

# Perfluoroalkyl phosphonic and phosphinic acids: Environment tier II assessment

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## CAS Registry Numbers: 68412-68-0, 68412-69-1.

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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](http://www.nicnas.gov.au).

## Disclaimer

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### Acronyms & Abbreviations

## Grouping Rationale

This Tier II assessment considers the environmental risks associated with industrial uses of two substances which are, respectively, UVCB mixtures of perfluorinated alkyl phosphonic acids (PFPA), and perfluorinated alkyl phosphinic acids (PFPIA). The organic acid constituents of these mixtures are perfluoroalkyl acids (PFAA) in which there is a perfluorinated carbon chain attached to either a phosphonic acid or a phosphinic acid functional group through a carbon-phosphorus (C-P) bond. The perfluoroalkyl chains in the various constituent acids of both substances contain even numbers of fully fluorinated carbon atoms in the range from six to 12.

Perfluorinated alkyl and cycloalkyl acids are extremely persistent environmental contaminants. A subset of extremely persistent PFAAs such as the perfluorinated carboxylic acid, perfluorooctanoic acid (PFOA; CAS RN 335-67-1), and the perfluorinated sulfonic acid, perfluorooctanesulfonic acid ((H-)PFOS; CAS RN 1763-23-1), are also both highly bioaccumulative and chronically toxic. These chemicals and their precursors have been (or are being) phased out of use globally because of the risks they pose to the environment and human health (NICNAS, 2018a, c).

The substances in this group or some of their discrete chemical constituents have been identified as potential precursors to PFOA and longer-chain perfluorinated carboxylic acids (PFCA) in Canada and the European Union (EU). As a result, industrial uses of these substances are currently prohibited in Canada and they are restricted in the EU in accordance with regulatory actions undertaken on other indirect precursors to PFOA and longer-chain PFCAs (ECCC, 2017, European Commission, 2017).

In response to the risks posed by some classes of PFAAs, NICNAS developed an action plan which provides advice on assessing and managing chemicals which may degrade to PFCAs, perfluoroalkylsulfonates (PFSA), and similar chemicals. Perfluorinated alkyl phosphonic acids and perfluorinated alkyl phosphinic acids are not specifically discussed in the NICNAS action plan for assessing and managing chemicals with four or more perfluorinated carbon atoms but meet the definition of chemicals covered by the plan (NICNAS, 2018b). This assessment will evaluate the information currently available on the environmental fate and effects of PFPAs and PFPIAs and consider (a) whether these two classes of PFAAs both degrade to

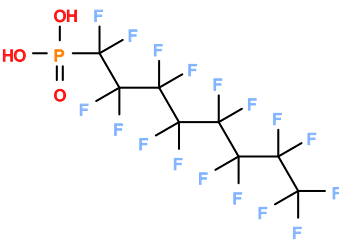
PFCAs, and (b) whether PFPAs pose similar concerns to the environment and human health as PFCAs and PFSAAs with the same number of perfluorinated carbon atoms.

## Chemical Identity

The substances in this group are produced industrially from perfluorinated organic chain compounds that are made by the telomerisation process (Buck, et al., 2011, Wang, et al., 2016). This process produces a mixture of homologous linear perfluoroalkyl chain compounds where the chain length increases in increments of two perfluorinated carbon atoms. Based on an analysis of commercial product formulations containing these two substances (D'Eon and Mabury, 2010, De Silva, et al., 2016), they are mixtures of discrete fully fluorinated organic phosphonic acids (RP(O)(OH)<sub>2</sub>) or fully fluorinated organic phosphinic acids

(RR'P(O)OH), wherein the organic groups (R and R') are linear perfluorinated chains containing six, eight, 10 or 12 carbon atoms.

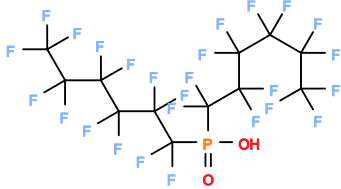
The perfluoroalkyl chain substituent in technical perfluorophosphonic acid mainly contains six, eight or 10 carbon atoms (D'Eon and Mabury, 2010). Representative chemical structure information is provided below for the homologue with eight perfluorinated carbon atoms (C8 PFPA):

|                                   |   |
|-----------------------------------|---|
| CAS RN                            | 68412-68-0  |
| Chemical Name                     | Phosphonic acid, perfluoro-C6-12-alkyl derivatives                                  |
| Synonyms                          | C6–12 PFPA<br>perfluoroalkyl (C6–C12) phosphonic acid                               |
| Representative Structural Formula |  |
| Molecular Formula                 | C <sub>8</sub> H <sub>2</sub> F <sub>17</sub> O <sub>3</sub> P                      |
| Molecular Weight (g/mol)          | 500.05  |
| SMILES                            | FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)P(=O)(O)O                  |

Technical perfluoroalkylphosphonic acid is a mixture of symmetrically di-substituted organic phosphonic acids, where the two fully fluorinated carbon chains are of the same length, and unsymmetrically substituted phosphonic acids, where the two fully

fluorinated carbon chains are of different lengths. An analysis of a commercial product formulation containing this substance found that the majority of PFPIAs present were the symmetrical congeners with either two chains of six carbon atoms (C6/C6 PFPIA) or two chains of eight carbon atoms (C8/C8 PFPIA). The unsymmetrical PFPIA congener with both a six carbon atom chain and an eight carbon atom chain (C6/C8 PFPIA) was present at comparable levels to the individual symmetrical congeners (Lee and Mabury, 2011). Other unsymmetrical congeners, C6/C10, C8/C10 and C6/C12 PFPIA, were also identified in the product formulation (D'Eon and Mabury, 2010).

Representative chemical structure information is provided below for C6/C6 PFPIA:

|                                   |  |
|-----------------------------------|--|
| CAS RN                            | 68412-69-1   |
| Chemical Name                     | Phosphinic acid, bis(perfluoro-C6-12-alkyl) derivatives  |
| Synonyms                          | C6-12/C6-12 PFPIA<br>bis(perfluoroalkyl) (C6-C12) phosphinic acid                              |
| Representative Structural Formula |              |
| Molecular Formula                 | C <sub>12</sub> HF <sub>26</sub> O <sub>2</sub> P  |
| Molecular Weight (g/mol)          | 702.07   |
| SMILES                            | FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)P(=O)(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |

## Physical and Chemical Properties

No specific physical or chemical property data were identified for the substances in this group. According to descriptive information in the patent literature (Heid, et al., 1975), mixtures of PFPAs and PFPIAs are stable towards heat, acid and oxidation.

The acid dissociation constants ( $pK_A$ ) for PFPAs and PFPIAs with long perfluoroalkyl chain substituents were inferred by Lee and Mabury (2017) from the measured  $pK_A$  of homologous phosphonic and phosphinic acids with short perfluoroalkyl chain substituents: PFFA (methyl and propyl homologues;  $pK_{A1} = 0.9-1.2$ ;  $pK_{A2} = 3.9$ ); PFPIA (dimethyl homologue;  $pK_A < 1$ ). The low measured  $pK_A$  values for these analogues indicate that the constituent acids of the substances in this group are expected

to be strong organic acids. Therefore, they are expected to readily dissociate in water to release organic mono- and di-anions from PFFPA, and mono-anions from PFPIA.

The substances in this group are expected to be surface active. According to application testing information in the patent literature (Heid, et al., 1975), mixtures of PFPAs and PFPIAs with chains of six to 12 perfluorinated carbon atoms are useful for their intended purpose as foam-dampening agents over a wide pH range (1–12) at concentrations in the range 0.001 to 0.1 grams per litre.

## Import, Manufacture and Use

### Australia

No specific Australian use, import, or manufacturing information has been identified for the substances in this group.

The constituent organic acids of both substances may be present in the environment due to their release from articles treated with these substances. However, emissions to the environment from this source are beyond the scope of this assessment.

### International

Mixtures of PFPAs and PFPIAs with chains of six to 12 perfluorinated carbon atoms are foam-dampening agents with a range of potential applications, including in the textile industry for textile finishing procedures (Heid, et al., 1975).

C6–12 PFFPA (CAS RN 68412-68-0) and C6–12/C6–12 PFPIA (CAS RN 68412-69-1) are both used in commercial fluorinated surfactant products. Two products, Masurf FS-710 and Masurf FS-780, containing both substances, are reported to have uses in the following product categories: aerosols; antimicrobial and cleaning products; industrial and automotive chemicals; polishes and floor maintenance products (Mason Chemical Company, 2018). According to the description of these products, they have anti-foam properties (Pilot Chemical, 2018). Both substances were reported to be used in Sweden in 2004 as antifoaming agents in the textile industry, and in lubricants (Keml, 2006).

C6–12 PFFPA and C6–12/C6–12 PFPIA were also reported to have uses as stain, soil, water or grease repellents in aftermarket cleaning formulations for carpets and rugs in the United States of America (USA) (Berrier, 2013a, b).

Non-industrial uses of these substances in pesticide formulations have also been identified (Keml, 2006, Mason Chemical Company, 2018, Nordic Council of Ministers, 2016).

These substances were produced in moderate volumes in the USA (4.5 to 226.8 tonnes annually) based on historical production volume information from 1998 and 2002 (Howard and Muir, 2010). Analysis of publically accessible records from Sweden, Denmark and Norway by Wang, et al. (2016) indicates that a minimum of 4.33 tonnes of C6–12 PFFPA and 3.33 tonnes of C6–12/C6–12 PFPIA were used in the period between 1999 and 2011.

The aluminium salts of C6–C12 PFFPA and C6–C12/C6–C12 PFPIA (CAS RNs 90481-10-0 and 93062-53-4) are potential direct precursors to PFAAs derived from the substances in this group. However, these two aluminium salts are not listed on the Australian Inventory of Chemical Substances and they are, therefore, assumed not to be in use in Australia (OECD, 2007).

## Environmental Regulatory Status

### Australia

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

A factsheet published by NICNAS recommends that industry seek alternatives to PFOA and chemicals that may degrade to PFOA, and ultimately aim to phase out use of these substances (NICNAS, 2016).

## United Nations

Some of the possible discrete chemical constituents of C6–12/C6–12 PFPIA are compounds that can degrade into PFOA according to the Persistent Organic Pollutant Review Committee of the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2017a). The Committee has defined any chemicals which can degrade into PFOA to be 'PFOA-related compounds'. It 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, 2017b). If this recommendation is adopted, uses of these chemicals may be severely restricted globally, in advance of their eventual elimination from production and use (UNEP, 2001).

According to the Committee, C6–12 PFPA is not a PFOA-related compound.

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

## OECD

The OECD has been leading an international collaboration on the scientific assessment of, and surveys of, perfluorinated chemicals. Since July 2000, Australia has been actively involved in this work through NICNAS. Surveys conducted by the OECD in 2004 and 2006 on the production and use of PFOS, PFSA, PFOA, PFCAs and their related substances, identified both substances in this group as present on multiple national chemical inventories. They were both categorised as substances that potentially degrade to PFCAs (OECD, 2007).

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

## Canada

The two substances in this group are considered to be precursors both to PFOA and to long-chain (C9–C20) PFCAs 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). Long-chain PFCAs are defined as perfluoroalkyl carboxylic acids with nine to 20 carbon atoms (ECCC, 2013).

PFOA and long-chain PFCAs 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 in Canada which prohibit PFOA and long-chain PFCAs and products containing them, unless they are present in manufactured items, or they are imported for use under a limited number of exemptions (ECCC, 2017).

## European Union

The substances in this group have been pre-registered, but have not yet undergone the full registration process, under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2014a, 2015). 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).

Perfluorophosphonic and phosphinic acids with chains of eight perfluorinated carbon atoms are identified as PFOA-related substances in the European Union (EU) (ECHA, 2014c). 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 substances (including 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

The definitions for both substances in this group include discrete chemical constituents which meet the category definition of long-chain perfluoroalkyl carboxylate (LCPFAC) chemicals under the Long-Chain Perfluorinated Chemicals Action Plan developed by the US Environmental Protection Agency (EPA) (US EPA, 2009). There is a Final Significant New Use Rule (SNUR) in place for substances in this category under Section 5(a)(2) of the Toxic Substances Control Act. Under the Rule, approval must be sought from the US EPA before manufacture, importation, or processing of C6–C12 PFPA or C6–C12/C6–C12 PFPIA for use as part of carpets or to treat carpets. Approval is not required when these two substances are to be used as surfactants in aftermarket carpet cleaning products (US EPA, 2013).

## Environmental Exposure

Both substances in this group have potential ongoing applications in consumer and commercial floor treatment products and in the textile finishing industry, which may result in emission of their constituent perfluoroalkyl acids to the environment.

No information on current industrial uses of C6–C12 PFPA and C6–C12/C6–C12 PFPIA in Australia was identified for this assessment. Based on composition information for fluorosurfactant products available internationally, both substances are assumed to have some ongoing uses in products such as floor polishes and waxes, and in aftermarket carpet cleaning formulations. These predominantly indoor use patterns can result in diffuse environmental emissions of PFAAs through the exchange of both air and particles between indoor and outdoor environments. Emissions can also occur indirectly through transfer of the chemicals on indoor dust into waste water that is disposed of into sewers from domestic and commercial cleaning operations (Müller, et al., 2011). Treatment of these waste waters in sewage treatment plants (STP) emits PFAAs originally on dust from indoor sources into the environment in the treated effluents and biosolids that are produced by these plants. There is also potential for release of constituent PFAAs into industrial waste water as a result of the use of the substances in this group as anti-foaming agents in textile finishing operations (OECD, 2004).

No organic derivatives of perfluorophosphonic and perfluorophosphinic acids have been identified as having industrial uses in this assessment. Hence, it is assumed that the occurrence of individual congeners of C6–C12 PFPA and C6–C12/C6–C12 PFPIA in the environment results primarily from uses of the two substances in this group. However, it should be noted that PFPIAs can be metabolised to PFPAs as outlined further below. As a result, PFPIAs are now established as indirect precursor to PFPAs. Environmental exposure to perfluoroalkyl phosphonic acids should, therefore, be considered to be a product both of emissions of PFPAs and the environmental transformation of PFPIAs.

## Environmental Fate

### Dissolution, Speciation and Partitioning

PFPAs and PFPIAs will occur as anions in the water compartment under typical environmental exposure conditions. PFPIAs with chains of six to 12 perfluorinated carbon atoms are expected to partition to soil and sediment, whereas PFPAs with similar chain lengths will be present both in the sediment and water compartments.

PFPAs and PFPIAs are strong acids and it can be assumed that dissolution of the acids in water will involve dissociation into the conjugate base anions. These will be the predominant species in water under typical environmental conditions. The environmental partitioning (water – sediment) of PFPAs and PFPIAs is dependent on the number of perfluorinated carbons, the charge on the head-group, and the chemistry of the solid phase. PFPAs (which will occur in water primarily as di-anions) have been observed to desorb from soils, suggesting they are more likely to occur as contaminants in water than comparable PFPIAs (Lee and Mabury, 2017).

PFPIAs with long perfluoroalkyl chains are likely to preferentially sorb to solid phases in the environment. In a study by Lee and Mabury (2017), the sorption of PFPIAs to soils was found to be greater than that for PFSAs, PFPAs and PFCAs, and sorption

generally increased with perfluoroalkyl chain length. However, no significant correlation was observed between degree of sorption and the organic carbon content (%OC) of the seven soils that were tested. A recent review demonstrated that a range of soil and sediment properties are important in the partitioning behaviour of per- and poly-fluorinated alkyl substances (PFAS), including organic carbon content, pH, and clay content (Li, et al., 2018).

## Degradation

PFPA and PFPIA are resistant to abiotic degradation. PFPIA are metabolised to PFPA and 1*H*-perfluoroalkanes in fish and mammals. Biotransformation of PFPA has not been observed.

Abiotic hydrolysis of the C–P bond in PFPIA has been previously reported to yield the corresponding PFPA at high temperatures which are not expected in the environment (Mahmood and Shreeve, 1986).

Metabolism of PFPIA in both fish and rats has been observed (Joudan, et al., 2017, Lee, et al., 2012). In fish, PFPA was detected as a product of this biotransformation. In rats, both the PFPA and corresponding 1*H*-perfluoroalkane metabolite were observed, confirming that cleavage of the C–P bond had occurred. The PFPA degradation products in fish were observed at the highest concentrations in the liver, blood and kidneys, suggesting that the liver and kidneys may be the sites of biotransformation (Lee, et al., 2012). High liver-to-blood concentration ratios for both PFPIA and PFPA in rats also suggested the liver as a site of biotransformation (Joudan, et al., 2017). The same study reported that intestinal biotransformation was unlikely, as PFPIA were administered as a single dose and formation of the PFPA metabolites was observed to continue for an extended time period following administration of the dose of PFPIA.

Metabolism of PFPIA releases 1*H*-perfluoroalkanes as biotransformation products. As noted by Joudan, et al. (2017), some 1*H*-perfluoroalkanes are known to undergo further biotransformation to PFCAs. A short-chain 1*H*-perfluoroalkane, pentafluoroethane (HFC 125; CAS RN 354-33-6), was previously observed to be metabolised in rats to produce trifluoroacetic acid. This transformation requires defluorination and oxidation of the terminal difluorinated carbon atom of HFC 125 (Harris, et al., 1992). In an atmospheric reaction chamber, oxidation of 1*H*-perfluorobutane and 1*H*-perfluoroethane (HFC 125) produced small amounts of the corresponding PFCAs wherein the terminal difluorinated carbon atoms of the parent chemicals had been defluorinated and oxidised to carboxy groups (Young, et al., 2009). Based on the biotic and abiotic transformation of these short-chain analogues, long-chain 1*H*-perfluoroalkanes liberated by metabolism of congeners from C6–C12/C6–C12 PFPIA have the potential to be degraded to long-chain PFCAs such as PFOA.

Biotransformation of PFPA has not been observed. In a metabolism study, rats dosed with C8 PFPA did not produce 1*H*-perfluorooctane, indicating that PFPA are not metabolised in the same way as PFPIA (Joudan, et al., 2017). A microbial degradation study conducted according to OECD Test Guideline (TG) 309 found no evidence of biodegradation of C6, C8 or C10 PFPA after incubation for 30 days (Llorca-Casamayor, 2012).

Microorganisms are capable of cleaving the C–P bond of organophosphonates (Agarwal, et al., 2011, Quinn, et al., 2007, Wackett, et al., 1987). One bacterial enzyme pathway (the C–P lyase pathway) produces inorganic phosphate and the corresponding alkane from the cleavage of organophosphonate compounds (Villarreal-Chiu, et al., 2012, Wackett, et al., 1987). This pathway has low substrate specificity, demonstrated in a study by Wackett, et al. (1987) in which bacterial growth was supported by several organophosphonates including 2-aminoethylphosphonic acid, hydroxymethylphosphonic acid and phenylphosphonic acid. One bacterial strain was capable of cleaving the C–P bond of isopropylphosphonic acid, although this was very slow, indicating that steric hindrance impacts the rate of transformation. This presents a possible degradation pathway for PFPA, which would result in the production of 1*H*-perfluoroalkanes, which may further transform to PFCAs. However, the environmental degradation of PFPA has yet to be demonstrated.

## Bioaccumulation

C6–C12/C6–C12 PFPIA has high bioconcentration potential in fish and uncertain biomagnification potential in air-breathing animals. C6–12 PFPA has low bioconcentration potential in fish and uncertain biomagnification potential in air-breathing animals.

Similar to other perfluorinated chemicals, PFPA and PFPIA have high affinities for proteins (i.e., they are proteophilic) and they tend to partition to protein-rich tissues (D'Eon and Mabury, 2010, Ng and Hungerbühler, 2014). This behaviour is distinct from lipophilic bioaccumulative substances, which typically partition to fatty tissues.



In a bioconcentration study conducted according to OECD TG 305 (Chen, et al., 2016), zebrafish were exposed to a technical mixture of PFPAs and PFPIAs. Measured bioconcentration factor (BCF) values indicated that PFPIAs had very high bioconcentration potential, with a lowest measured whole-body BCF for C6/C6 PFPIA of 41 700 L/kg, significantly exceeding the domestic categorisation threshold of 2000 L/kg.

In a biomagnification study, dietary exposure of a mixture of C6/C6, C6/C8 and C8/C8 PFPIAs in juvenile rainbow trout gave biomagnification factors (BMF) of less than one for each congener (Lee, et al., 2012). The biotransformation of PFPIAs in fish as an additional depuration pathway contributed to these low BMF values. BMFs of less than one indicate that these chemicals have low potential to accumulate through aquatic food webs. However, the biomagnification potential of PFASs are known to differ between piscivorous and marine mammalian food webs (Kelly, et al., 2009), indicating that these measured BMF values cannot be used to infer the biomagnification potential of PFPIAs in air-breathing animals.

PFPAs are eliminated rapidly from rats. After dosing by oral gavage, the elimination half-life of C8 PFPA was calculated to be 0.95 days, with no C8 PFPA able to be detected in blood samples after 4 days (Joudan, et al., 2017). The elimination half-life for C8/C8 PFPIA administered to rats by oral gavage is 2.8 days. These elimination half-lives are shorter than those observed for PFOA (< 6 days) and PFOS (43 days) (Joudan, et al., 2017). Metabolism of PFPIAs to PFPAs and excretion of this di-anionic PFAA may be responsible for the faster elimination of PFPIAs from rats than other mono-anionic PFAAs.

The bioconcentration and biomagnification potential of PFPAs were also investigated in the studies discussed above (Chen, et al., 2016, Lee, et al., 2012). PFPAs were found to have low bioconcentration potential in zebrafish, with a measured whole-body BCF of 204 L/kg for C10 PFPA (Chen, et al., 2016), which is significantly less than the domestic categorisation threshold. Dietary exposure gave BMFs significantly less than one for the C6, C8 and C10 homologues in juvenile rainbow trout, indicating low biomagnification potential in fish (Lee, et al., 2012).

While these studies apparently indicate low bioaccumulation potential for PFPAs, the bioaccumulation characteristics, including uptake and elimination kinetics, of related perfluorinated alkyl acids such as PFCAs and PFSAAs are known to be highly variable (Wang, et al., 2016). Given the expected extremely persistent characteristics of PFPAs and the known complexity of bioaccumulation of related perfluoroalkyl acid substances, the currently available information is not considered sufficient to allow for definitive categorisation of the bioaccumulation potential of PFPAs.

## Transport

The long-range transport potential of PFPAs and PFPIAs is uncertain.

PFPAs and PFPIAs have been identified in multiple locations worldwide (Chen, et al., 2018, D'Eon, et al., 2009, De Silva, et al., 2016, Esparza, et al., 2011, Hlouskova, et al., 2013, Loi, et al., 2013). These PFAAs have also been measured in biological samples on three continents (Wang, et al., 2016). The high persistence and water solubility of PFPAs may lead to these chemicals being transported in water to remote regions.

## Predicted Environmental Concentration (PEC)

PECs for the constituent PFAAs of the substances in this group have not been calculated. No Australian environmental monitoring data are available for these chemicals.

The constituent PFAAs of the substances in this group are widely dispersed environmental contaminants based on several international monitoring studies which have measured PFPAs and PFPIAs in the environment (Wang, et al., 2016). PFPAs have been measured in Canadian, German, Japanese and Chinese surface waters at concentrations ranging from below 1 nanogram per litre (ng/L) to low ng/L levels. PFPAs have also been measured in sewage treatment plant effluents in Canada and Germany at similar concentrations. C6/C6 PFPIA and C6/C8 PFPIA were measured in domestic STP sludge from the US prior to 1996 at concentrations in the range of 2 to 3 nanograms per gram (ng/g). PFPAs and PFPIAs have been measured in indoor dust samples in Canada at levels below 1 ng/g up to 944 ng/g (C6/C8 PFPIA). A recent study measured PFPIAs in sediments taken from Lake Ontario (Guo, et al., 2016).

PFPIAs have been detected in biota in a number of different studies. C6/C6 and C6/C8 PFPIAs were found at concentrations below 1 ng/g in trout fillet samples from Lake Ontario and Lake Erie (Guo, et al., 2012), while C6/C8 and C8/C8 PFPIAs were found in benthic worms in the Hong Kong area at concentrations up to 1.9 and 0.295 ng/g respectively (Loi, et al., 2013). A

range of PFPIA congeners were found in a study investigating PFAAs in blood plasma, with total PFPIAs present at up to low ng/g levels in double-crested cormorants, northern pike, and bottlenose dolphins (De Silva, et al., 2016). PFPAs were not detected. PFCAs and PFSAAs were found at concentrations more than one order of magnitude greater than those of the PFPIAs. While the contribution of perfluoroalkyl phosphinic acids to total amounts of PFASs in blood and tissues is relatively low, these studies do demonstrate the ubiquity of PFPIAs in biota from several trophic levels.

## Environmental Effects

### Acute and chronic toxicity

The potential long-term toxicity of these substances and their constituent PFAAs is uncertain as there are no standard aquatic or terrestrial toxicity data available.

In juvenile rainbow trout, significantly lower whole-body and liver growth rates were observed in populations dosed with Masurf-780 compared to the control populations (Lee, et al., 2012), with no mortality occurring in dosed or control populations. In a 24 day uptake study of a mixture of perfluorinated chemicals in adult female zebrafish (Chen et al., 2016), no significant differences in mortality, growth, behaviour and swimming pattern were observed in all three groups (control, low and high exposure concentrations).

A study on the effects of PFPAs on the green algae *Chlamydomonas reinhardtii* (Sanchez, et al., 2015) found no difference in cellular viability after 72 h exposure to C8 and C10 PFPAs. Increased reactive oxygen species concentrations and increased lipid peroxidation were detected following exposure to C10 PFPA. Both C8 and C10 PFPA were able to alter transcription of genes related to the cell antioxidant defence system.

Developmental toxicity for a mixture of PFPAs and PFPIAs was investigated in a preliminary study in which 5–40 milligrams per kilogram body-weight per day (mg/kg bw/day) Masurf-780 was fed to pregnant mice daily through the gestation period (Tatum, et al., 2012). Neonatal survival and growth was unaffected except in the highest dose group of 40 mg/kg bw/day. Increased maternal liver weight was observed at 30 and 40 mg/kg bw/day.

There are insufficient data available to evaluate whether the toxicity of perfluorinated phosphonic or phosphinic acids can be considered similar to comparable long-chain perfluoroalkyl acid substances. The primary toxicity concern for these substances is chronic, intergenerational toxicity. The high environmental persistence and possible bioaccumulation of both PFPAs and PFPIAs increases the potential for chronic toxic effects. The potential of the constituent chemicals of the substances in this group to have high chronic toxicity is, therefore, currently assessed as uncertain.

### Predicted No-Effect Concentration (PNEC)

Use of the substances in this group will result in the environmental release of PFPAs and PFPIAs, which are extremely persistent and may be bioaccumulative. These hazard characteristics combined have the potential to result in a range of long-term effects on organisms exposed to the chemicals which cannot be readily identified through standard ecotoxicity tests. For such chemicals, it is not currently possible to estimate a safe exposure concentration using standard extrapolation methods based on laboratory screening level tests. PNECs have therefore not been derived for the chemicals in this group.

## Categorisation of Environmental Hazard

The categorisation of the substances in this group according to domestic environmental hazard thresholds (EPHC, 2009) is presented below:

### Persistence

C6–C12 PFPA

Persistent (P). PFPAs are resistant to degradation. This substance is therefore categorised as Persistent.

#### *C6–C12/C6–C12 PFPIA*

Persistent (P). PFPIAs may be metabolised into the corresponding PFPAs with no evidence of further degradation. This substance is therefore categorised as Persistent.

## Bioaccumulation

#### *C6–C12 PFPA*

Uncertain (Uncertain B). PFPAs have low bioconcentration potential in fish, but the biomagnification potential in air-breathing animals is uncertain.

#### *C6–C12/C6–C12 PFPIA*

Bioaccumulative (B). PFPIA congeners with a chain of six perfluorinated carbon atoms have a very high bioconcentration potential in fish and this substance is, therefore, categorised as Bioaccumulative.

## Toxicity

Uncertain (Uncertain T). The primary toxicity concern for the substances in this group is chronic toxicity. There is currently insufficient information available to conclude whether the long-term aquatic and terrestrial toxicity of the constituent PFAAs of the substances in this group is similar to other long-chain PFAAs. The toxicity of these substances is, therefore, categorised as Uncertain.

## Summary

C6–C12 PFPA is categorised as:

- P
- Uncertain B
- Uncertain T

C6–C12/C6–C12 PFPIA is categorised as:

- P
- B
- Uncertain T

## Risk Characterisation

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

The substances in this group have been identified as having constituent PFAAs that are persistent and bioaccumulative or potentially bioaccumulative. Chemicals with these characteristics remain in the environment and accumulate in biota over an extended period of time, even if new emissions of the chemicals cease. These characteristics can cause long-term toxic effects that are not readily identified through standard testing protocols. Substances with constituent chemicals with these hazard characteristics are, therefore, considered to be of concern for the environment.

C6–C12/C6–C12 PFPIA can be metabolised to chemicals that are potential precursors to PFCAs, including PFOA. Long-chain PFCAs such as PFOA are of high environmental concern due to their PBT properties and because they are globally distributed environmental contaminants.

## Key Findings

The substances in this group are PFAAs that are composed of discrete perfluoroalkyl phosphonic and phosphinic acids that have chains of six to 12 perfluorinated carbon atoms. They have a number of specialised industrial applications in floor treatment products and textile finishing which have the potential to release the constituent acids to the environment. Both substances are subject to regulatory controls in Canada and Europe, and C8 PFPIA is a PFOA-related compound that is being considered for listing as a persistent organic pollutant under the Stockholm Convention.

All of the constituent acids of both substances are expected to be resistant to abiotic degradation and to be extremely persistent environmental contaminants. They are widely dispersed in the environment and in biota, although they are typically present at lower levels than other PFAAs, such as PFOA and PFOS. C6/C6 PFPIA has a very high bioconcentration potential in fish and close homologues of this chemical are also expected to be bioconcentration hazards in fish. PFPAs with long perfluoroalkyl chains do not bioconcentrate in fish to a significant extent and are not considered to be an aquatic bioaccumulation hazard. The bioaccumulation potential of the constituent acids of C6–C12 PFPA and C6–C12/C6–C12 PFPIA in air-breathing animals is currently uncertain. Although PFPAs and PFPIAs are eliminated more rapidly from rats than comparable PFCAs and PFSAs, there is insufficient information to reliably extrapolate from these findings to the bioaccumulation potential in upper trophic level air-breathing animals, especially humans and other apex predators.

A plausible pathway has been identified for the biotransformation of PFPIAs to PFCAs. This pathway involves cleavage of the C–P bond of PFPIAs to release 1*H*-perfluoroalkanes which are defluorinated and oxidised to give a PFCA with one less perfluorinated carbon atom than is present in the 1*H*-perfluoroalkane metabolite. According to this scheme, PFPIAs with a perfluorooctyl chain can be metabolised to perfluorooctanoic acid. Hence, PFPIAs with at least one perfluorooctyl substituent are indirect precursors to PFOA, which is of high concern to human health and the environment. Under the NICNAS action plan, industrial uses of PFPIAs with a perfluorooctyl or longer-chain substituent should be restricted to only essential uses in Australia and less hazardous alternatives should be used for all non-essential uses.

PFPAs with long perfluoroalkyl chains have been identified as being of lower overall concern than PFPIAs with long perfluoroalkyl chain substituents. They are considered to be extremely persistent environment contaminants, but it is uncertain whether they have the same biomagnification potential and chronic toxicity as PFCAs and PFSAs with the same carbon chain length. Therefore, it is not considered appropriate to use hazard data for PFOA and PFOS as indicative of the hazard characteristics of PFPAs. However, if further hazard information becomes available for PFPAs this finding could be reconsidered.

## Recommendations

C6–C12/C6–C12 PFPIA has been assessed as having the potential to give rise to adverse outcomes for the environment. 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.

There is currently limited information regarding the biomagnification potential of PFPAs in aquatic and terrestrial mammals. This is a significant gap in the environmental hazard information for this class of PFAAs considering the demonstrated biomagnification of PFOS and PFOA in mammalian food webs. C6–C12 PFPA should, therefore, be treated as being of equivalent concern to PFOA and PFOS.

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.

## Action Plan

Perfluoroalkyl phosphinic acids (PFPIA) have been identified as indirect precursors to perfluorocarboxylic acids. It is therefore recommended that the action plan outlined in the **Data requirements for notification of new chemicals containing a perfluorinated carbon chain** should be updated to indicate that PFPIAs with a perfluoroalkyl chain containing eight or more carbon atoms are indirect precursors to long-chain PFCAs.

No change to the action plan can be recommended for PFPAs.

## 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 phosphonic acid, perfluoro-C6-12-alkyl derivatives and phosphinic acid, bis(perfluoro-C6-12-alkyl) derivatives according to the third edition of the United Nations' Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is presented below (UNECE, 2009):

| Hazard          | GHS Classification (Code) | Hazard Statement                                       |
|-----------------|---------------------------|--|
| Chronic Aquatic | Category 4 (H413)         | May cause long lasting harmful effects to aquatic life |

There are insufficient reliable data to classify the acute aquatic hazards of the substances in this group. The substances in this group were classified as Chronic Category 4 (i.e. the "safety net" classification), as they contain constituent chemicals that are extremely persistent and there are concerns that they may be bioaccumulative in aquatic ecosystems (UNECE, 2007).

It is noted that PFOA has been classified as Chronic Aquatic Category 1 (H410: Very toxic to aquatic life with long lasting effects) under the GHS (NICNAS, 2018c).

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