

Potential PFOA Precursors

Literature study and theoretical
assessment of abiotic degradation
pathways leading to PFOA.

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Preface

The Norwegian Environment Agency, in cooperation with German Environment Authorities, is preparing a report proposing regulations on PFOA (perfluorooctanoic acid), its salts and precursors. PFOA (or its ammonium salt), is mainly used as a processing aid in the production of fluoropolymers; i.e. polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). Other PFOA sources are fluorotelomers, which are not produced using PFOA, but which may contain low levels of PFOA. There are a number of products containing PFOA such as carpet care solutions, sealants, floor waxes, paints, impregnating agents, fire fighting foam, ski wax and surface coatings of carpets, textiles, paper and leather. PFOA is found in the environment and in people all over the world. PFOA is degraded very slowly in nature and is long-range transported to the Arctic. PFOA is listed as a priority pollutant covered by the national goal that emissions should be eliminated by 2020.

The overall objective of the present project is to summarize relevant information available in the open literature to provide an overall assessment of relevant precursors including possible grouping, and to evaluate possible routes to provide documentation, where missing, on the potential of abiotic degradation resulting in PFOA

The present report summarises a classification of potential PFOA precursors and outlines the transformation routes leading to PFOA.

The project has achieved its targets.

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Executive Summary

The open literature on substances included in the list of potential PFOA precursors has been reviewed with respect to abiotic environmental degradation. Experimental data and theoretical assessments of abiotic degradation pathways of potential PFOA precursors is summarized by substance class and by perfluoroalkyl chain structure. In general, substances containing a perfluorinated alkyl chain with the formula $F(CF_2)_n-$ ($n=7$ or 8) and is directly bonded to any chemical moiety other than a fluorine, chlorine or bromine atom and other than a phosphonic, phosphinic or sulfonic group will undergo abiotic degradation resulting in release of PFOA.

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1 Literature study on abiotic degradation processes of potential PFOA precursors

A list of potential PFOA precursors was compiled based on a list published by OECD (2007) and Environment Canada (2012) and results of searching the internet. The list is presented in the ANNEX (page 36) and includes the following compound classes:

- PFOA salts
- Fluorotelomer alcohols
- Fluorotelomer acrylates
- Fluorotelomer methacrylates
- Polyfluoroalkyl phosphoric acid mono- and diesters
- Polyfluorinated olefins
- Polyfluorinated iodides
- Polyfluorinated amides
- Other potential PFOA precursors
- Unknown or Variable compositions, Complex reaction products and Biological materials (UVCBs)
- Polymers

The literature on potential pentadecafluorooctanoic acid (PFOA, CAS 335-67-1) precursors referenced in the Chemical Abstract Service (CAS) by 30.09.2013 and other publicly available information, including data on www, has been examined.

Terminology, classification and origins of perfluoroalkyl and polyfluoroalkyl substances in the environment was reviewed in 2011 [Buck *et al.*, 2011]. An overview of research on perfluoroalkyl acids (PFAAs) including perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), their potential precursors and related substances was also published in 2011 [Lindstrom *et al.*, 2011].

The atmospheric gas phase chemistry of perfluorinated acid precursors was reviewed in 2010 [C. J. Young and Mabury, 2010]. The review summarizes results from around 200 scientific publications and provides detailed information on fluorotelomer iodides (FTIs), fluorotelomer olefins (FTOs), fluorotelomer alcohols (FTOHs), and fluorotelomer acrylates (FTAs). Recently, a study on the atmospheric photo-oxidation of polyfluorinated amides was published [Jackson *et al.*, 2013].

The atmospheric aqueous phase chemistry, including aqueous surface layer chemistry, of potential PFOA precursors has received little attention. The rationale behind this neglect is based on the low solubility of the known PFOA precursors, i.e. $137 \mu\text{g L}^{-1}$ at $25 \text{ }^\circ\text{C}$ for 8:2 FTOH [Kaiser *et al.*, 2004]. However, many PFOA precursors are surfactants and will conceivably undergo photo-oxidation in aqueous surface layers. Herrmann and co-workers have previously reviewed atmospheric aqueous phase chemistry [Zellner and Herrmann, 1995; Herrmann and Zellner, 1996; Herrmann, 2003; 2007]. Chemical reactions in the atmospheric aqueous phase are generally triggered by free radicals such as OH, NO₃ and SO₄⁻. In addition O₃ may contribute to the overall removal of dissolved trace gases.

Currently the only results in the open literature on PFOA related aqueous phase chemistry stem from a qualitative study of 8:2 FTOH photo-oxidation [Gauthier and Mabury, 2005], and from a study of PFOA degradation in the presence of Fe(III) under natural sunlight conditions [Liu *et al.*, 2013].

2 Abiotic degradation pathways of potential PFOA precursors

2.1 PFOA Salts

The list provided in the annex includes four PFOA salts: 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctanoic acid, ammonium salt (APFO, CAS RN 3825-26-1)
 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-octanoic acid, sodium salt (CAS RN 335-95-5)
 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-octanoic acid, potassium salt (CAS RN 2395-00-8)
 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-octanoic acid, silver salt (CAS RN 335-93-3)

The silver salt is the least soluble of the four PFOA salts with a solubility of the around 0.003 mol/L (estimated from thermodynamic measurements [Fan *et al.*, 1988]) This corresponds to around 1.6 g/L. Consequently, the commercially available PFOA salts in the list in the annex will all dissolve in water resulting in release of PFOA.

2.2 Fluorotelomer alcohols

The atmospheric gas phase lifetime of “odd-numbered” oFTOHs, $\text{CF}_3(\text{CF}_2)_x\text{CH}_2\text{OH}$, is determined by reaction with OH radicals and is in the order of 4-5 months [Chen *et al.*, 2000; M. D. Hurley *et al.*, 2004; Papadimitriou *et al.*, 2007]. The sole primary product from the reactions is the corresponding aldehyde (oFTAL) [M. D. Hurley *et al.*, 2004]. Further atmospheric photo-oxidation of oFTALs will result in the corresponding PFCA [Sulbaek Andersen *et al.*, 2003; Sulbaek Andersen *et al.*, 2004]

The atmospheric gas phase lifetime of FTOHs, $\text{CF}_3(\text{CF}_2)_x\text{CH}_2\text{CH}_2\text{OH}$, is determined by reaction with OH radicals and is in the order of 10-20 days [D. A. Ellis *et al.*, 2003; Kelly *et al.*, 2004; Michael D. Hurley *et al.*, 2005; Papadimitriou *et al.*, 2007]. The dominant primary product from the reactions is the corresponding aldehyde, FTAL [David A. Ellis *et al.*, 2004; M. D. Hurley *et al.*, 2004; Kelly *et al.*, 2004; Michael D. Hurley *et al.*, 2005; Wallington *et al.*, 2006; Papadimitriou *et al.*, 2007; Chiappero *et al.*, 2008]. The atmospheric lifetimes of FTALs, *i.e.* $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$, is determined by reaction with OH radicals and is in the order of a few days [Sellevåg *et al.*, 2004; Chiappero *et al.*, 2006; Solignac *et al.*, 2007].

The atmospheric chemistry of 8:2 FTOH (CAS RN 678-39-7) was studied by Wallington *et al.* [Wallington *et al.*, 2006], who also reported a simplified mechanism for the atmospheric degradation of 8:2 FTOH illustrating its conversion via the intermediate $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ (8:2 FTAL), and the competition between NO and HO_2 (or RO_2) radicals that limits the formation of perfluorocarboxylic acids. The mechanism is also applicable to larger FTOHs. Results from a 3-D global atmospheric chemistry model showed that PFNA (perfluorononanoic acid), PFOA, and other smaller PFCAs are significant products of the atmospheric oxidation of 8:2 FTOH, and that the PFOA yield is somewhere between 3 and 6% on a per-emissions basis in the Northern Hemisphere [Wallington *et al.*, 2006].

The aqueous phase photo-oxidation of 8:2 FTOH was investigated in 2005 [Gauthier and Mabury, 2005]. The major products detected were ~60% 8:2 FTCA ($\text{C}_8\text{F}_{17}\text{CH}_2\text{COOH}$) and ~40% PFOA; 8:2 FTAL was observed as a short-lived intermediate that underwent further photo-oxidation to PFOA. 8:2 FTCA was shown to undergo aqueous phase photo-oxidation leading to PFOA as the major product. It therefore appears that aqueous phase photo-oxidation of 8:2 FTOH will result in close to 100% PFOA. Although the study is only of qualitative nature (no rate coefficients reported), it shows that fluorotelomer alcohols and other related compounds will undergo photo-oxidation in aqueous surface layers and in the atmospheric aqueous phases (cloud droplets and deliquescent particles). Since the PFOA yield from 8:2 FTOH photo-oxidation is close to 100% in the aqueous phase (compared to 3-6% in the gas phase), aqueous phase photo-oxidation may turn out to be very important in spite of the low solubility. Any quantitative statements will require multiphase modelling.

2.2.1 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanol

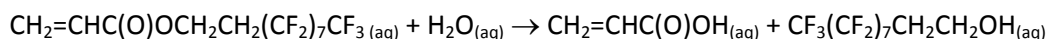
Both atmospheric gas phase and aqueous phase photo-oxidation of 8:2 FTOH (CAS RN 678-39-7) will result in release of PFOA.

2.3 Fluorotelomer acrylates and methacrylates

In general, carboxylic acid esters will undergo hydrolysis resulting in the corresponding alcohols and carboxylic acids. It is reported that hydrolysis of perfluorinated telomer acrylates (and methacrylates) may be fast in landfills, but that they have half-lives in the range of years in marine systems. Polymeric perfluorinated telomer acrylates are expected to be hydrolysed more slowly with half-lives from several centuries to millennia [Hilal *et al.*, 2003; Rayne and Forest, 2010].

2.3.1 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl acrylate

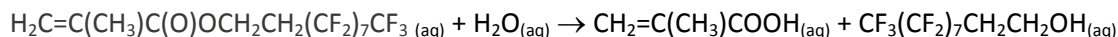
CAS RN 27905-45-9, also known as 8:2 FTAc, will hydrolyse to acrylic acid and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanol (8:2 FTOH, CAS: 678-39-7):



Hydrolysis of 8:2 FTAc (CAS RN 27905-45-9) will lead to release of 8:2 FTOH, which is a PFOA precursor, see section 2.2.

2.3.2 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl methacrylate

CAS RN 1996-88-9, also known as 8:2 FTMAC, will hydrolyse to 2-methacrylic acid (CAS RN 79-41-4) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanol (8:2 FTOH, CAS: 678-39-7):



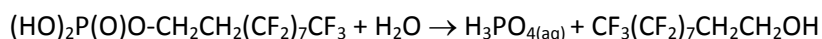
Hydrolysis of 8:2 FTMAC (CAS RN 1996-88-9) will lead to release of 8:2 FTOH, which is a PFOA precursor, see section 2.2.

2.4 Polyfluoroalkyl phosphoric acid mono- and diesters

Mono- and di- 8:2 fluorotelomer phosphoric acid esters (FTPAPs) are reported to undergo slow hydrolysis at environmental conditions (estimated lifetimes >26 years) resulting in 8:2 FTOH and phosphoric acid [D'Eon and Mabury, 2007]. It is explicitly noted that the experimental hydrolysis rates cannot be reproduced by existing models [Rayne and Forest, 2010].

2.4.1 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decanol 1-(Dihydrogen Phosphate)

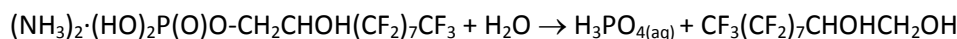
CAS RN 57678-03-2, also known as 8:2 monoPAP, will hydrolyse to 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanol (8:2 FTOH, CAS: 678-39-7):



Hydrolysis of 8:2 monoPAP (CAS RN 57678-03-2) will lead to release of 8:2 FTOH, which is a PFOA precursor, see section 2.2.

2.4.2 Diammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-hydroxyundecyl phosphate

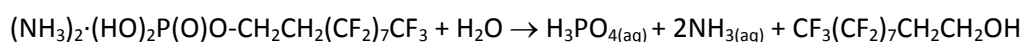
CAS RN 94200-45-0 is a diammonium phosphoric acid ester and will hydrolyse to 1,2-undecanediol, 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro- (CAS RN 94159-84-9):



Hydrolysis of the diammonium phosphoric acid ester (CAS RN 94200-45-0) will lead to release of 8:2 FTOH, which is a PFOA precursor, see section 2.2.

2.4.3 Diammonium 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadeca-fluorodecyl phosphate

CAS RN 93857-44-4, also known as 8:2 FTOH phosphate monoester ammonium salt, will hydrolyse to 3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,10-heptadecafluor-1-decanol (8:2 FTOH, CAS: 678-39-7):

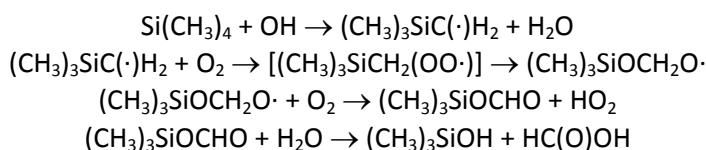


Hydrolysis of the diammonium phosphoric acid ester (CAS RN 93857-44-4) will lead to release of 8:2 FTOH, which is a PFOA precursor, see section 2.2.

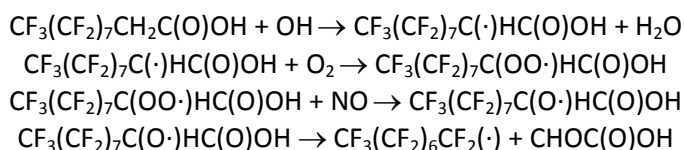
2.5 Polyfluorinated silanes

In the presence of water halo silanes and silane esters undergo hydrolysis resulting in the corresponding silanols. Silanols, in turn, will under operational conditions take part in condensation and/or polymerisation reactions resulting in bonding to substrates via Si–O– links. No relevant information concerning hydrolytic lifetimes of condensed or polymerized polyfluorinated silanes was found in the open literature.

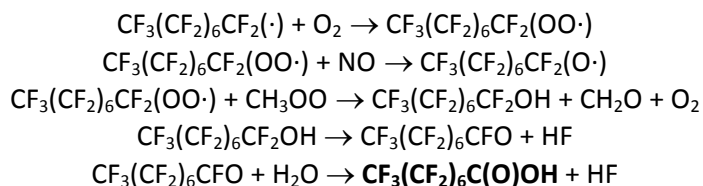
Silanes have appreciable vapour pressures and may in principle evaporate and undergo photo-oxidation in the atmosphere. It is also conceivable that small siloxanes may partition to the atmosphere and undergo photo-oxidation there. Atkinson studied the kinetics of OH reactions with a series of organosilicon compounds including siloxanes and reported atmospheric lifetimes of >10 days [Atkinson, 1991]. Tuazon *et al.* have investigated the products formed in the atmospheric degradation of volatile methyl-silicon compounds [Tuazon *et al.*, 2000]. For tetramethylsilane the first steps in the photo-oxidation are reported to be:



For telomer-substituted silanes and/or siloxanes the corresponding reactions will lead to the corresponding FTCA as product. The subsequent gas phase photo-oxidation of $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{C}(\text{O})\text{OH}$ will eventually lead to some PFOA. The first steps are expected to be:



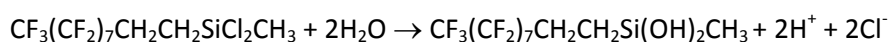
The reactions of the perfluoroalkyl radical leading to PFOA are [Wallington *et al.*, 2006]:



Established aqueous phase photo-oxidation reactions resemble the above and lead to the same product.

2.5.1 Dichloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)methylsilane

$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SiCl}_2\text{CH}_3$ (CAS RN 3102-79-2) has a melting point of 26-27 °C and a boiling point of 205-207 °C (1 atm) [Gelest_Inc, 2013]; evaporation at environmental conditions is therefore possible. Hydrolysis of the compound will result in the corresponding silanediol (CAS RN 160447-73-4):

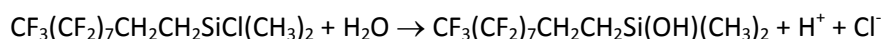


Evaporation of $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SiCl}_2\text{CH}_3$ or $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si(OH)}_2\text{CH}_3$ will, via the photo-oxidation reactions described above, eventually result in release of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanoic acid (8:2 FTCA, CAS RN 27854-31-5). Alternatively, aqueous phase photo-oxidation of the silanediol will result in the same release of 8:2 FTCA.

Atmospheric gas phase and/or aqueous phase photo-oxidation of the silane (CAS RN 3102-79-2) will result in the release of 8:2 FTCA, which is a PFOA precursor, see also section 2.2.

2.5.2 Chloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilane

$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SiCl}(\text{CH}_3)_2$ (CAS RN 74612-30-9) has a boiling point of 197-198 °C [Gelest_Inc, 2013]; evaporation at environmental conditions is therefore possible. Hydrolysis of the compound will result in the corresponding silanol (CAS RN 128194-56-9):

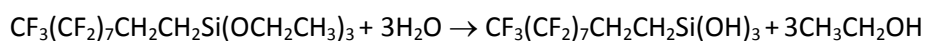


Evaporation of $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SiCl}(\text{CH}_3)_2$ or $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si(OH)}(\text{CH}_3)_2$ will eventually lead to release of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanoic acid (8:2 FTCA, CAS RN 27854-31-5). Alternatively, aqueous phase photo-oxidation of the silanediol will result in the same release of 8:2 FTCA.

Atmospheric gas phase and/or aqueous phase photo-oxidation of the silane (CAS RN 3102-79-2) will result in the release of 8:2 FTCA, which is a PFOA precursor, see also section 2.2.

2.5.3 Trietoxy(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane

$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_3)_3$ (CAS RN 101947-16-4) has a boiling point of 103-106 °C [Gelest_Inc, 2013]; evaporation at environmental conditions is therefore possible. Hydrolysis of the compound will result in the corresponding silanetriol (CAS RN 115781-18-5):



Evaporation of $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_3)_3$ or $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si(OH)}_3$ will eventually lead to release of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanoic acid (8:2 FTCA, CAS RN 27854-31-5).

Alternatively, aqueous phase photo-oxidation of the silanediol will result in the same release of 8:2 FTCA.

Atmospheric gas phase and/or aqueous phase photo-oxidation of the silane (CAS RN 3102-79-2) will result in the release of 8:2 FTCA, which is a PFOA precursor, see also section 2.2.

2.5.4 *Trichloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane*

$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SiCl}_3$ (CAS RN 78560-44-8) has a boiling point of 216-218 °C [*Gelest_Inc*, 2013]; evaporation at environmental conditions is therefore possible. Hydrolysis of the compound will result in the corresponding silanetriol (CAS RN 115781-18-5):

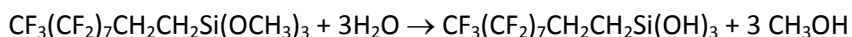


Evaporation of $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SiCl}_3$ or $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OH})_3$ will eventually lead to release of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanoic acid (8:2 FTCA, CAS RN 27854-31-5). Alternatively, aqueous phase photo-oxidation of the silanediol will result in the same release of 8:2 FTCA.

Atmospheric gas phase and/or aqueous phase photo-oxidation of the silane (CAS RN 3102-79-2) will result in the release of 8:2 FTCA, which is a PFOA precursor, see also section 2.2.

2.5.5 *(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)trimethoxysilane*

$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ (CAS RN 83048-65-1) has a boiling point of 247 °C [*Gelest_Inc*, 2013]; evaporation at environmental conditions is therefore possible. Hydrolysis of the compound will result in the corresponding silanetriol (CAS RN 115781-18-5):



Evaporation of $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ or $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OH})_3$ will eventually lead to release of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecanoic acid (8:2 FTCA, CAS RN 27854-31-5). Alternatively, aqueous phase photo-oxidation of the silanediol will result in the same release of 8:2 FTCA.

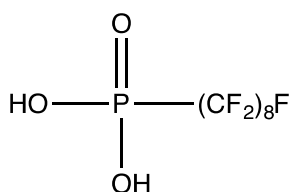
Atmospheric gas phase and/or aqueous phase photo-oxidation of the silane (CAS RN 3102-79-2) will result in the release of 8:2 FTCA, which is a PFOA precursor, see also section 2.2.

2.6 Per- and polyfluorinated phosphonic acids

Phosphonic acids is a group of compounds with the general formula $\text{R-P}(\text{O})(\text{OH})_2$, where R is either a hydrogen atom or an organic fragment. No experimental information relevant to abiotic environmental degradation of phosphonic acids was found in the open literature.

2.6.1 *Perfluorooctyl phosphonic acid*

The compound (CAS RN 40143-78-0), also known as C8-PFPA, has the following structure:



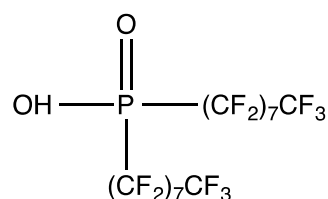
No abiotic degradation routes found.

2.7 Per- and polyfluorinated phosphinic acids

Phosphonic acids is a group of compounds with the general formula $RR'P(O)(OH)$, where R and R' are either hydrogen ato or organic fragments. No experimental information relevant to abiotic environmental degradation of phosphonic acids was found in the open literature.

2.7.1 Bis(perfluorooctyl) phosphinic acid

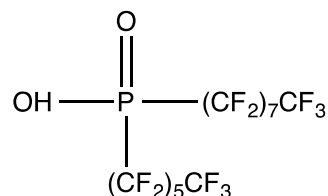
The compound (CAS RN 40143-79-1), also known as C8/C8-PFPIA, has the following structure:



No abiotic degradation routes found.

2.7.2 Bis(perfluorooctyl) phosphinic acid

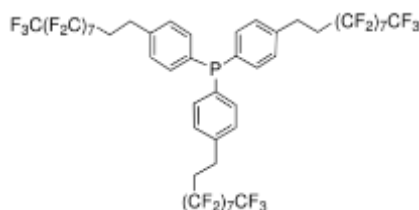
The compound (CAS RN 40143-34-5), also known as C6/C8-PFPIA, has the following structure:



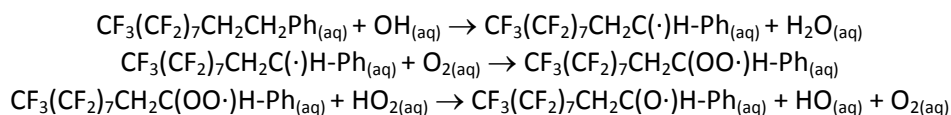
No abiotic degradation routes found.

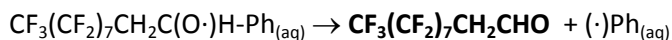
2.7.3 Tris[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)phenyl]phosphine

The compound (CAS RN 325459-92-5) has the following structure:



The compound will not have sufficient vapour pressure to make gas phase photo-oxidation important. Aqueous phase photo-oxidation may take place (1) via OH addition to the benzene ring resulting in a wide variety of products, (2) via H-abstraction from the CH_2 -groups leading to 8:2 FTAL, which is an intermediate in the 8:2 FTOH photo-oxidation, see section 2.2:

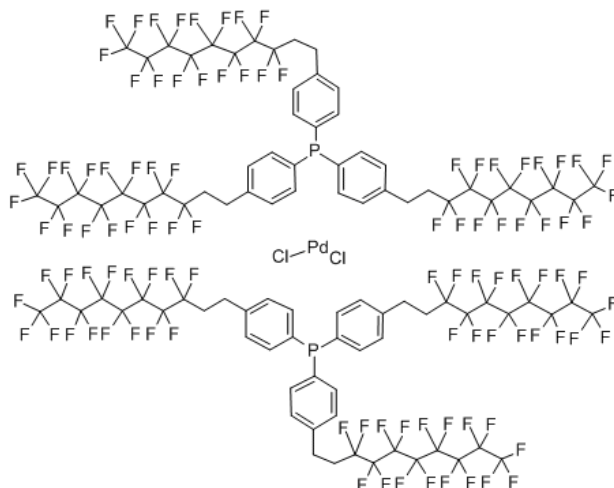




Aqueous phase photo-oxidation of (CAS RN 325459-92-5) will result in 8:2 FTAL, which is a PFOA precursor.

2.7.4 Tris[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)phenyl]phosphine

The compound (CAS RN 326475-46-1) has the following structure:

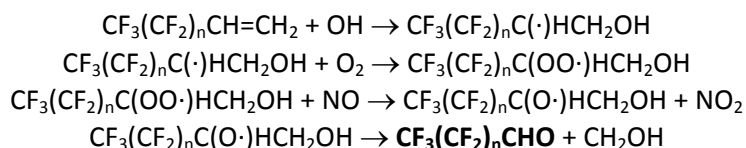


The compound will not have sufficient vapour pressure to make gas phase photo-oxidation important. Aqueous phase photo-oxidation may take place (1) via OH addition to the benzene ring resulting in a wide variety of products, (2) via H-abstraction from the CH₂-groups leading to 8:2 FTAL, see section 2.7.3.

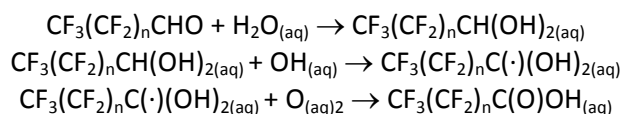
Aqueous phase photo-oxidation of (CAS RN 326475-46-1) will result in 8:2 FTAL, which is a PFOA precursor.

2.8 Polyfluorinated olefins

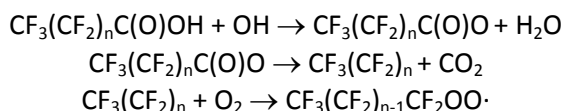
The atmospheric lifetimes of polyfluorinated olefins (PTOs) are around 8 days and determined by reaction with OH radicals. [Andersen *et al.*, 2005] The major product (around 90 % yield) in the atmospheric photo-oxidation is the corresponding PFAL [Vésine *et al.*, 2000; Nakayama *et al.*, 2007]:



The atmospheric lifetimes of PFALs are estimated to be around 90 days with respect to reaction with OH. It is therefore likely that PFALs in part will partition to the atmospheric aqueous phase and undergo photo-oxidation there:



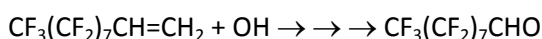
Because the PFCA is close to 100% protolysed in the aqueous phase, further oxidation is essentially blocked. Upon transfer to the gas phase the photo-oxidation reactions will continue (lifetime with respect to OH is around 130 days) [M. D. Hurley *et al.*, 2003]:



See section 2.5 for subsequent steps in the degradation leading to PFCAs.

2.8.1 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decene

The compound (CAS RN 21652-58-4), also known as 8:2 FTO, will undergo atmospheric photo-oxidation leading to 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-nonanal (CAS RN 63967-40-8)

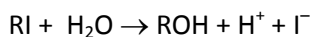


Subsequent atmospheric photo-oxidation of the perfluorononanal will result in release of PFOA, see section 2.2.

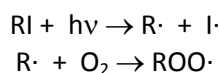
The compound (CAS RN 21652-58-4) will undergo gas phase photo-oxidation resulting in release of PFOA.

2.9 Polyfluorinated iodides

Perfluorinated telomer iodides are reported to have hydrolytic half-lives of about 4 months [Adachi *et al.*, 1974; Glowa and Wren, 2003; Rayne and Forest, 2010]. The hydrolysis results in the corresponding alcohol:

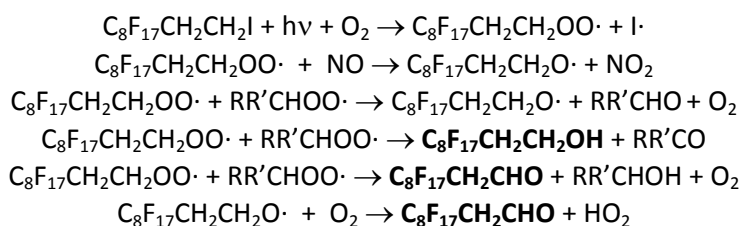


The atmospheric gas phase lifetime of fluorotelomer iodides (and polyfluorinated iodides) is limited by photolysis with lifetimes ranging from 1 to 7 days [Cora J. Young *et al.*, 2008], depending on time of year and latitude:

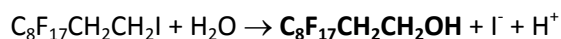


2.9.1 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iododecane

The gas phase photolysis of CAS RN 2043-53-0, also known as 8:2 FTI, will result in 8:2 FTOH and 8:2 FTAL (CAS RN 135984-68-8):



Hydrolysis of 8:2 FTI will result in 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanol (8:2 FTOH, CAS RN 678-39-7):



The atmospheric fate of 8:2 FTOH, which is a PFOA precursor, was discussed in section 2.2.

Gas phase photolysis of the fluorotelomer iodide (CAS RN 2043-53-0) will lead to the release of 8:2 FTOH (CAS RN 678-39-7) and 8:2 FTA (CAS RN 135984-68-8), which are both PFOA precursors.

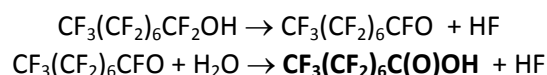
2.9.2 Perfluorooctyl iodide

Gas phase photolysis of the PFI (CAS RN 507-63-1) will result in various PFCAs including PFOA [David A. Ellis et al., 2004; C. J. Young and Mabury, 2010].

Hydrolysis of the PFI will result in perfluorooctanol (CAS RN 647-42-7):



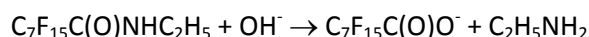
The alcohol is unstable and will eliminate HF and react with H₂O resulting in PFOA:



Gas phase photolysis and aqueous phase hydrolysis of the perfluorooctyl iodide iodide (CAS RN 507-63-1) will lead to the release of PFOA.

2.10 Polyfluorinated amides

Jackson and Mabury [Jackson and Mabury, 2012] investigated the hydrolysis of the PFAM *N*-ethyl-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-octanamide (CAS RN 89685-57-4) in 1 M NaOH solution, in 5 mM Tris buffer pH 8.5, and in 50 mM borate buffer. They found quantitative hydrolysis to PFOA in 1 M NaOH solution. No hydrolysis to PFOA was observed after 8 days at pH 8.5. Rapid degradation was observed in the borate buffer, but not to PFOA unless at pH 14:



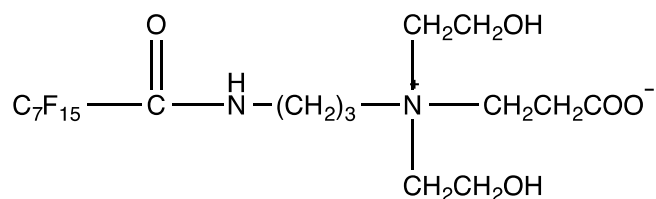
It can be inferred from the experiments that polyfluorinated amides have long hydrolytic lifetimes at environmental conditions. They do, however, hydrolyse.

Jackson et al. [Jackson et al., 2013] studied the atmospheric photo-oxidation of *N*-ethyl-2,2,3,3,4,4,4-heptafluoro-butanamide (C₃F₇C(O)NHCH₂CH₃, CAS RN 70473-76-6) and identified C₃F₇C(O)NH₂ as intermediate, and PFCAs and HNCO (isocyanic acid) as products. They presented a general mechanism based on the observed product distribution.

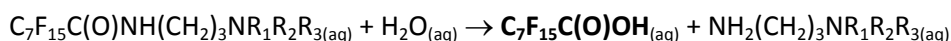
Martin et al. [Martin et al., 2005] studied the atmospheric photo-oxidation of *N*-Ethyl perfluorobutanesulfonamide (C₄F₉S(O)₂NHCH₂CH₃, CAS RN 40630-67-9) and identified C₄F₉S(O)₂NHC(O)CH₃, C₄F₉S(O)₂NHCH₂CHO and C₄F₉S(O)₂NHCHO as intermediates, and SO₂, COF₂ and PFCAs as stable products. They presented a general mechanism based on the observed product distribution.

2.10.1 2-Carboxyethylbis(2-hydroxyethyl)-3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]propylammonium hydroxide inner salt

The compound (CAS RN 39186-68-0) is an amide with following structure:



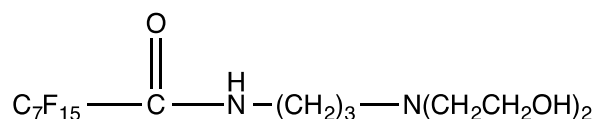
The compound is an internal salt and it is unlikely that the vapour pressure will be sufficient to make gas phase photo-oxidation important. Hydrolysis, although slow, will release PFOA:



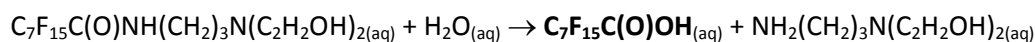
Hydrolysis of the amide (CAS RN 39186-68-0) will result in release of PFOA.

2.10.2 *N*-[3-[bis(2-hydroxyethyl)amino]propyl]-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide

The amine/amide (CAS RN 41358-63-8) has the following structure:



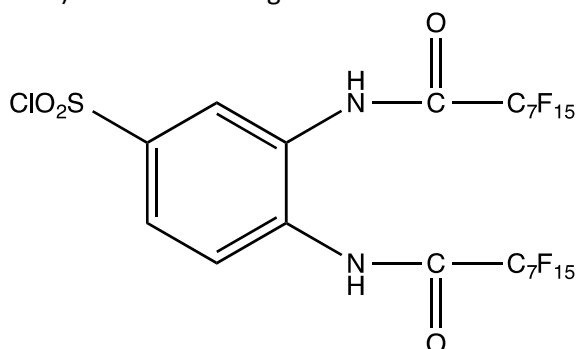
The compound will likely have a too low vapour pressure to make gas phase photo-oxidation important. Hydrolysis, although slow, will release PFOA:



Hydrolysis of the amine/amide (CAS RN 41358-63-8) will result in the release of PFOA.

2.10.3 3,4-bis[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]benzenesulphonyl chloride; 3,4-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctylamino)benzenesulfonyl chloride

The amide (CAS RN 24216-05-5) has the following structure:

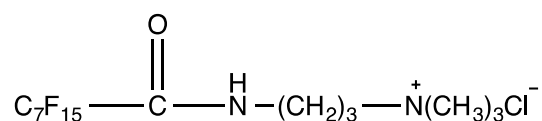


The compound will likely have a too low vapour pressure to make gas phase photo-oxidation important. Hydrolysis, although slow, will release PFOA:

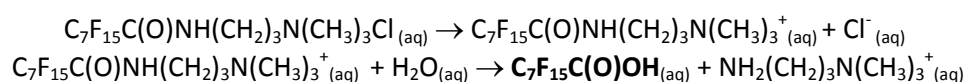
Hydrolysis of the amide (CAS RN 24216-05-5) will result in the release of PFOA.

2.10.4 1-Propanaminium,N,N,N-trimethyl-3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]-, chloride

The amide/aminium salt (CAS RN 53517-98-9) has the following structure:



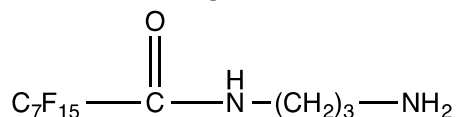
The compound is a salt and it is unlikely that the vapour pressure will be sufficient to make gas phase photo-oxidation important. Hydrolysis, although slow, will release PFOA:



Hydrolysis of the amide/aminium salt (CAS RN 53517-98-9) will result in the release of PFOA.

2.10.5 N-(3-aminopropyl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide

The amide (CAS RN 85938-56-3) has the following structure:

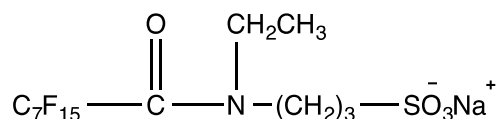


The compound may have sufficient vapour pressure to make gas phase photo-oxidation important. Gas phase photo-oxidation will release PFOA. Hydrolysis, although slow, will also release PFOA:

Both gas phase photo-oxidation and hydrolysis of the amide (CAS RN 85938-56-3) will result in the release of PFOA.

2.10.6 1-Propanesulfonic acid, 3-[ethyl(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]-, sodium salt

The compound (CAS RN 89685-61-0) is both an amide and an amine, and has the following structure:



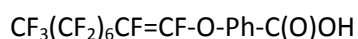
The compound is a salt and it is unlikely that the vapour pressure will be sufficient to make gas phase photo-oxidation important. Hydrolysis, although slow, will release PFOA:

Hydrolysis of the amide (CAS RN 89685-61-0) will result in the release of PFOA.

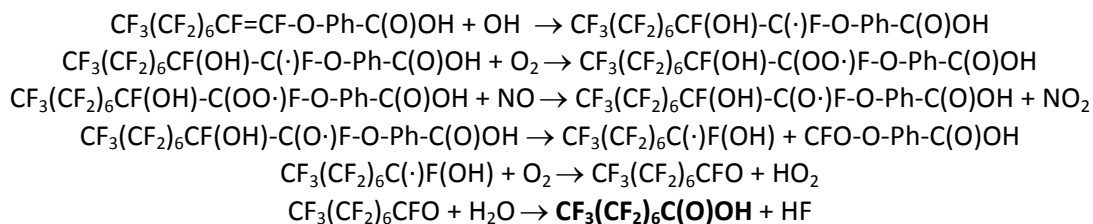
2.11 Other potential PFOA precursors

2.11.1 4-[(heptadecafluoro-nonyl)oxy]-Benzoic acid

The compound (CAS RN 58253-65-9) has the following structure:



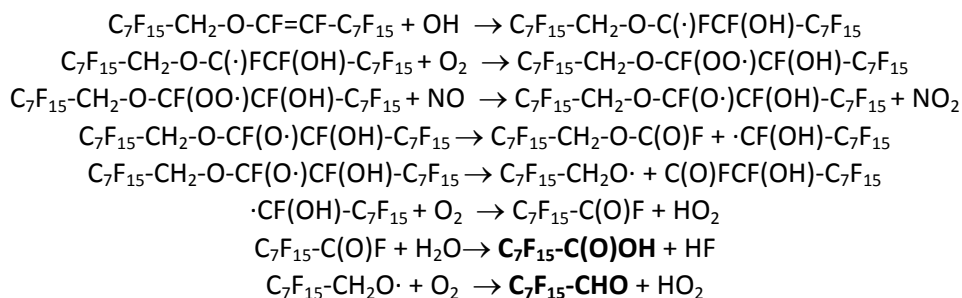
Gas phase photo-oxidation will result in a wide suite of products following OH addition to the benzene ring. The OH radical may also add to the –CF=CF–O double bond resulting in PFOA:



Gas phase photo-oxidation of the compound (CAS RN 58253-65-9) will lead to release of PFOA.

2.11.2 Heptadecafluoro-1-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]nonene

The compound (CAS RN 84029-60-7) has the formula $\text{C}_7\text{F}_{15}\text{-CH}_2\text{-O-CF}=\text{CF-C}_7\text{F}_{15}$ and can be characterized as a perfluorinated unsaturated ether. The compound will undergo atmospheric gas phase photo-oxidation via OH radical addition to the double bond:

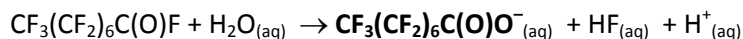


The atmospheric chemistry of the aldehyde $\text{C}_7\text{F}_{15}\text{CHO}$ was addressed in section 2.2, and atmospheric photo-oxidation of the compound will lead to release of PFOA.

Gas phase photo-oxidation of the compound (CAS RN 84029-60-7) will lead to release of PFOA.

2.11.3 Pentadecafluoro-octanoyl fluoride

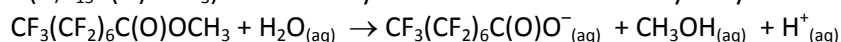
Acid fluorides generally react fast with water resulting in the corresponding acid and HF. Pentadecafluoro-octanoyl fluoride (CAS RN 335-66-0) will hydrolyse relatively fast:



Hydrolysis of PFOA acid fluoride (CAS RN 335-66-0) will result in the release of PFOA.

2.11.4 Pentadecafluoro-octanoic acid methyl ester

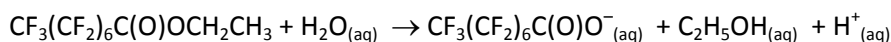
CAS RN 376-27-2 ($\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{OCH}_3$) is the methyl ester of PFOA and will hydrolyse relatively fast:



Hydrolysis of the PFOA ester (CAS RN 376-27-2) will result in the release of PFOA.

2.11.5 Pentadecafluoro-octanoic acid ethyl ester

CAS RN 3108-24-5 ($\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{OCH}_2\text{CH}_3$) is the ethyl ester of PFOA and will hydrolyse relatively fast to PFOA:

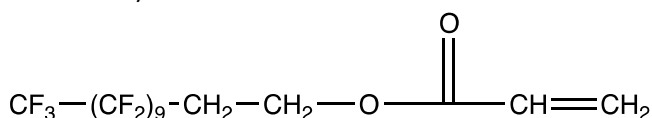


Hydrolysis of the PFOA ester (CAS RN 3108-24-5) will result in the release of PFOA.

2.11.6 2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecyl 2-propenoate, alpha-(2-methyl-1-1-oxo-2-2-propenyl)-omega-[(2-methyl-1-oxo-2-propenyl)oxy]poly(oxy-1, 2-ethanediyl), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-nonacosafuorohexadecyl 2-propenoate, octadecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafuorotetradecyl 2-propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-tritriacontafuorooctadecyl 2-propenoate

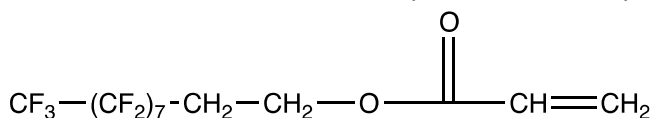
The substance (CAS RN 116984-14-6) is co-polymer based on the following compounds:

2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecyl ester (CAS RN 17741-60-5):



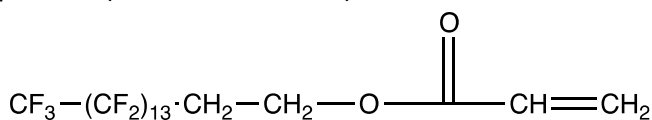
The constituent is an acrylic acid ester and will hydrolyse releasing 9:2 FTOH, which is a PFOA precursor (see section 2.2).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecyl 2-propenoate (CAS RN 27905-45-9):



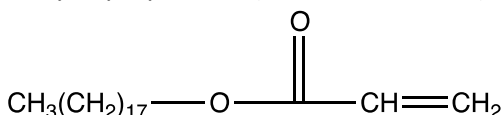
The constituent is an acrylic acid ester and will hydrolyse releasing 8:2 FTOH, which is a PFOA precursor (see section 2.2).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-nonacosafuorohexadecyl 2-propenoate (CAS RN 34362-49-7):



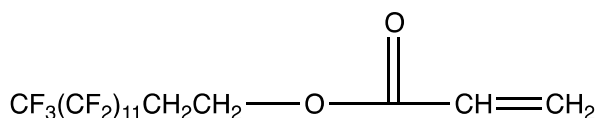
The constituent is an acrylic acid ester and will hydrolyse releasing 14:2 FTOH, which is a PFOA precursor (see section 2.2).

Octadecyl 2-propenoate (CAS RN 4813-57-4):



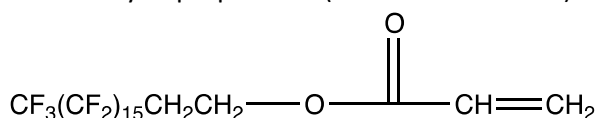
The constituent is an acrylic acid ester and will hydrolyse releasing octadecanol.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafuorotetradecyl 2-propenoate (CAS RN 34395-24-9):



The constituent is an acrylic acid ester and will hydrolyse releasing 12:2 FTOH, which is a PFOA precursor (see section 2.2).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-tritriacontadecyl 2-propenoate (CAS RN 65150-93-8):

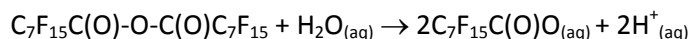


The constituent is an acrylic acid ester and will hydrolyse releasing 16:2 FTOH, which is a PFOA precursor (see section 2.2).

The substance (CAS RN 116984-14-6) is an acrylic acid ester co-polymer, which will undergo slow hydrolysis releasing PFOA precursors.

2.11.7 Pentadecafluorooctanoic anhydride

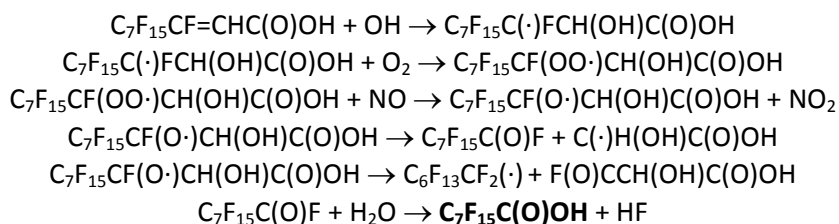
Carboxylic acid anhydrides normally hydrolyse relatively fast. Pentadecafluorooctanoic anhydride (CAS RN 33496-48-9) will hydrolyse as shown:



Hydrolysis of the PFOA anhydride (CAS RN 33496-48-9) will result in the release of PFOA.

2.11.8 2-Decenoic acid, 3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-

CAS RN 70887-84-2 ($\text{C}_7\text{F}_{15}\text{CF}=\text{CHC}(\text{O})\text{OH}$), also known as 8:2 FTUCA, is expected to be water soluble and to have a vapour pressure above 1 Pa. The compound may therefore undergo photo-oxidation in both in the gas phase and in deliquescent particles. The gas phase photo-oxidation will proceed via addition of OH to the double bond eventually forming some PFOA:



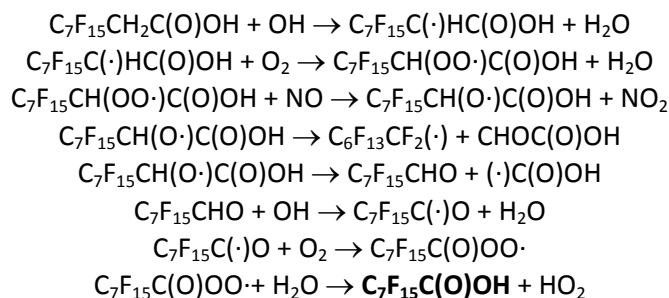
Established aqueous phase photo-oxidation reactions lead to the same product.

The compound (8:2 FTUCA, CAS RN 70887-84-2) will undergo gas phase and/or aqueous phase photo-oxidation leading to the release of PFOA.

2.11.9 Decanoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluoro-

CAS RN 27854-31-5 ($\text{C}_7\text{F}_{15}\text{CH}_2\text{COOH}$) is expected to be water soluble and to have a vapour pressure above 1 Pa. The compound may therefore undergo photo-oxidation in both in the gas phase and in

deliquescent particles. The gas phase photo-oxidation will proceed via hydrogen abstraction from the $-CH_2-$ group eventually resulting in some PFOA:



Established aqueous phase photo-oxidation reactions lead to the same product.

The compound (CAS RN 70887-84-2) will undergo gas phase and/or aqueous phase photo-oxidation leading to the release of PFOA.

2.12 UVCBs

The UVCBs (Unknown or Variable compositions, Complex reaction products and Biological materials), included on the list in the annex, are discussed in the following sub-sections.

2.12.1 Fatty acids, C7-13, perfluoro

CAS RN 68333-92-6 is a generic registration and should be combined with text terms for complete reference search results. The acids are slightly watersoluble and have sufficiently high vapour pressures to partition to the gas phase. A fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Consequently, "C7-C13 perfluorinated fatty acids" may contain both PFOA, and longer chain saturated/unsaturated PFCAs that can be degraded to PFOA.

"C7-C13 perfluorinated fatty acids" (CAS RN 68333-92-6) may contain both PFOA, and longer chain saturated/unsaturated PFAs that can be degraded to PFOA.

2.12.2 Fatty acids, C7-13, perfluoro, compds. with ethylamine

CAS RN 69278-80-4 is a generic registration and should be combined with text terms for complete reference search results. A fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Fatty acid ethylamine (CAS RN 75-04-7) salts are generally about as soluble as the fatty acids themselves. Consequently, "ethylamine salts of C7-C13 perfluorinated fatty acids" may contain both PFOA, and longer chain saturated/unsaturated PFAs that can be degraded to PFOA.

"Ethylamine salts of C7-C13 perfluorinated fatty acids" (CAS RN 69278-80-4) may contain both PFOA, and longer chain saturated/unsaturated PFCAs that can be degraded to PFOA.

2.12.3 Fatty acids, C6-18, perfluoro, ammonium salts

CAS RN 72623-77-9 is a generic registration and should be combined with text terms for complete reference search results. A fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Fatty acid ammonium salts are about as soluble as the fatty acids themselves. Consequently, "ammonium salts of C7-C13 perfluorinated fatty acids" may contain both PFOA, and longer chain saturated/unsaturated PFAs that can be degraded to PFOA.

“Ammonium salts of C7-C13 perfluorinated fatty acids” (CAS RN 72623-77-9) may contain both PFOA, and longer chain saturated/unsaturated PFCAs that can be degraded to PFOA.

2.12.4 Carboxylic acids, C7-13, perfluoro, ammonium salts

CAS RN 72968-38-8 is a generic registration and should be combined with text terms for complete reference search results. The acids are slightly watersoluble and have sufficiently high vapour pressures to partition to the gas phase. Carboxylic acid ammonium salts are about as soluble as the carboxylic acids themselves. Consequently, “ammonium salts of C7-C13 perfluorinated carboxylic acids” may contain both PFOA, and longer chain PFCAs that can be degraded to PFOA.

“Ammonium salts of C7-C13 perfluorinated carboxylic acids” (CAS RN 72968-38-8) may contain both PFOA, and longer chain PFCAs that can be degraded to PFOA.

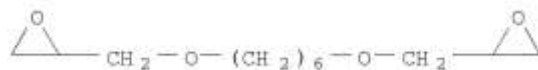
2.12.5 Octanoic acid, pentadecafluoro-, mixed esters with 2,2'-[1,4-butanediylbis(oxymethylene)]-bis[oxirane] and 2,2'-[1,6-hexanediylbis(oxymethylene)]bis[oxirane]

CAS RN 90480-57-2 is a generic registration and should be combined with text terms for complete reference search results. The generic registration covers unspecified mixtures of PFOA with C₁₂H₂₂O₄ (CAS RN 2425-79-8) and C₁₀H₁₈O₄ (CAAS RN 16096-31-4):

CAS RN 2425-79-8 C₁₂H₂₂O₄



CAS RN 16096-31-4 C₁₀H₁₈O₄



The esters are expected to hydrolyse reasonably fast whereby PFOA is released.

The unspecified mixture of esters (CAS RN 90480-57-2) will hydrolyse resulting in PFOA release.

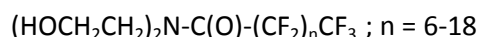
2.12.6 Fatty acids, C7-19, perfluoro

CAS RN 91032-01-8 is a generic registration and should be combined with text terms for complete reference search results. A fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Consequently, “C7-C19 perfluorinated fatty acids” may contain both PFOA, and longer chain saturated/unsaturated PFCAs that can be degraded to PFOA.

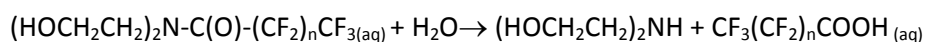
“C7-C19 perfluorinated fatty acids” (CAS RN 91032-01-8) may contain both PFOA, and longer chain saturated/unsaturated PFCAs that can be degraded to PFOA.

2.12.7 Amides, C7-19, α-ω-perfluoro-N,N-bis(hydroxyethyl)

CAS RN 90622-99-4 is a generic registration and should be combined with text terms for complete reference search results. The chemical structure of this class of compounds is:



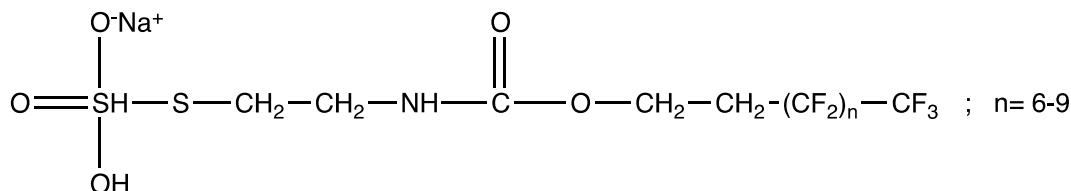
The compounds can be classified as amides and are expected to undergo slow hydrolysis in the environment (see section 0) releasing PFOA and longer chain PFCAs that can be degraded to PFOA:



The compound class (CAS RN 90622-99-4) will undergo hydrolysis resulting in the release of PFOA and longer chain PFCAs that can be degraded to PFOA.

2.12.8 Carbamic acid, [2-(sulfothio)ethyl]-, C-(γ-ω-perfluoro-C6-9-alkyl) esters, monosodium salts

CAS RN 95370-51-7 is a generic registration and should be combined with text terms for complete reference search results. The chemical structure of this class of compounds is:

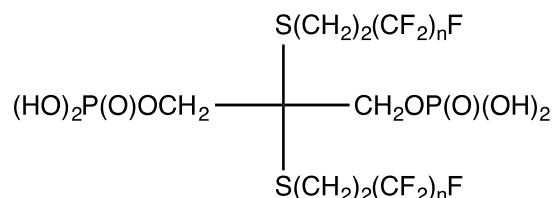


Carbamic acid esters, $\text{R}_1\text{R}_2\text{N}-\text{C}(\text{O})-\text{O}-\text{R}_3$, may in principle undergo hydrolysis resulting in an amine ($\text{R}_1\text{R}_2\text{NH}$), an alcohol (R_3OH) and CO_2 . In the present case, the alcohol will be $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$, which for $n \geq 6$ is a PFOA precursor. The hydrolysis of simple alkyl carbamic esters is very slow at environmental conditions. No hydrolytic lifetimes were found in the open literature for perfluoro-alkyl carbamates.

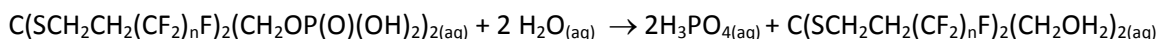
The compound class of carbamic acid esters (CAS RN 95370-51-7) may undergo slow hydrolysis resulting in the release of PFOA and longer chain PFCAs that can be degraded to PFOA.

2.12.9 1,3-Propanediol, 2,2-bis(γ-ω-perfluoro-C4-10-alkyl)thiomethyl derivs., phosphates, ammonium salts

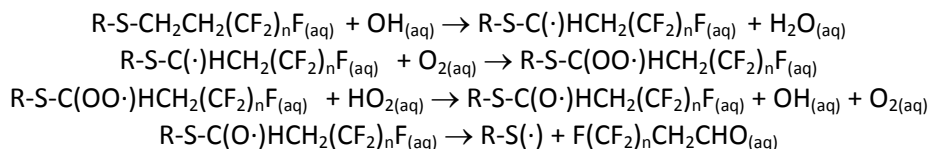
The substance (CAS RN 148240-85-1) is a generic registration and should be combined with text terms for complete reference search results. The substance contains $\text{F}(\text{CF}_2)_n\text{CH}_2\text{CH}_2$ -fragments ($n=4-10$) and has the general structure (ammonium not included):



The substance is a phosphate ester ammonium salt and will undergo hydrolysis, see section 2.4:



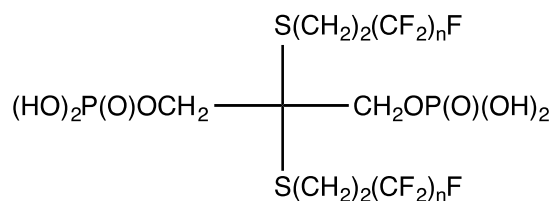
The two sulphide bridges will not undergo abiotic hydrolysis at environmental conditions. Sulphides are not reported to hydrolyse under environmental conditions, but they may undergo photo-oxidation in aqueous surfaces, in the atmospheric aqueous phase and in the gas phase. The substance will not have sufficient vapour pressure for gas phase photo-oxidation to be of relevance. Established aqueous phase photo-oxidation reactions will eventually result in dissociation of the C-S bond leading to n:2 PFAL as one of the products:



Hydrolysis of the substance (CAS RN 148240-85-1) followed by aqueous phase photo-oxidation will result if n:2 FTALs that for n>7 will lead to release of PFOA.

2.12.10 1,3-Propanediol, 2,2-bis(γ - ω -perfluoro-C6-12-alkyl)thiomethyl derivs., phosphates, ammonium salts

The substance (CAS RN 148240-87-3) is a generic registration and should be combined with text terms for complete reference search results. The substance contains $F(CF_2)_nCH_2CH_2$ -fragments (n=6-12) and has the general structure (ammonium not included):

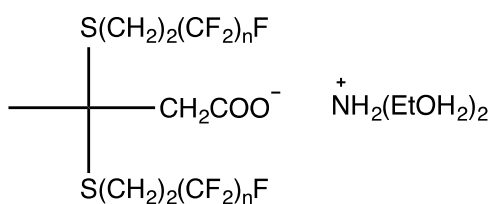


The two sulphide bridges will not undergo abiotic hydrolysis at environmental conditions Sulphides are not reported to hydrolyse under environmental conditions, but they may undergo photo-oxidation in aqueous surfaces, in the the atmospheric aqueous phase and in the gas phase. The substance will not have sufficient vapour pressure for gas phase photo-oxidation to be of relevance. Established aqueous phase photo-oxidation reactions will eventually results in dissociation of the C-S bond leading to n:2 PFAL as one of the products, see section 2.12.10.

Hydrolysis of the substance (CAS RN 148240-87-3) followed by aqueous phase photo-oxidation will result if n:2 FTALs that for n>7 will lead to release of PFOA.

2.12.11 Pentanoic acid, 4,4-bis(γ - ω -perfluoro-C8-20-alkyl)thio derivs., compds. with diethanolamine; 4,4-Bis[(γ - ω -perfluoro-alkyl(C=8-20))thio]pentanoic acid derivs. compds. with diethanolamine

The substance (CAS RN 71608-61-2) is a generic registration and should be combined with text terms for complete reference search results. The substance contains $F(CF_2)_nCH_2CH_2$ -fragments (n=8-20) and has the general structure:



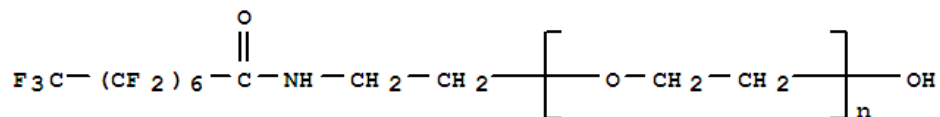
The two sulphide bridges will not undergo abiotic hydrolysis at environmental conditions Sulphides are not reported to hydrolyse under environmental conditions, but they may undergo photo-oxidation in aqueous surfaces, in the the atmospheric aqueous phase and in the gas phase. The substance will not have sufficient vapour pressure for gas phase photo-oxidation to be of relevance. Established aqueous phase photo-oxidation reactions will eventually results in dissociation of the C-S bond leading to n:2 PFAL as one of the products, see section 2.12.10.

Hydrolysis of the substance (CAS RN 71608-61-2) followed by aqueous phase photo-oxidation will result if n:2 FTALs that for n>7 will lead to release of PFOA.

2.13 Polymers

2.13.1 Poly(oxy-1,2-ethanediyl), α -[2-[2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl) amino]ethyl]- ω -hydroxy

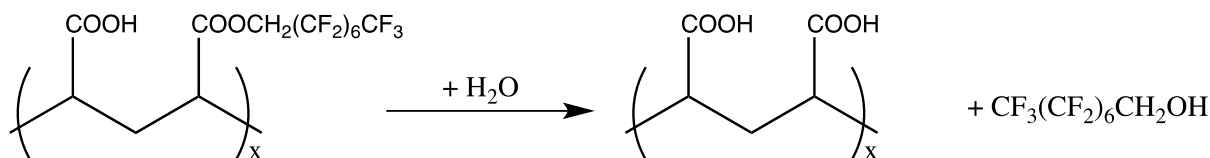
The substance (CAS RN 93480-00-3) has the following structure:



The substance (CAS RN 93480-00-3) is an amide and will hydrolyse releasing PFOA.

2.13.2 2-Propenoic acid, 2-methyl-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl ester, polymer with 2-propenoic acid

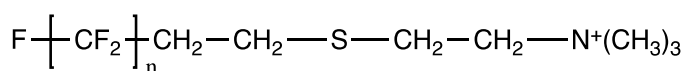
This polyacrylate co-polymer (CAS RN 53515-73-4) contains (ester) side-chains $>\text{C}-\text{C}(\text{O})\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ and will slowly undergo hydrolysis (see section 2.3) to give 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octanol (CAS RN 307-30-2).



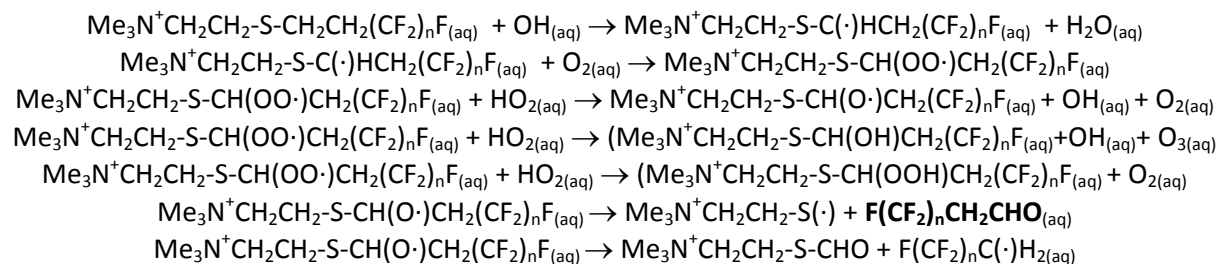
Aqueous phase photo-oxidation of $\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{OH}$ will result in PFOA. Gas phase photo-oxidation will lead to $\text{CF}_3(\text{CF}_2)_6\text{CHO}$ and subsequently in part to PFOA, see section 2.2.

2.13.3 Poly(difluoromethylene), α -fluoro- ω -[[2-[(trimethylammonio)ethyl]thio]ethyl]-, methyl sulphate

The substance (CAS RN 65530-57-6) is a salt of $\text{CH}_3\text{OS}(\text{O})_2\text{OH}$ with the following trimethylamine:



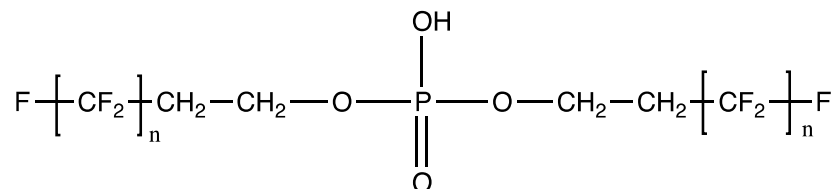
Sulphides are not reported to hydrolyse under environmental conditions, but they may undergo photo-oxidation in aqueous surfaces, in the the atmospheric aqueous phase and in the gas phase. The substance will not have sufficient vapour pressure for gas phase photo-oxidation to be of relevance. Established aqueous phase photo-oxidation reactions will eventually results in dissociation of the C-S bond leading to n:2 PFAL as one of the products:



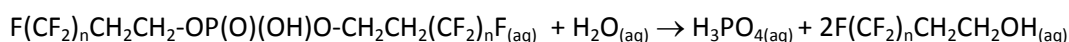
Hydrolysis followed by aqueous phase photo-oxidation of the substance (CAS RN 65530-57-6) will lead to $F(CF_2)_nCOOH$ (PFOA for $n=7$).

2.13.4 Poly(difluoromethylene), α,α' -phosphinicbis(oxy-2,1-ethanediyl)bis n -fluoro-

The compound (CAS RN 65530-62-3) is a phosphoric acid ester with the following structure:



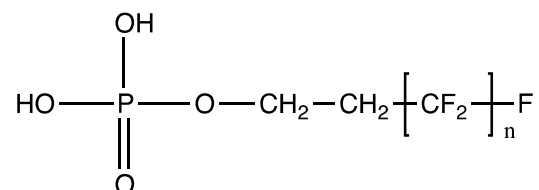
The phosphoric acid ester will hydrolyse and release $n:2$ FTOHs, see section 2.4:



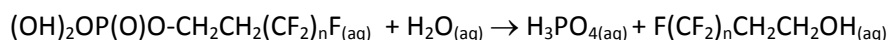
Hydrolysis of the phosphate ester $(OH)_2OP(O)O-CH_2CH_2(CF_2)_nF$ will result in $n:2$ FTOHs that will undergo photo-oxidation in aqueous surfaces, in the the atmospheric aqueous phase and in the gas phase eventually leading to PFOA for $n \geq 8$, see section 2.2.

2.13.5 Poly(difluoromethylene), α -fluoro- ω -[2-(phosphonooxy)ethyl]-

The compound (CAS RN 65530-61-2) is a phosphoric acid ester with the following structure:



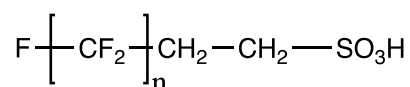
The phosphoric acid ester will hydrolyse and liberate the $n:2$ FTOH:



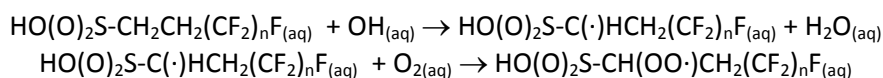
Hydrolysis of the phosphate ester $(OH)_2OP(O)O-CH_2CH_2(CF_2)_nF$ will result in $n:2$ FTOHs that will undergo photo-oxidation in aqueous surfaces, in the the atmospheric aqueous phase and in the gas phase eventually leading to PFOA for $n \geq 8$, see section 2.2.

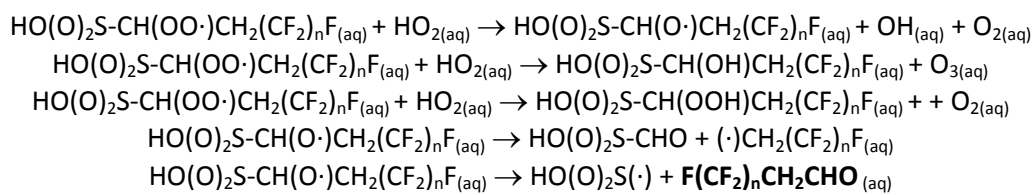
2.13.6 Poly(difluoromethylene), α -fluoro- ω -(2-sulfoethyl)-

This class of sulfonic acids (CAS RN 80010-37-3) has the following chain structure:



Sulfonic acids have low vapour pressures and are not reported to hydrolyse, but they may undergo photo-oxidation in aqueous surfaces, in the the atmospheric aqueous phase and in the gas phase. Established aqueous phase photo-oxidation reactions will eventually result in dissociation of the C-S bond leading to $n:2$ FTAL as one of the products:





Abiotic degradation of $\text{F}(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ will result in the formation of n:2 FTALs, which eventually will lead to PFOA for $n \geq 8$, see section 2.2. The environmental lifetime of the sulfonic acid is highly uncertain.

3 Grouping of substances

The experimental data and theoretical assessments of abiotic degradation pathways of potential PFOA precursors can be summarized either by substance class or by perfluoroalkyl chain structure.

3.1 Summary by substance class

There are 7 commercially available PFOA salts listed in CAS – 5 inorganic and 2 organic: Na^+ , 335-95-5; NH_4^+ , 3825-26-1; K^+ , 2395-00-8; Ag^+ , 335-93-3; Cr^{3+} , 68141-02-6; NEt_4^+ , 98241-25-9; 1-Phenyl-piperazine- H^+ , 1514-68-7. All are soluble in water, and they can therefore be considered as a class of substances leading to release of PFOA.

Fluorotelomer alcohols (FTOHs) undergoes photo-oxidation in the atmospheric gas and aqueous phases as well as in aqueous surfaces. FTOH's, having formulas $\text{F}(\text{CF}_2)_n(\text{CH}_2)_m\text{OH}$ with $n \geq 7$ and $m \geq 1$, can therefore be considered as a group leading to release of PFOA.

Mono- and di- 8:2 FT-PAPs are reported to undergo slow hydrolysis at environmental conditions (estimated lifetimes >26 years) resulting in 8:2 FTOH and phosphoric acid [D'Eon and Mabury, 2007]. It is explicitly noted that the experimental hydrolysis rates cannot be reproduced by existing models [Rayne and Forest, 2010]. Polyfluoroalkyl phosphoric acid mono- and diesters, mono- and diPAPs of n:m FTOHs with $n \geq 7$ and $m \geq 1$, including their polymers, can therefore be considered as a class of substances leading to release of PFOA.

Acrylates and methacrylates will all hydrolyse within a few years in the environment. Polymeric acrylates and methacrylates are expected to be hydrolysed more slowly with half-lives from several centuries to millennia [Hilal et al., 2003; Rayne and Forest, 2010]. Acrylates and methacrylates of n:m FTOHs with $n \geq 8$ and $m \geq 1$, including their polymers, can therefore be considered as a class of substances leading to release of PFOA.

Polyfluorinated halo silanes and silane esters undergo hydrolysis resulting in the corresponding silanols. Silanols, in turn, will under operational conditions take part in condensation and/or polymerisation reactions resulting in bonding to substrates via Si–O– links. No relevant information concerning hydrolytic lifetimes of condensed or polymerized polyfluorinated silanes was found in the open literature.

Polyfluorinated olefins (PFOs) undergo photo-oxidation in the atmosphere resulting in aldehydes (PFALs), which undergo further photo-oxidized to give PFAs. FTOs, a sub-class of PFOs having the structure $\text{F}(\text{CF}_2)_n(\text{CH}_2)_m\text{CX}=\text{CYZ}$ with $n \geq 7$ and $m \geq 0$, can therefore be considered as a class of substances leading to release of PFOA.

Per- and polyfluorinated phosphonic acids are not reported to undergo hydrolysis. In general, this group of substances cannot be considered as a class of substances leading to release of PFOA. However, the sub-class of phosphonic acids containing $\text{F}(\text{CF}_2)_n(\text{CH}_2)_m$ -groups with $n \geq 7$ and $m \geq 1$ will undergo photo-oxidation in the atmospheric aqueous phase and in aqueous surfaces, and can therefore be considered as a class of substances leading to release of PFOA.

Per- and polyfluorinated phosphinic acids are not reported to undergo hydrolysis. In general, this group of substances cannot be considered as a class of substances leading to release of PFOA. However, the sub-class of phosphinic acids containing $\text{F}(\text{CF}_2)_n(\text{CH}_2)_m$ -groups with $n \geq 7$ and $m \geq 1$ will undergo photo-oxidation in the atmospheric aqueous phase and in aqueous surfaces, and can therefore be considered as a class of substances leading to release of PFOA.

Polyfluorinated iodides (PFIs) undergo both hydrolysis and photolysis. In general, this group of substances cannot be considered as a class of substances leading to release of PFOA. However, the sub-class of PFIs containing $F(CF_2)_n(CH_2)_m$ -groups with $n \geq 7$ and $m \geq 1$ can be considered as a class of substances leading to release of PFOA.

Polyfluorinated amides, PFAMs, will undergo slow hydrolysis at environmental conditions. In general, this group of substances cannot be considered as a class of substances leading to release of PFOA. However, hydrolysis of PFAMs from n:m FTOHs with $n \geq 7$ and $m \geq 1$ will result in release of n:m FTOHs and can therefore be considered as a class of substances leading to release of PFOA.

Other potential PFOA precursors and UVCBs cannot in general be classified as classes of substances leading to release of PFOA. However, substances containing $F(CF_2)_n(CH_2)_m$ -groups with $n \geq 7$ and $m \geq 1$ will result in release of n:m FTOHs and can therefore be considered as a class of substances leading to release of PFOA, see section 3.2.

3.2 Summary by perfluoroalkyl chain structure

Substances containing a perfluorinated alkyl chain with the formula $F(CF_2)_n$ - ($n=7$ or 8) and is directly bonded to any chemical moiety other than a fluorine, chlorine or bromine atom and other than a phosphonic, phosphinic or sulfonic group will undergo abiotic degradation resulting in release of PFOA.

4 Literature

Adachi, M., Eguchi, W., and Haoka, T. (1974), Reactions of methyl iodine in aqueous sodium hydroxide solutions, *Journal of Chemical Engineering of Japan*, 7(5), 364-367.

Andersen, M. P. S., Nielsen, O. J., Toft, A., Nakayama, T., Matsumi, Y., Waterland, R. L., Buck, R. C., Hurley, M. D., and Wallington, T. J. (2005), Atmospheric chemistry of $C_xF_{2x+1}CH=CH_2$ (x=1, 2, 4, 6, and 8): Kinetics of gas-phase reactions with Cl atoms, OH radicals, and O_3 , *Journal of Photochemistry and Photobiology A: Chemistry*, 176(1-3), 124-128.

Atkinson, R. (1991), Kinetics of the gas-phase reactions of a series of organosilicon compounds with hydroxyl and nitrate (NO_3) radicals and ozone at 297 \pm 2 K, *Environmental Science & Technology*, 25(5), 863-866.

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., and van Leeuwen, S. P. J. (2011), Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins, *Integrated Environmental Assessment and Management*, 7(4), 513-541.

Chen, L., Fukuda, K., Takenaka, N., Bandow, H., and Maeda, Y. (2000), Kinetics of the gas-phase reaction of $CF_3CF_2CH_2OH$ with OH radicals and its atmospheric lifetime, *International Journal of Chemical Kinetics*, 32(2), 73-78.

Chiappero, M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., and Buck, R. C. (2006), Atmospheric Chemistry of Perfluoroaldehydes ($C_xF_{2x+1}CHO$) and Fluorotelomer Aldehydes ($C_xF_{2x+1}CH_2CHO$): Quantification of the Important Role of Photolysis, *The Journal of Physical Chemistry A*, 110(43), 11944-11953.

Chiappero, M. S., Argüello, G. A., Hurley, M. D., and Wallington, T. J. (2008), Atmospheric chemistry of $C_8F_{17}CH_2CHO$: Yield from $C_8F_{17}CH_2CH_2OH$ (8:2 FTOH) oxidation, kinetics and mechanisms of reactions with Cl atoms and OH radicals, *Chemical Physics Letters*, 461(4-6), 198-202.

D'Eon, J. C., and Mabury, S. A. (2007), Production of perfluorinated carboxylic acids (PFCAs) from the biotransformation of polyfluoroalkyl phosphate surfactants (PAPS): Exploring routes of human contamination, *Environmental Science & Technology*, 41(13), 4799-4805.

Ellis, D. A., Martin, J. W., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., and Wallington, T. J. (2003), Atmospheric Lifetime of Fluorotelomer Alcohols, *Environmental Science & Technology*, 37(17), 3816-3820.

Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., and Wallington, T. J. (2004), Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids, *Environmental Science & Technology*, 38(12), 3316-3321.

Environment Canada, Health Canada (2012): Screening Assessment Report, Perfluorooctanoic Acid, its Salts, and its Precursors

Fan, X. J., Colic, M., Kallay, N., and Matijevic, E. (1988), Precipitation of surfactant salts. III. Metal perfluoroalkancarboxylates, *Colloid Polym. Sci.*, *266*, 380-384.

Gauthier, S. A., and Mabury, S. A. (2005), Aqueous photolysis of 8:2 fluorotelomer alcohol, *Environmental Toxicology and Chemistry*, *24*(8), 1837-1846.

Gelest_Inc (2013), Metal-Organics Catalog, Gelest, Inc. of Morrisville, Pennsylvania (US).

Glowa, G. A., and Wren, J. C. (2003), Aqueous-gas phase partitioning and hydrolysis of organic iodides, *81*, 230-243.

Herrmann, H., and Zellner, R. (1996), *Reactions of NO₃-radicals in aqueous solution*, 1-71 pp., Alfassi, Wiley, New York.

Herrmann, H. (2003), Kinetics of aqueous phase reactions relevant for atmospheric chemistry, *Chem Rev*, *103*(12), 4691-4716.

Herrmann, H. (2007), On the photolysis of simple anions and neutral molecules as sources of O[•]/OH, SO_x⁻ and Cl in aqueous solution, *Physical Chemistry Chemical Physics*, *9*(30), 3935-3964.

Hilal, S. H., Karickhoff, S. W., Carreira, L. A., and Shrestha, B. P. (2003), Estimation of Carboxylic Acid Ester Hydrolysis Rate Constants, *QSAR & Combinatorial Science*, *22*(9-10), 917-925.

Hurley, M. D., Sulbaek Andersen, M. P., Wallington, T. J., Ellis, D. A., Martin, J. W., and Mabury, S. A. (2003), Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes, *The Journal of Physical Chem. A*, *108*(4), 615-620.

Hurley, M. D., Wallington, T. J., Sulbaek Andersen, M. P., Ellis, D. A., Martin, J. W., and Mabury, S. A. (2004), Atmospheric Chemistry of Fluorinated Alcohols: Reaction with Cl Atoms and OH Radicals and Atmospheric Lifetimes, *The Journal of Physical Chemistry A*, *108*(11), 1973-1979.

Hurley, M. D., Misner, J. A., Ball, J. C., Wallington, T. J., Ellis, D. A., Martin, J. W., Mabury, S. A., and Sulbaek Andersen, M. P. (2005), Atmospheric Chemistry of CF₃CH₂CH₂OH: Kinetics, Mechanisms and Products of Cl Atom and OH Radical Initiated Oxidation in the Presence and Absence of NO_x, *The Journal of Physical Chemistry A*, *109*(43), 9816-9826.

Jackson, D. A., and Mabury, S. A. (2012), Polyfluorinated Amides as a Historical PFCA Source by Electrochemical Fluorination of Alkyl Sulfonyl Fluorides, *Environmental Science & Technology*, *47*(1), 382-389.

Jackson, D. A., Wallington, T. J., and Mabury, S. A. (2013), Atmospheric Oxidation of Polyfluorinated Amides: Historical Source of Perfluorinated Carboxylic Acids to the Environment, *Environmental Science & Technology*, *47*(9), 4317-4324.

- Kaiser, M. A., Cobranchi, D. P., Chai Kao, C.-P., Krusic, P. J., Marchione, A. A., and Buck, R. C. (2004), Physicochemical Properties of 8-2 Fluorinated Telomer B Alcohol, *Journal of Chemical & Engineering Data*, 49(4), 912-916.
- Kelly, T., Bossoutrot, V., Magneron, I., Wirtz, K., Treacy, J., Mellouki, A., Sidebottom, H., and Le Bras, G. (2004), A Kinetic and Mechanistic Study of the Reactions of OH Radicals and Cl Atoms with 3,3,3-Trifluoropropanol under Atmospheric Conditions, *The Journal of Physical Chemistry A*, 109(2), 347-355.
- Lindstrom, A. B., Strynar, M. J., and Libelo, E. L. (2011), Polyfluorinated Compounds: Past, Present, and Future, *Environmental Science & Technology*, 45(19), 7954-7961.
- Liu, D., Xiu, Z., Liu, F., Wu, G., Adamson, D., Newell, C., Vikesland, P., Tsai, A.-L., and Alvarez, P. J. (2013), Perfluorooctanoic acid degradation in the presence of Fe(III) under natural sunlight, *Journal of Hazardous Materials*, 262(0), 456-463.
- Martin, J. W., Ellis, D. A., Mabury, S. A., Hurley, M. D., and Wallington, T. J. (2005), Atmospheric Chemistry of Perfluoroalkanesulfonamides: Kinetic and Product Studies of the OH Radical and Cl Atom Initiated Oxidation of N-Ethyl Perfluorobutanesulfonamide, *Environmental Science & Technology*, 40(3), 864-872.
- Nakayama, T., Takahashi, K., Matsumi, Y., Toft, A., Sulbaek Andersen, M. P., Nielsen, O. J., Waterland, R. L., Buck, R. C., Hurley, M. D., and Wallington, T. J. (2007), Atmospheric Chemistry of CF_3CHCH_2 and $\text{C}_4\text{F}_9\text{CHCH}_2$: Products of the Gas-Phase Reactions with Cl Atoms and OH Radicals, *The Journal of Physical Chemistry A*, 111(5), 909-915.
- OECD (2007): Lists of PFOS, PFAS, PFOA, PFCA related compounds and chemicals that may degrade to PFCA (as revised in 2007). ENV/JM/MONO(2006)15
- Papadimitriou, V. C., Papanastasiou, D. K., Stefanopoulos, V. G., Zaras, A. M., Lazarou, Y. G., and Papagiannakopoulos, P. (2007), Kinetic Study of the Reactions of Cl Atoms with $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$, $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$, and $\text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$, *The Journal of Physical Chemistry A*, 111(45), 11608-11617.
- Rayne, S., and Forest, K. (2010), Modeling the hydrolysis of perfluorinated compounds containing carboxylic and phosphoric acid ester functions and sulfonamide groups, *Journal of Environmental Science and Health, Part A*, 45(4), 432-446.
- Sellevåg, S. R., Kelly, T., Sidebottom, H., and Nielsen, C. J. (2004), A study of the IR and UV-Vis absorption cross-sections, photolysis and OH-initiated oxidation of CF_3CHO and $\text{CF}_3\text{CH}_2\text{CHO}$, *Physical Chemistry Chemical Physics*, 6(6), 1243-1252.
- Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., and Sidebottom, H. (2007), The gas phase tropospheric removal of fluoroaldehydes ($\text{C}_x\text{F}_{2x+1}\text{CHO}$, $x = 3, 4, 6$), *Physical Chemistry Chemical Physics*, 9(31), 4200-4210.
- Sulbaek Andersen, M. P., Hurley, M. D., Wallington, T. J., Ball, J. C., Martin, J. W., Ellis, D. A., and Mabury, S. A. (2003), - 381(- 1-2), - 21.

Sulbaek Andersen, M. P., Stenby, C., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J., Martin, J. W., Ellis, D. A., and Mabury, S. A. (2004), - 108(- 30), - 6330.

Tuazon, E. C., Aschmann, S. M., and Atkinson, R. (2000), Atmospheric Degradation of Volatile Methyl-Silicon Compounds, *Environmental Science & Technology*, 34(10), 1970-1976.

Vésine, E., Bossoutrot, V., Mellouki, A., Le Bras, G., Wenger, J., and Sidebottom, H. (2000), Kinetic and Mechanistic Study of OH- and Cl-Initiated Oxidation of Two Unsaturated HFCs: C₄F₉CHCH₂ and C₆F₁₃CHCH₂, *The Journal of Physical Chemistry A*, 104(37), 8512-8520.

Wallington, T. J., et al. (2006), Formation of C₇F₁₅COOH (PFOA) and Other Perfluorocarboxylic Acids during the Atmospheric Oxidation of 8:2 Fluorotelomer Alcohol, *Environ. Sci. Technol.*, 40, 924-930.

Young, C. J., Hurley, M. D., Wallington, T. J., and Mabury, S. A. (2008), - 112(- 51), - 13548.

Young, C. J., and Mabury, S. A. (2010), Atmospheric Perfluorinated Acid Precursors: Chemistry, Occurrence, and Impacts, in *Reviews of Environmental Contamination and Toxicology, Vol 208: Perfluorinated Alkylated Substances*, edited by D. M. Whitacre and P. DeVoogt, pp. 1-109, Springer, New York.


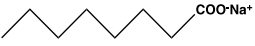
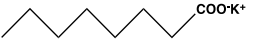

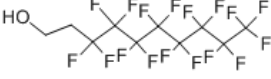
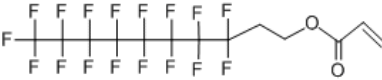

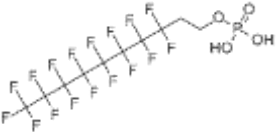
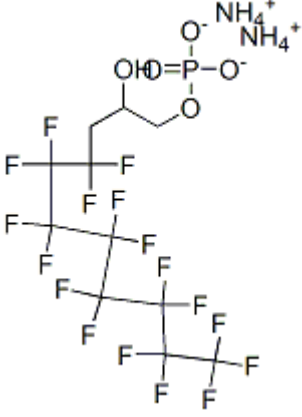
Zellner, R., and Herrmann, H. (1995), Free radical chemistry of the aqueous atmospheric phase, in *Spectroscopy in environmental science*, edited by R. J. H. Clark and R. E. Hester, pp. 381-451, Wiley, London.

ANNEX

List of abbreviations

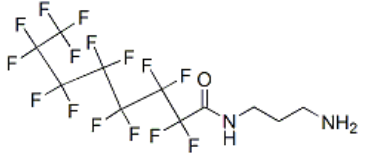
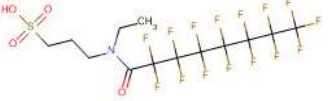
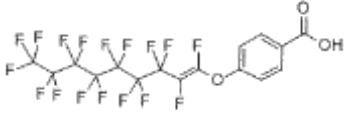
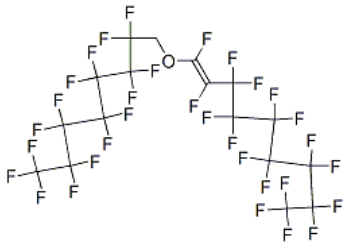
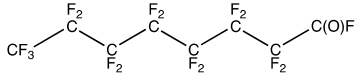


Acronym	Name	Structure
FTAc	Fluorotelomer acrylate	$F(CF_2)_nCH_2CH_2OC(O)CH=CH_2$
FTAL	Fluorotelomer aldehyde	$F(CF_2)_nCH_2CHO$
oFTAL	Odd-numbered Fluorotelomer aldehyde	$F(CF_2)_nCHO$
FTCA	Fluorotelomer carboxylic acid	$F(CF_2)_nCH_2C(O)OH$
FTI	Fluorotelomer iodide	$F(CF_2)_nCH_2CH_2I$
FTMAc	Fluorotelomer metacrylate	$F(CF_2)_nCH_2CH_2OC(O)C(CH_3)=CH_2$
FTOH	Fluorotelomer alcohol	$F(CF_2)_nCH_2CH_2OH$
oFTOH	Odd-numbered Fluorotelomer alcohol	$F(CF_2)_nCH_2OH$
FTO	Fluorotelomer olefin	$F(CF_2)_nCH_2CH_2CH=CH_2$
FTPAP	Fluorotelomer phosphate	$F(CF_2)_nCH_2CH_2OP(O)(OH)_2$
FTUCA	Fluorotelomer unsaturated carboxylic acid	N/A
PAP	Polyfluoro Alkyl Phosphate	N/A
PFA	Perfluorinated acid	N/A
PFAL	Perfluorinated aldehyde	N/A
PFAM	Polyfluorinated amide	N/A
PFCA	Perfluorocarboxylic acid	$F(CF_2)_nC(O)OH$
PFI	Perfluorinated iodide	N/A
PFNA	Perfluorononanoic acid	$F(CF_2)_8C(O)OH$
PFOA	Perfluorooctanoic acid	$F(CF_2)_7C(O)OH$

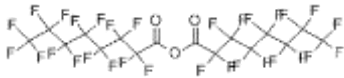
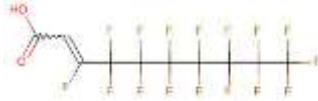

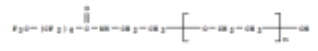
List of potential PFOA precursors.

Name	CAS-No.	Abbr.	Chem. Structure
PFOA salts			
2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-penta-deca-fluoro-octanoic acid, ammonium salt	3825-26-1	APFO	
2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-penta-deca-fluoro-octanoic acid, sodium salt	335-95-5		
2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-penta-deca-fluoro-octanoic acid, potassium salt	2395-00-8		
2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-penta-deca-fluoro-octanoic acid, silver salt	335-93-3		
Fluorotelomer alcohols			
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecan-1-ol	678-39-7	8:2 FTOH	
Fluorotelomer acrylates			
8:2 Fluorotelomer acrylate	27905-45-9	8:2 FTAC	
Fluorotelomer methacrylates			
8:2 Fluorotelomer methacrylate	1996-88-9	8:2 FTMAC	
Polyfluoroalkyl phosphoric acid monoesters			
8:2 Fluorotelomer phosphate monoester	57678-03-2	8:2 monoPAP	
Diammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-hydroxyundecyl phosphate	94200-45-0		

8:2 Fluorotelomer phosphate monoester ammonium salt	93857-44-4		
Polyfluoroalkyl phosphoric acid diesters			
8:2 Fluorotelomer phosphate diester	678-41-1	8:2 diPAP	
Polyfluorinated silanes (PFSi)			
Perfluorodecyldichloromethylsilane	3102-79-2		
Perfluorodecyldimethylchlorosilane	74612-30-9		
Perfluorooctylethyltriethoxysilane	101947-16-4		
Perfluorodecyltrichlorosilane	78560-44-8		
Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane	83048-65-1		
Per- and polyfluorinated phosphonic acids			
Perfluorooctyl phosphonic acid	40143-78-0	C8-PFPA	
Per- and polyfluorinated phosphinic acid			
Bis(perfluorooctyl) phosphinic acid	40143-79-1	C8/C8-PFPIA	
Bis(perfluorooctyl) phosphinic acid	610800-34-5	C6/C8-PFPIA	$O=P(OH)(C_8F_{17})_2$

Tris[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)phenyl]phosphine	325459-92-5		
bis[tris(4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)phenyl)phosphine]palladium(ii) dichloride	326475-46-1		
Polyfluorinated olefines			
8:2 Fluorotelomer olefin	21652-58-4	8:2 FTO	
Polyfluorinated iodines			
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iododecane	2043-53-0	8:2 PFI	
Perfluorooctyl iodide	507-63-1		
Polyfluorinated amides			
2-carboxyethylbis(2-hydroxyethyl)-3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]propylammonium hydroxide	39186-68-0		
N-[3-[bis(2-hydroxyethyl)amino]propyl]-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide	41358-63-8		
3,4-bis[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]benzenesulphonyl chloride;3,4-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctylamino)benzenesulfonyl chloride	24216-05-5		
1-Propanaminium,N,N,N-trimethyl-3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]-, chloride	53517-98-9		

N-(3-aminopropyl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide;Einecs 288-891-4	85938-56-3		
1-Propanesulfonic acid, 3-[ethyl(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino] -, sodium salt	89685-61-0		
Others			
4-[(heptadecafluoro-nonyl)oxy]-Benzoic acid	58253-65-9		
heptadecafluoro-1-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]nonene	84029-60-7		
Pentadecafluoro-octanoyl fluoride	335-66-0		
Pentadecafluoro-octanoic acid methyl ester	376-27-2		
Pentadecafluoro-octanoic acid ethyl ester	3108-24-5		
2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-propenoate, alpha-(2-methyl-1-1-oxo-2-2-propenyl)-omega-[(2-methyl-1-oxo-2-propenyl)oxy]poly(oxy-1, 2-ethanediyl), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-nonacosafuorohexadecyl 2-propenoate, octadecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafuorotetradecyl 2-propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-tritriacontafuorooctadecyl 2-propenoate	116984-14-6 17741-60-5 34362-49-7 4813-57-4 34395-24-9 65150-93-8	(Co-polymer made by a mix where some are PFOA precursors)	

Pentadecafluorooctanoic anhydride	33496-48-9		
2-Decenoic acid, 3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-	70887-84-2		
Decanoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluoro-	27854-31-5		
UVCBs			
Fatty acids, C7-13, perfluoro	3-92-6		
Fatty acids, C7-13, perfluoro, compds. with ethylamine	69278-80-4		
Fatty acids, C6-18, perfluoro, ammonium salts	72623-77-9		
Carboxylic acids, C7-13, perfluoro, ammonium salts	72968-38-8		
Octanoic acid, pentadecafluoro-, mixed esters with 2,2'-[1,4-butanediylbis(oxymethylene)]bis[oxirane] and 2,2'-[1,6-hexanediylbis(oxymethylene)]bis[oxirane]	90480-57-2		
Fatty acids, C7-19, perfluoro	91032-01-8		
Amides, C7-19, alpha-omega-perfluoro-N,N-bis(hydroxyethyl)	90622-99-4		
Carbamic acid, [2-(sulfothio)ethyl]-, C-(gamma-omega-perfluoro-C6-9-alkyl) esters, monosodium salts	95370-51-7		
1,3-Propanediol, 2,2-bis(.gamma.-.omega.-perfluoro-C4-10-alkyl)thiomethyl derivs., phosphates, ammonium salts	148240-85-1		
1,3-Propanediol, 2,2-bis(.gamma.-.omega.-perfluoro-C6-12-alkyl)thiomethyl derivs., phosphates, ammonium salts	148240-87-3		
Pentanoic acid, 4,4-bis(.gamma.-.omega.-perfluoro-C8-20-alkyl)thio derivs., compds. with diethanolamine;4,4-Bis[(gamma-omega-perfluoro-alkyl(C=8-20))thio]pentanoic acid derivs. compds. with diethanolamine	71608-61-2		
Polymers			
Poly(oxy-1,2-ethanediyl),a-[2-[2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]ethyl]-w-hydroxy	93480-00-3		
2-Propenoic acid, 2-methyl-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl ester, polymer with 2-propenoic acid	53515-73-4		
Poly(difluoromethylene), alpha-fluoro-omega-[2-[[2-(trimethylammonio)ethyl]thio]ethyl]-, methyl sulfate	65530-57-6		
Poly(difluoromethylene), .alpha.,.alpha.-phosphonicobis(oxy-2,1-ethanediyl)bis.omega.-fluoro-	65530-62-3		
Poly(difluoromethylene), .alpha.-fluoro-.omega.-2-(phosphonoxy)ethyl-	65530-61-2		

Poly(difluoromethylene), .alpha.-fluoro-.omega.-(2-sulfoethyl)-	80010-37-3		
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