

PFAS Degradation/Transformation Examples

TURI materials prepared for:
Toxics Use Reduction Science Advisory Board

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PFAS to FOCUS ON

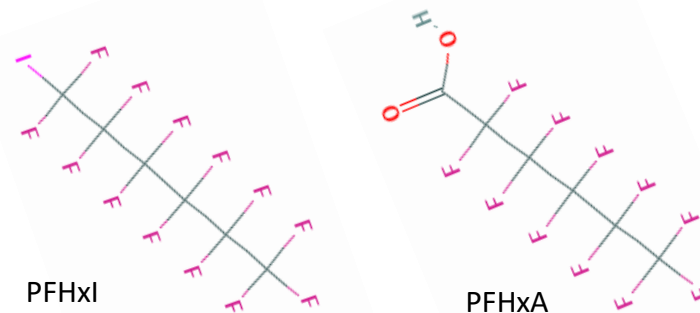
Perfluoroalkyl Substances

Examples

Perfluoroalkyl halides

Perfluorohexyl Iodide - PFHxI

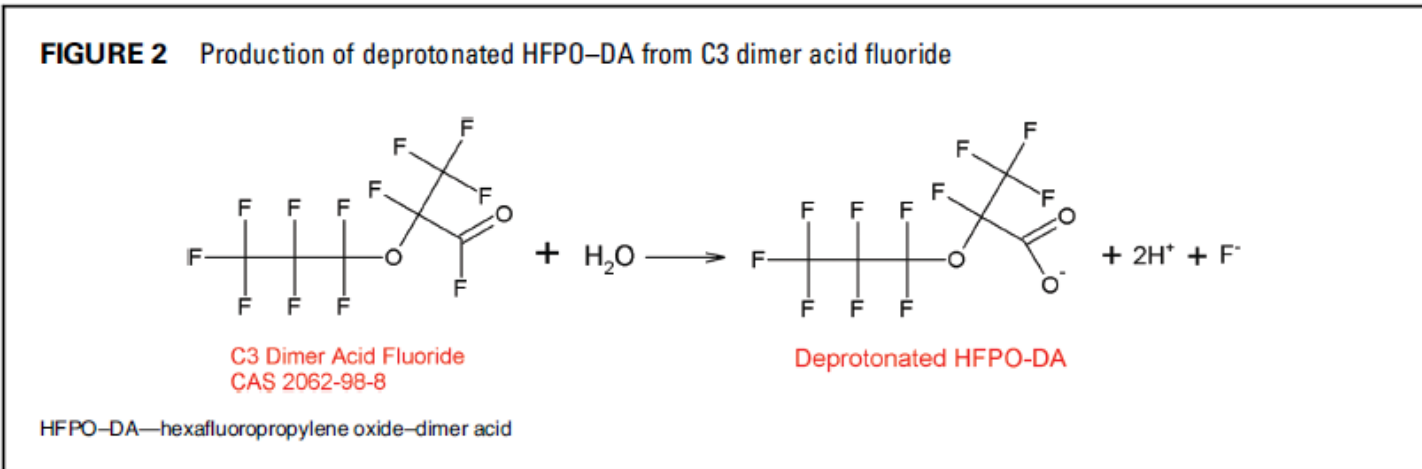
PFHxA



Example: Perfluoroalkyl iodide

Korzeniowski & Buck; "The PFAS Universe: Uses, Classification & Degradation" Webinar for IC2 & MA TURI. 30 January 2019

Perfluoroether acyl halides - hydrolysis



Hopkins et al, 2018. *Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids*, Journal AWWA July 2018, 110:7.

Short-chain Fluorotelomer – C6 Biodegradation Pathway



Short-chain Fluorotelomer-based Products and Raw Materials

Transient Biodegradation Intermediates

e.g., 6:2 FTOH, 6:2 FTSA, 6:2 FTCA, 6:2 FTUCA, 5:3 Acid



Short-chain PFCA Terminal Degradation Products

PFCA_s

PFBA

PFPeA

PFHxA

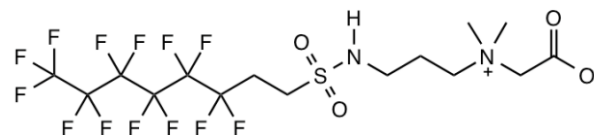
PFHpA

Degradation products formed and yields vary by substance, matrix (e.g., soil, sediment, air,) and mode (biotic vs. abiotic)

Korzeniowski & Buck; "The PFAS Universe: Uses, Classification & Degradation" Webinar for IC2 & MA TURI. 30 January 2019. slide 59

Example:

6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) (34455-29-3)
Aqueous photolysis



L.J. Trouborst, 2016. *Aqueous photolysis of 6:2 fluorotelomer sulfonamide alkylbetaine*

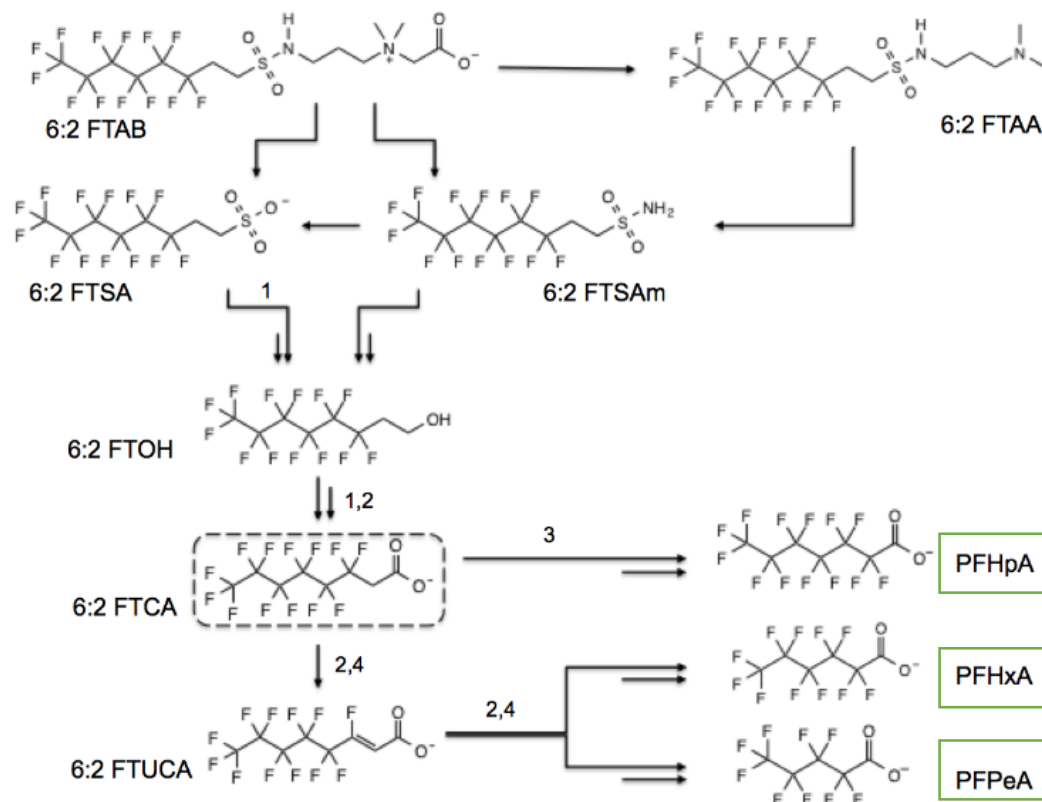


Figure 2.6: Proposed aqueous photodegradation for 6:2 FTAB. Double arrows indicate that a reaction occurs in multiple steps. Only 6:2 FTCA, in the dashed box, was not

Short-chain ECF Biodegradation Pathway



ECF-based Products and Raw Materials

Transient Biodegradation Intermediates

e.g., FASA, FASE, FASAA, etc.



PFSA and PFCAs Terminal Degradation Products

PFASs: PFBS, PFPeS, PFHxS, PFHpS, PFOS

PFCAs: PFBA, PFPeA, PFHxA, PFHpA, PFOA

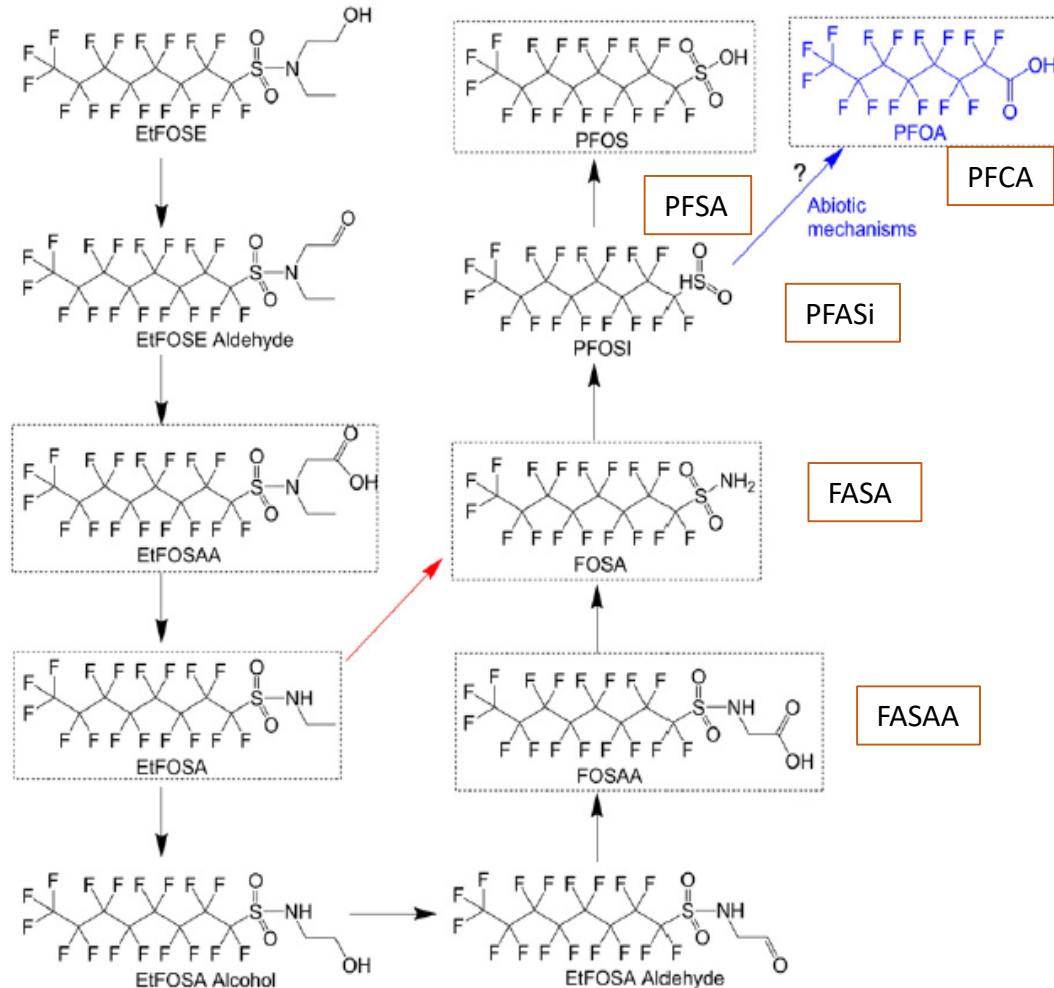
Degradation products formed and yields vary by substance, matrix (e.g., soil, sediment, air), and mode (biotic vs. abiotic)

Korzeniowski & Buck; "The PFAS Universe: Uses, Classification & Degradation" Webinar for IC2 & MA TURI. 30 January 2019. Slide 61

Example:

Long chain Urethanes, acrylates, etc. based on EtFOSE - N-ethyl perfluorooctane sulfonamide ethanol
Aerobic biodegradation in activated sludge

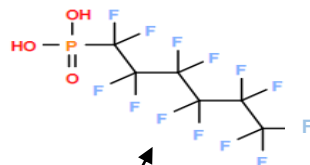
J. Liu, S. Mejia Avendaño / Environment International 61 (2013) 98-114



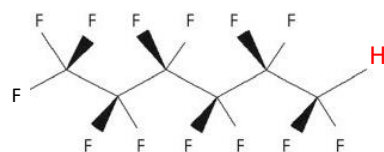
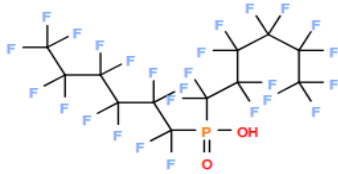
J Liu and S Mejia Avendano, 2013. Microbial degradation of polyfluoroalkyl chemicals in the environment: A review.

Perfluoroalkyl Phosphonic Acid (PFPIA)

Perfluoroalkyl Phosphonic Acid (PFPA)

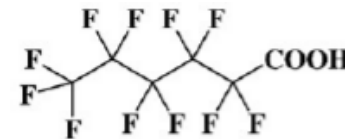


Cleavage of C-P bond



1-H Perfluoroalkanes
(Metabolite)

Defluorinated and
Oxidized



Perfluoroalkyl Carboxylic Acids (PFCA)

Perfluoroalkyl Phosphonic Acid (PFPIA)

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 1H-perfluoroalkanes which are defluorinated and oxidized to give a PFCA with one less perfluorinated carbon atom than is present in the 1H-perfluoroalkane metabolite. According to this scheme, PFPIAs with a perfluorooctyl chain can be metabolized 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.

In fish, PFPA was detected as a product of this biotransformation. In rats, both the PFPA and corresponding 1H-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. High liver-to-blood concentration ratios for both PFPIAs and PFPAs in rats also suggested the liver as a site of biotransformation.

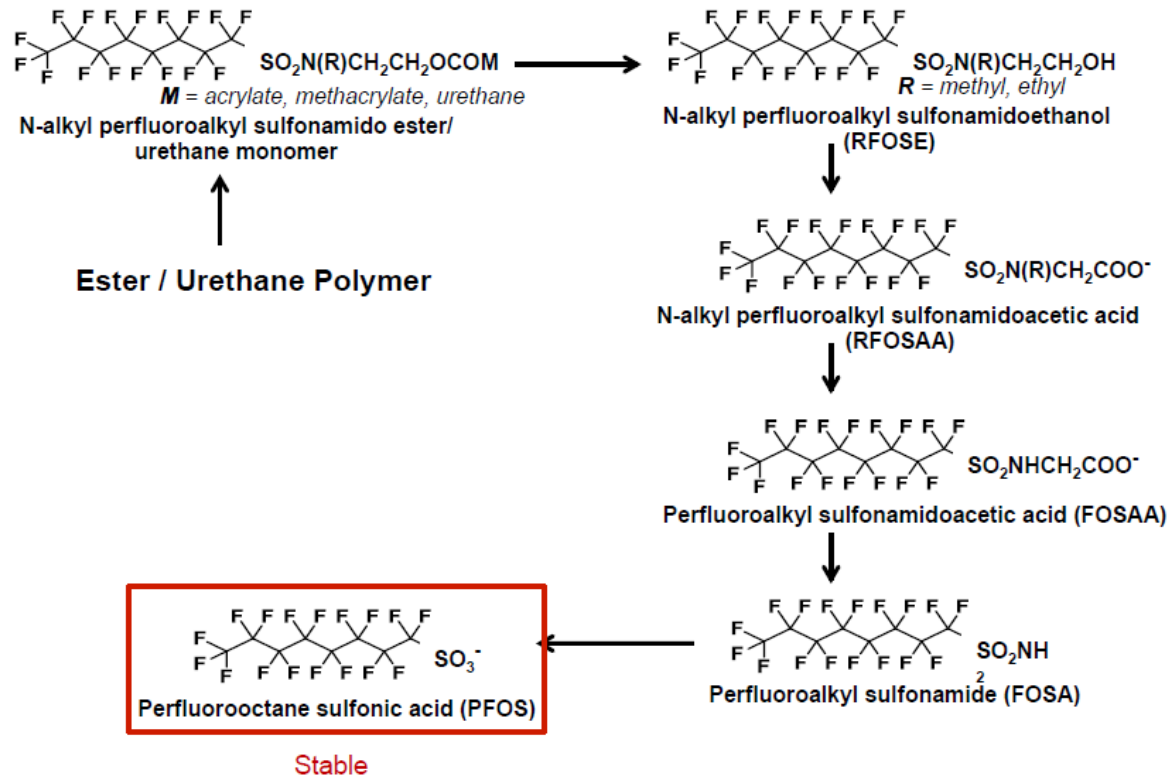
Joudan, S., Yeung, L., & Mabury, S. A. (2017). *Biological Cleavage of the C–P Bond in Perfluoroalkyl Phosphonic Acids in Male Sprague-Dawley Rats and the Formation of Persistent and Reactive Metabolites*. *Environmental health perspectives*, 125(11), 117001. doi:10.1289/EHP1841

Holly Lee, Amila O. De Silva, and Scott A. Mabury (2012). *Dietary Bioaccumulation of Perfluorophosphonates and Perfluorophosphinates in Juvenile Rainbow Trout: Evidence of Metabolism of Perfluorophosphinates*. *Environmental Science & Technology*, 46 (6), 3489-3497. DOI: 10.1021/es204533m

Example:

Sulfonamide derivatives: e.g., Urethane Polymers - Perfluoroalkyl sulfonamido ester

Oxidative Transformation to form PFOS



Ref: Mills, M. Per- and Polyfluoroalkyl Substances (PFAS): Source/Site Characterization and Treatment/Remediation.. Emerging Contaminants Summit 2018, Westminster, CO, March 06 - 07, 2018.

Accessed at: https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=538492&Lab=NRMRL

PFBS Precursors Abiotic Degradation

The PFBS-related substances identified in the study by Nielsen, 2017, include

- PFBS salts,
- sulfonic acid halides,
- sulfonic alkyl/olefinic/aryl esters,
- sulfonamides,
- sulfones and
- side-chain fluorinated polymers containing the PFBS moiety.
- Perfluorobutane sulfinic acid also represents a precursor to PFBS through oxidation to the required sulfonic acid group

“Contributions to the overall amount of PFBS in the environment come from production, use and emissions of PFBS and its salts, as well as from degradation of PFBS-related substances during use, in the waste stage, or in the environment. However, the concern is first and foremost associated with the ultimate degradation product PFBS. On this basis the scope of the present SVHC-dossier has been selected to be PFBS and its salts.”



R = any chemical group, in particular R = -OH, -F, -Cl, -OR', -NR'R''
where R' and R'' represent any chemical group.

Related substances include e.g. sulfonic halides, sulfonic acid salts,
sulfonic esters, sulfonamides, sulfones and sulfinic acid.

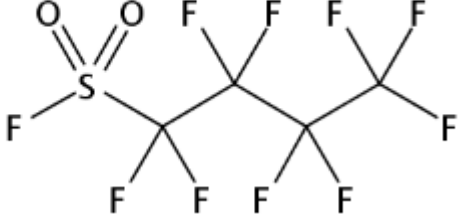
Figure 2: Chemical structure of PFBS-related substances

Ref: ECHA 2019. Proposal for Identification of a Substance of Very High Concern on the Basis of the Criteria set out in REACH Article 57; Perfluorobutane Sulfonic Acid (PFBS) and its Salts. Submitted by Norway 05.08.2019. p. 22.

<https://echa.europa.eu/documents/10162/1e516c08-d91e-6da3-87f7-cc0679135422>

PFBS Precursors – Sulfonyl Halides

Abiotic Degradation - hydrolysis

CAS RN	Name	Structure
* 375-72-4	1-Butanesulfonyl fluoride, 1,1,2,2,3,3,4,4,4-nonafluoro-	

The PFBS and PFHxS sulfonyl fluorides do not hydrolyse readily in pure water, but they will eventually do so. The PFBS and PFHxS sulfonyl fluorides are reported to hydrolyse reasonably fast in the presence of traces of NH₃ [Honda and Takano, 2013]. The PFBS and PFHxS sulfonyl chlorides and -bromides readily hydrolyses upon contact with water

PFBS and PFHxS sulfonyl halides will eventually undergo hydrolysis resulting in the release of respectively PFBS and PFHxS.

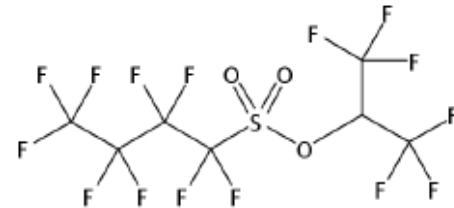
Ref: Nielsen 2017. Potential PFBS and PFHxS Precursors: Literature study and theoretial assessment of abiotic degradation pathways leading to PFBS and PFHxS.

<https://www.miljodirektoratet.no/globalassets/publikasjoner/M792/M792.pdf>

PFBS Precursors – Fluoroalkyl Esters of PFBS Abiotic Degradation – hydrolysis and photo-oxidation

Example:

118334-96-6 1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,2-trifluoro-1-(trifluoromethyl)ethyl ester



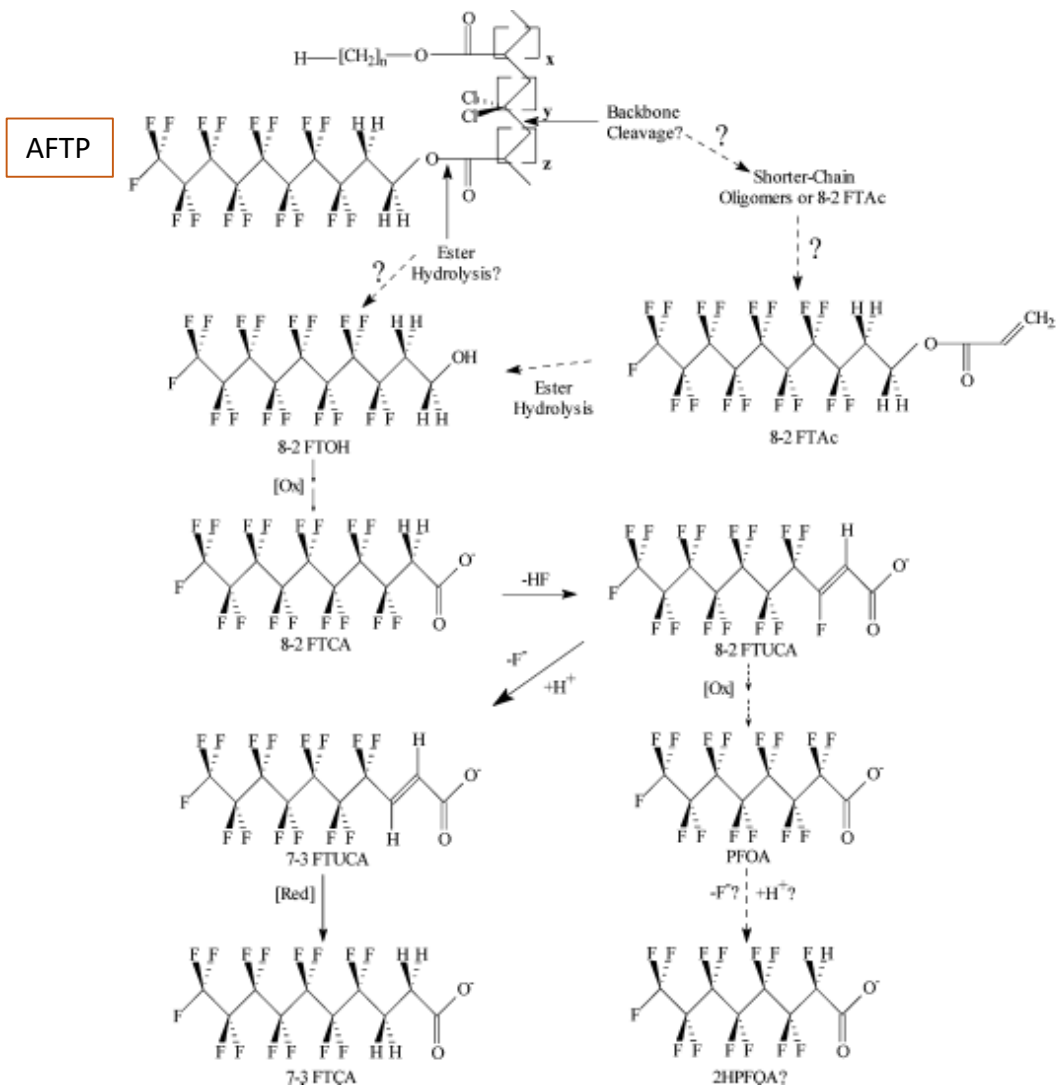
All commercially available PFBS (nonaflate) and PFHxS fluoroalkyl esters (n-C₄F₉SO₂-O-R and n-C₆F₁₃SO₂-O-R) will eventually undergo hydrolysis; no relevant information concerning hydrolytic lifetimes of the alkyl esters listed was found in the open literature. The vapour pressures available for some of the nonaflate fluoroalkyl esters listed in Table 2.3.2 are relatively high and they are therefore also expected to undergo photo-oxidation in the atmosphere. They all have H-atom(s) in α -position, and they will follow the same mechanism as outlined for the PFBS alkyl esters, see section 2.3.2.

Fluorinated alkyl esters of PFBS and PFHxS will eventually hydrolyse / alternatively undergo photo-oxidation resulting in the release of respectively PFBS and PFHxS. Photo-oxidation of PFBS and PFHxS fluorinated alkyl esters may also result in the release of C₂ – C₆ PFCA's.

Ref: Nielsen 2017. Potential PFBS and PFHxS Precursors: Literature study and theoretical assessment of abiotic degradation pathways leading to PFBS and PFHxS.

<https://www.miljodirektoratet.no/globalassets/publikasjoner/M792/M792.pdf>

Washington 2009: Degradability of an Acrylate-Linked Fluorotelomer Polymer in Soil

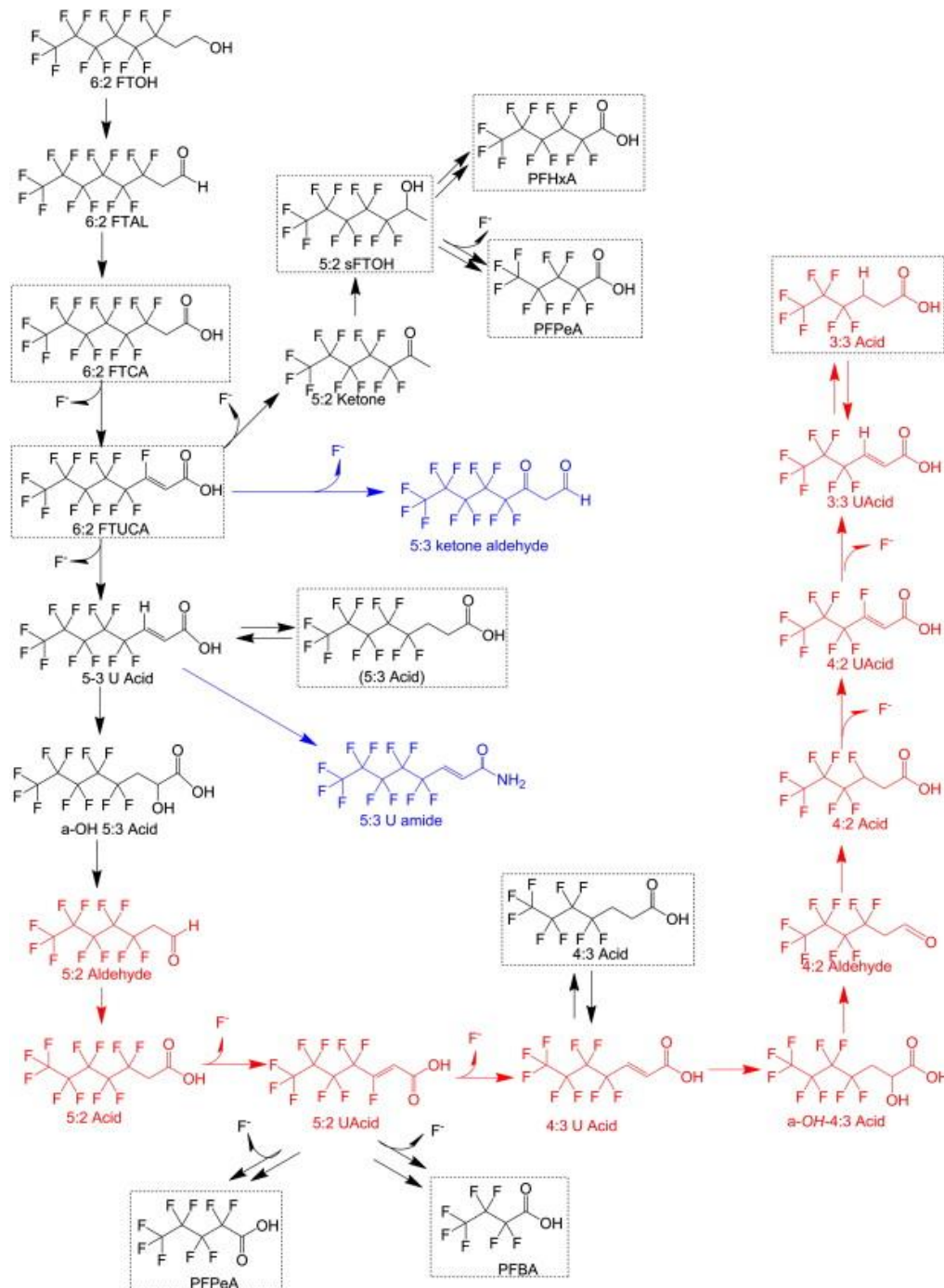


Potential pathways for AFTP degradation include cleavage of the carbon backbone to form the 8-2 fluorotelomer acrylate (8-2FTAc), or hydrolysis of the ester linkage between the perfluorinated chain and the carbon backbone to form the 8-2 fluorotelomer alcohol (8-2FTOH; Figure 1) (20). If 8-2FTAc is formed, it likely is subject to degradation to form 8-2FTOH.

Further degradation of 8-2FTOH has been shown via oxidation to 8-2 fluorotelomer carboxylic acid (8-2FTCA) and then to 8-2 fluorotelomer unsaturated carboxylic acid (8-2FTUCA) (21). -oxidation of 8-2FTUCA is known to occur through a series of transitory intermediates to form PFOA, the conventionally inferred terminal compound identified for this oxidative degradation sequence (Figure 1) (21). Degradation of 8-2FTUCA also can yield the 7-3 fluorotelomer unsaturated carboxylic acid (7-3FTUCA) and then the 7-3 fluorotelomer carboxylic acid (7-3FTCA) which possibly can undergo oxidation to PFOA (21).

Example: 6:2 fluorotelomer

Aerobic biodegradation pathways of 6:2 FTOH in activated sludge and aerobic soils



The double arrows indicate multiple transformation steps. Defluorination reactions are indicated by release of fluoride ions (F⁻).

Blue pathways have been observed only in soil (Liu et al., 2010b), while

red pathways have been observed only in sludge (Wang et al., 2012).

Stable and semi-stable compounds are shown inside dashed boxes.

Ref: Liu and Avendano, 2013. Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. Environment International Nov 2013.

Accessed at:

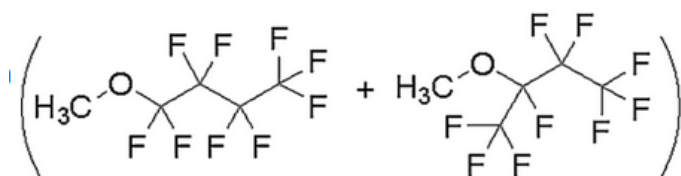
<https://www.sciencedirect.com/science/article/pii/S0160412013001931?via%3Dihub#f0005>

Hydrofluoroethers: Atmospheric Degradation

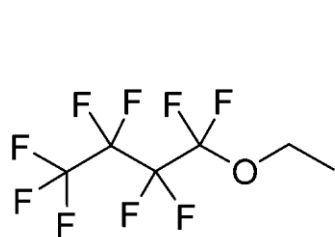
Among HFEs, **HFE-7100** and **7200/8200** can react with OH radicals and form $C_4F_9OC(O)H$ as well as $C_4F_9OC(O)CH_3$ and $C_4F_9OC(O)H$, respectively (Chen et al., 2011b; Christensen et al., 1998; Wallington et al., 1997). These intermediates can undergo further reaction with OH radicals and form PFBA (for a detailed mechanistic analysis, see Chen et al., 2011b).

In addition, the atmospheric oxidation of **HFE-7500** forms $C_3F_7CF(OC(O)CH_3)CF(CF_3)_2$ and $C_3F_7CF(OC(O)H)CF(CF_3)_2$ (Goto et al., 2002). The authors also suggested that both degradation products will likely be hydrolysed by moist air and form $C_3F_7CF(OH)-CF(CF_3)_2$, which can likely be further oxidized to $C_3F_7C(O)CF(CF_3)_2$ (Goto et al., 2002). By analogy with the atmospheric degradation of $C_2F_5C(O)CF(CF_3)_2$ (Jackson et al., 2011), it is expected that $C_3F_7C(O)-CF(CF_3)_2$ can further undergo direct photolysis (under low No_x conditions) or hydrolysis (rather slow) to yield PFBA.

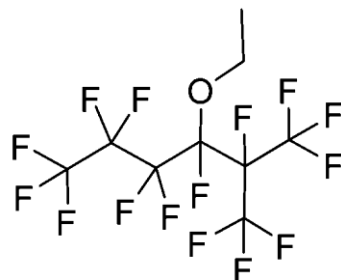
Wang, Cousins, Scheringer, Buck, Hungerbuhler, 2014. "Global emission inventories for C_4-C_{14} perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part II: The remaining pieces of the puzzle." *Environment International* 69 (2014) 166-176.



HFE-7100



HFE-7200



HFE-7500



PFBA