substance is not currently identified as an ozone depleting substance (UNEP, 1987), or a hazardous substance for the purpose of international trade (UNEP & FAO, 1998).

OECD

This substance has been identified as a fluorinated chemical that potentially degrades to PFCAs (OECD, 2007). It has not been sponsored for assessment under the Cooperative Chemicals Assessment Programme (CoCAP) (OECD, 2017).

Canada

This substance is considered to be a precursor to PFOA by Canada. Precursors to PFOA are defined as those substances where the perfluorinated alkyl moiety has the formula C_nF_{2n+1} (where n = 7 or 8) and is directly bonded to any chemical moiety other than a fluorine, chlorine or bromine atom (ECCC, 2012).

PFOA and precursors to PFOA are listed under Schedule 1 of the *Canadian Environmental Protection Act, 1999* (The List of Toxic Substances) (Government of Canada, 2018). Controls have been introduced on uses of these chemicals which include a prohibition on the manufacture, use, sale, offer for sale, or import of PFOA and PFOA precursors unless the substances are present in manufactured items (ECCC, 2017).

European Union

This substance is pre-registered, but has not yet undergone the full registration process under the European Union (EU) Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2017). Under the phase-in arrangements of the REACH legislation, full registration was required for chemicals used at volumes greater than 100 tonnes per annum in 2013 (ECHA, 2014b).

Substances containing a chain of seven perfluorinated carbon atoms (with the formula C_7F_{15}) directly attached to another carbon atom are identified as PFOA-related substances in the EU (ECHA, 2014a). There are restrictions on the manufacture, use and placing on the market of PFOA-related substances in the EU under Annex XVII of the REACH legislation. From 4 July 2020, perfluorooctanoic acid, its salts and any related substance (including its salts and polymers) shall not be manufactured, or placed on the market as substances on their own. PFOA-related substances are also not to be used in the production of, or placed on the market in another substance, as a constituent; a mixture; or an article, in a concentration equal to or above 1000 parts per billion (ppb) of one or a combination of these substances (European Commission, 2017).

United States of America

This substance is not listed on the United States (US) Toxic Substances Control Act (TSCA) Chemical Substance Inventory of existing chemicals (US EPA, 2018).

Environmental Exposure

This assessment did not identify any industrial uses of this substance either domestically or internationally. Emissions of this substance to the environment from current industrial uses in Australia are, therefore, unlikely.

The organic acid components of this substance are expected to be susceptible to hydrolysis of their carbamate groups in the environment (Nielsen, 2012, 2014). Hydrolysis of these groups will release FTOHs, such as 7:2 FTOH. Biotransformation of FTOHs to PFCAs occurs by a mechanism which involves defluorination of the first perfluorinated methylene carbon atom in the chain (Butt, et al., 2014, De Voogt, 2010, Dinglasan, et al., 2004). Hence, 7:2 FTOH released by hydrolysis of the substance is expected to be metabolised to PFHpA.

If released to the atmosphere, volatile FTOHs are expected to be oxidised by chlorine and hydroxyl radicals, resulting in an ‘unzipping cycle’ that forms PFCAs of various lengths (De Voogt, 2010, Ellis, et al., 2004).

Shorter-chain FTOHs may also be released from the hydrolysis of this substance. These hydrolysis products will undergo biotic and abiotic transformation to produce short-chain PFCAs including perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutanoic acid (PFBA) (NICNAS, 2018a).

Studies have identified PFCAs, including PFHpA, in various locations worldwide including in 100% of samples taken from the Parramatta River (main tributary to Sydney Harbour) and in other locations such as Antarctica and the European Alps (Cai, et al., 2012, Kirchgeorg, et al., 2013, Thompson, et al., 2011, Zhao, et al., 2012). Perfluorocarboxylic acids are extremely persistent in the environment and they are globally distributed pollutants (NICNAS, 2015b, c, d).

Environmental Effects

There is no information available on the environmental effects of this substance.

The substance is expected to be degraded to the extremely persistent perfluorocarboxylic acid, PFHpA, in the environment. The currently available environmental hazard data for this PFCA are presented in the IMAP Environment Tier II assessment for PFHpA and its direct precursors (NICNAS, 2015a). The primary toxicity concern for PFCAs is chronic toxicity, especially intergenerational

toxicity. There is currently insufficient information to conclude whether the long-term toxicity of PFHpA is comparable to toxic long-chain homologues or to less toxic short-chain perfluorocarboxylic acids. Under the NICNAS action plan, PFHpA is assumed to be of equivalent concern to PFOA which is an extremely persistent and bioaccumulative chemical with high chronic toxicity.

The environmental effects data available for the short-chain PFCA degradants of the parent UVCB substance are presented in the IMAP Environment Tier II assessment for short-chain perfluorocarboxylic acids and their direct precursors (NICNAS, 2015d).

Categorisation of Environmental Hazard

Insufficient data are presented in this assessment to categorise this substance according to domestic environmental hazard thresholds (EPHC, 2009). The potential terminal degradant, PFHpA, is categorised as being persistent (P), and as having uncertain bioaccumulation potential (uncertain B) and uncertain toxicity (uncertain T) (NICNAS, 2015a).

Risk Characterisation

A risk quotient (RQ) has not been calculated for this substance.

The perfluorinated carboxylic acid terminal degradants assumed to be formed from the degradation of this substance may have multiple sources. Due to their extreme persistence in the environment, levels of PFCAs including PFHpA 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 PFCAs, currently remain unknown.

Key Findings

No industrial uses of this substance have been identified. It is a potential precursor to extremely persistent perfluorocarboxylic acids and if released to the environment it could contribute to the quantity of these recalcitrant pollutants present in the environment.

The substance is subject to regulatory controls in Canada and Europe including a prohibition on manufacture and use. The substance also meets the definition of a PFOA-related compound under a proposal to identify PFOA, its salts and PFOA-related compounds as persistent organic pollutants (POPs) under the *Stockholm Convention on Persistent Organic Pollutants*. This substance is, therefore, subject to significant and evolving global regulatory action.

The substance has been identified as an indirect precursor to PFHpA according to the NICNAS action plan for the assessment and management of chemicals with a perfluorinated chain of four or more carbons. The IMAP environment assessment of PFHpA has previously established that this PFCA is of equivalent concern to PFOA. Hence, industrial uses of this substance in Australia should be restricted to only essential uses and less hazardous alternatives should be used for all non-essential uses.

This substance has not been categorised according to domestic environmental hazard criteria. This finding does not indicate a lack of potential hazard for this substance, but rather a lack of suitable available data to characterise the potential hazard.

Recommendations

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

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

Environmental Hazard Classification

Insufficient data are available to classify the aquatic hazards of this substance according to the third edition of the United Nations' Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (UNECE, 2009).

It is noted that PFHpA is classified as Chronic Aquatic Category 4 (H413: May cause long lasting harmful effects to aquatic life) under the GHS (NICNAS, 2015a).

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