Performance

Study of PFASs applied to mechanical engineering

FIM/Cetim study

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Foreword

Industrial mechanical engineering companies took action at a very early stage to reduce the impact of their activities on the environment and are continuously striving to adapt their economic models and practices to regulatory and technological developments. Evidence of this commitment is demonstrated by their search for alternatives to dangerous chemical substances and the control of risks that these substances represent whenever no alternative is available.

The French Association of Mechanical Industries (FIM) actively promotes the continued strengthening of measures to protect human health and the environment through the substitution of high-risk chemicals by safer alternatives. The FIM believes that regular updating of the various regulations applicable to the substances, whether they are used in the manufacturing processes or as components of manufactured processes, must guarantee or even improve the competitiveness of companies and innovations. To do so, this update must take into account the available alternatives, the ability of user industries to adapt their practices and must be established in consistency with the various regulations applicable to a single product. This is especially vital as it relates to the circular economy which raises questions about the conditions under which waste containing hazardous substances are reused.

As part of its Chemicals Strategy for Sustainability, published in October 2020 the European Commission has set the objective of phasing out the use of per- and polyfluoroalkyl substances (PFAS) as a group unless their use is essential for society. The restriction of substances as a group and the definition of essential uses are new features in the regulatory framework applicable to the substances and are the subject of related legislative work.

The application of these new criteria is justified by the specific properties of PFASs, a "family" of 4,700 highly environmentally persistent chemicals, some of which can easily migrate into the environment. It is worth noting that several compounds belonging to the PFAS group have already been regulated at the European or global level due to their specific harmfulness. Moreover, this proposed general restriction of PFASs goes in hand with a specific project for the restriction of fire-retardant foams.

Due to the large number of substances belonging to the PFAS group, their various uses in industrial applications and the fact that there is no obligation of traceability for most of these compounds, there is a heightened need to assist mechanical engineering companies in identifying the relevant uses and the available or studied alternative solutions. The FIM commends the work performed by Cetim. This paper, provides an overview of various studies and existing data on PFASs and their uses in the industry, particularly those which have been identified as critical. It will provide industrial mechanical engineering companies with information so they are better able to anticipate the implementation of the upcoming restrictions on PFASs.

About the FIM:

The French Association of Mechanical Industries (FIM) acts on a European, national and regional level. It works to provide the companies that it represents with a favourable framework for their growth and competitiveness. It assists them with their modernisation efforts. It romotes the image of the mechanical engineering industry and its trades in order to attract talents, preserve know-how and foster recruitment. www.fim.net

1 Abbreviations

PFAS:	Per- and polyfluoroalkyl substances
PFCA:	Perfluorated carboxylic acid
PFOS:	Perfluorooctanesulfonic acid (CAS No.: 1763-23-1)
PFOA:	Perfluorooctanoic acid (CAS No.: 335-67-1)
PFHxS:	Perfluorohexanesulfonic acid (CAS No.: 355-46-4)
PFHxA:	Perfluorohexanoic acid (CAS No.: 307-24-4)
PFAA:	Perfluoroalkyl acids
PTFE:	Polytetrafluoroethylene (CAS No.: 9002-84-0)
TFE:	Tetrafluoroethylene
PVDF:	Polyvinylidene fluoride (CAS No.: 24937-79-9)
FEP:	Fluorinated Ethylene Propylene (CAS No.: 25067-11-2)
PFAP:	Perfluoroalkoxy polymers
PVF:	Polyvinyl fluoride (CAS No.: 95508-16-0)
FTOH:	Fluorotelomer alcohols
ETFE:	Ethylene tetrafluoroethylene (CAS No.: 25038-71-5)
HFE:	Hydrofluoroether
PFS:	Perfluoroalkane sulfonyl
PFDoDA:	Perfluorododecanoic acid (CAS No.: 307-55-1)
PFunDA:	Perfluoroundecanoic acid (CAS No.: 2058-94-8)
PFBA:	Perfluorobutyric acid (CAS No.: 375-22-4)
PFDA:	Perfluorodecanoic acid (CAS No.: 335-76-2)
PFNA:	Perfluorononanoic acid (CAS No.: 375-95-1)
FTS:	Fluorotelomer sulfonate
PFE:	Per- and polyfluoroalkyl ether
POSF:	Perfluorooctanesulfonyl fluoride (CAS No.: 307-35-7)
PMVE:	Perfluoromethylvinylether
PFSA:	Perfluorosulfonic acid
FASA:	Perfluoroalkane sulfonamide
FASE:	Perfluoroalkane sulfonamido ethanol
PFASAA:	Perfluoroalkane sulfonamido amine
PASF:	Perfluooroalkane sulfonyl fluoride
PFASNO:	Perfluoroalkane sulfonamido amine oxide
PACF:	Perfluoroalkane carbonyle fluoride
FTB:	Fluorotelomer betaine
FTAA:	Fluorotelomer sulfonamide alkylamine
FTPA:	Perfluorotripropylamine
PFPE:	Perfluoropolyether
PFSmA:	Perfluoroalkane sulfonyl (meth)acrylate
FTmAP:	n: 2 fluorotelomer-based (meth)acrylate polymers
FTUP:	n: 2 fluorotelomer-based urethane polymers

THV:	Terpolymer of tetrafluoroethylene
VDF-HFP:	Vinylidenefluoride-hexafluoropropylene
VDF:	Vinylidene
Mono/diPAP:	n: 2 Fluorotelomer phosphate mono/diester
FTP:	Fluorotelomer polymers
PFESA:	Per- or polyfluoroalkyl ether sulfonic acid
FTNP:	n: 2 fluorotelomer-based non-polymers
PFA:	Perfluoroalkanes
LE:	Liaison ether (Ether bond)
PFASmAP:	Perfluoroalkane sulfonyl (meth)acrylate polymer
FTS:	n: 2 fluorotelomer sulfonyl
PFS:	Perfluoroalkane sulfonyl
FTmA:	n: 2 fluorotelomer-based (meth)acrylate
FTsP:	n: 2 fluorotelomer-based side-chain fluorinated polymers
FTSi:	n: 2 fluorotelomer-based silanes
FTSix:	n: 2 fluorotelomer-based siloxanes/silicon polymers
SAmPAPs:	Perfluoroalkane sulfonyl amido ethanols, phosphate esters
PFECA:	Per- or polyfluoroalkyl ether carboxylic acid
PFESA:	Per- or polyfluoroalkyl ether sulfonic acid
xFASA/Es:	Perfluoroalkane sulfonyl amides/amido ethanols
PAP:	Perfluoroalkyl phosphate
FTSA:	Fluorotelomer sulfonic acid
PCTFE:	Polychlorotrifluoroethylene
PFPE:	Perfluoropolyether
FKM:	Fluorocarbon-based fluoroelastomer, generally made up of VDF, HFP, TFE or PMVE
FFKM:	Fluoroelastomers containing an even higher amount of fluorine than FKM fluoro-elastomers
FVMQ:	Fluorosilicones

2 Background of the study

PFASs are a broad group of substances that are often poorly identified, both in relation to their structures and the industrial uses that are made of these substances. However, over the past few years, there have been changes to regulations (e.g. REACh) and focus has been placed on these substances and on reducing their use.

Recent work has helped to identify a number of uses; however these studies are few in number and are lacking in data relative to available and potential alternatives as well as production tonnages.

The Netherlands and Germany, with support from Norway, Sweden and Denmark, are preparing a proposal to restrict all substances classified as PFAS. This proposal is expected to be submitted to the ECHA in January 2023.

The FIM asked Cetim to carry out a documentary study on PFASs, their general and critical uses in the various mechanical engineering fields, the release of these substances into the environment as well as data from public consultation.

3 Definition of PFASs

Per- and polyfluoroalkyl substances (PFAS) are a broad family of fluorinated molecules made up of oligomers, polymers and non-polymers. These molecules are generally surfactants (neutral or anionic) and exhibit great thermal, chemical and biological stability. There is no international consensus as to the definition of PFASs, nevertheless, there are a number of definitions which are broadly used in the scientific world and in regulations.

3.1 OECD and the REACh restriction file

A PFAS is a chemical substance with the following structure:

$X\text{-}(\text{-}CF_2\text{-})_n\text{-}X'$

Where $n \geq 1$ and X and X' are not hydrogen atoms.

According to this definition, a PFAS is any substance with at least one saturated and fully fluorinated carbon atom, i.e. a chemical substance comprising at least:

- one perfluorinated methyl group ($\text{-}CF_3$);
- OR one perfluorinated methylene group ($\text{-}CF_2\text{-}$).

The definition used for the REACh consultation dossier makes it possible to consider a very large number of substances as being PFASs. For reference, in 2018, the OECD published a database of 4,700 PFASs that was compiled using a more restrictive definition.

3.2 Bück et Al.

The previous generally accepted definition for characterising PFASs was that proposed by Bück et Al. in 2011:

Highly fluorinated aliphatic substances that contain 1 or more C atoms on which all the H substituents (present in the non fluorinated analogues from which they are notionally derived) have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety ($\text{-}C_nF_{2n+1}$).

This definition excludes aromatic compounds as well as those which do not comply with the ($-C_nF_{2n+1}$) rule.

Although this definition can still be used to define PFASs, the consultation file on PFASs uses the OECD definition to identify substances as a PFAS.

3.3 US EPA

The US Environmental Protection Agency has its own definition for a PFAS:

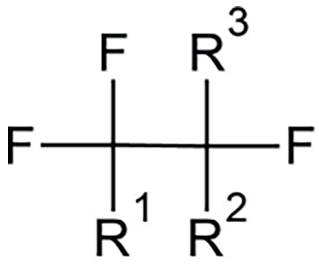


FIGURE 1: Definition of PFAS by the US EPA - R1, R2 and R3 are not hydrogen

The database compiled by the US EPA contains over 9,000 substances classified as a PFAS, without information being given as to the uses of each substance. This definition will not be used in this report however it is worth noting that it differs from that of the OECD.

3.4 Definition used in this study

As part of this report, the definition used will be that proposed by the OECD and also used in the restriction proposal submitted by Germany, the Netherlands, Norway, Sweden and Denmark. For ease of reference and to take advantage of the classification made by the OECD in its PFAS database, the other definitions and classifications will not be taken into consideration.

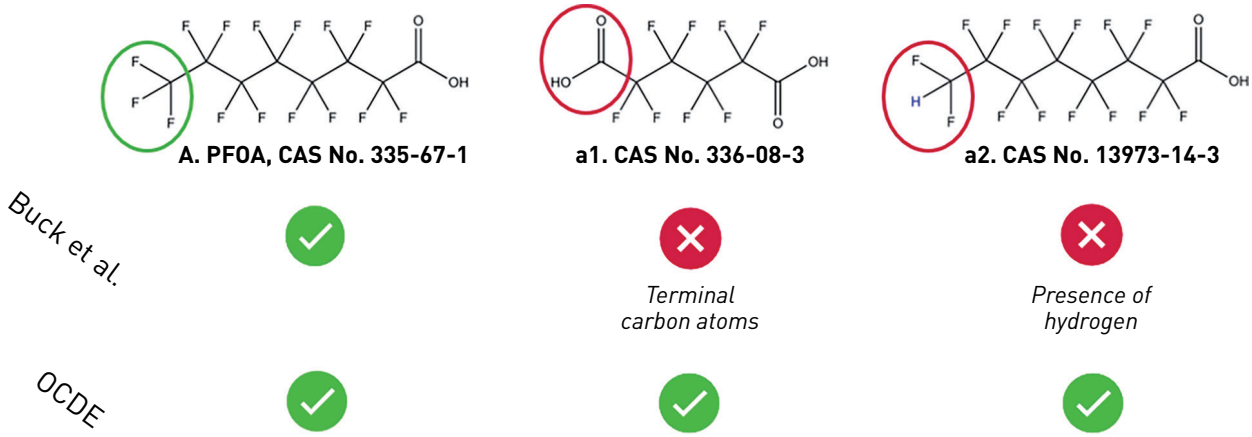


FIGURE 2: Comparison between the Bück et Al. and the OECD definitions

Using the OECD definition makes it possible to consider a larger number of substances as PFASs; for example, it is worth noting here that according to the Bück et Al. definition, the a1 substance cannot be a PFAS as the presence of two functional groups at the terminal carbon atoms prevents the structure from complying with the C_NF2_{N+1} rule.

The same applies to the a2 substance, where the presence of a hydrogen on the terminal carbon atom prevents compliance with this same rule. As such, polyfluorinated substances would be largely excluded from PFASs.

4 Classification of PFASs

A distinction is made between perfluorinated substances **(Figure 3)** and polyfluorinated substances **(Figure 4)**: perfluorinated substances are molecules where the carbon atoms are all saturated with fluorine, except for possible functional groups.

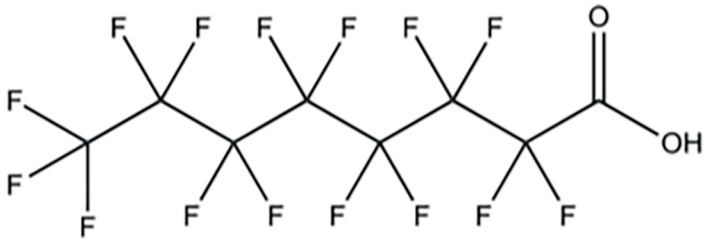


FIGURE 3: PFOA (CAS No.: 335-67-1) [5]

Polyfluorinated substances are similar, however they possess carbon atoms that are not saturated with fluorine, i.e., substituted with hydrogen atoms.

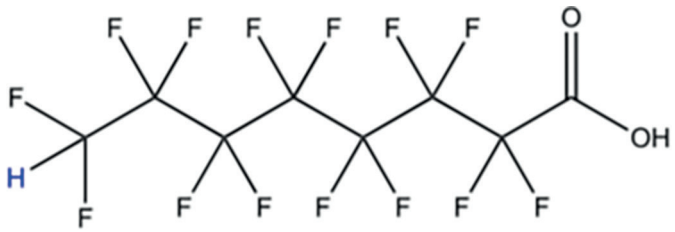


FIGURE 4: 8H-perfluorooctanoic acid (CAS No.: 13973-14-3) [5]

Likewise, on this molecule **(Figure 4)**, the terminal carbon atom has a hydrogen atom; therefore it is not fully substituted by fluorine atoms.

Beyond this initial difference between poly and perfluorinated substances, it is the size and the type (linear, branched, aromatic, cyclic, etc.) of the carbon chain as well as the types and numbers of functional groups in the molecule which will determine its properties and classification, at least according to the OECD. In the case of polymers, this will also be determined by the level of curing, the cross-linking and the presence of secondary branched chains.

Owing to the number and large range of PFASs, these substances need to be divided into sub-categories. A study carried out by the OECD in 2018 uses the functional groups and the chemical structure to divide the PFASs into categories and consistent sub-categories, so that the substances of the same subgroup share similar chemical structures and can potentially be studied together rather than individually.

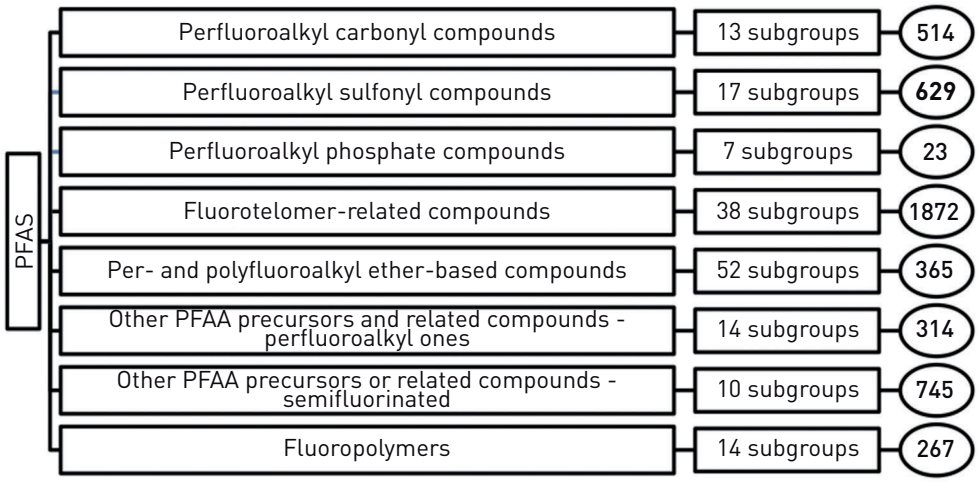


FIGURE 5: OECD PFAS structure categories

Based on the results of this study, 4,700 substances can be characterised as PFASs, broken down into 8 sub-categories. This is the most recent classification for such a large number of substances.

The US EPA also has a grouping of different databases on its Comptox site; however, this site does not categorise PFASs into groups or subgroups, even though the list comprises a greater number of substances.

It is worth noting that the classification proposed by the OECD does not take into account the uses of the PFASs, only their chemical structures.

A simplified classification is given by the BDI in its 2021 report on the PFAS restriction proposal. In one quick glance, the user can quickly identify the major types of PFASs (fluoropolymers, fluoro-elastomers, non-polymer substances).

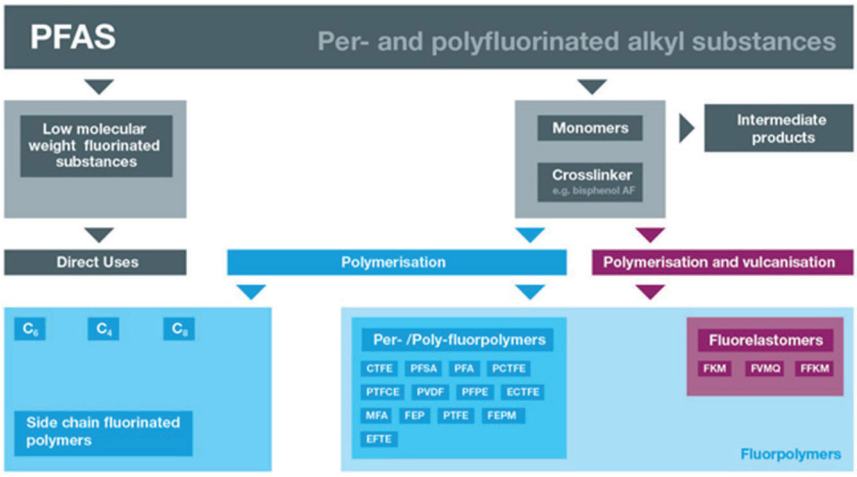


FIGURE 6: Presentation of PFASs (BDI, 2021)

4.1.1 Perfluoroalkyl carbonyl compounds

These substances are characterised by the presence of a carbonyl group in the substance so that the structure complies with the rule: C_nF2_{n+1}-C(=O)-R where R can be another carbon chain, a hydrogen, a salt, etc.

This group includes perfluoroalkyl carboxylic acids (PFCA), which are the PFASs identified as having the largest number of uses in the industry.

FIGURE 7: Perfluorooctanoic acid (CAS No. : 335-67-1)

This category covers compounds such as PFOA, a perfluoroalkyl carboxylic acid, as well as the salts, derivatives and esters of this acid. According to the OECD classification, this subcategory of PFAS consists of at least 514 substances.

4.1.2 Perfluoroalkyl sulfonyl compounds

These substances are characterised by the presence of a functional sulfonyl group or one of its derivatives, which fulfils the chemical structure C_nF2_{n+1}-S(=O)(=O)-R where R can be another carbon chain, a hydrogen, a salt, etc.

FIGURE 8: Perfluorooctanoic acid (CAS No.: 335-67-1)

This sub-category includes compounds such as PFOS or PFHxS. According to the OECD classification, this sub-category contains at least 629 substances.

4.1.3 Perfluoroalkyl phosphate compounds

These substances are characterised by the presence of one functional phosphate group or one of its derivatives, which fulfils the chemical structure C_nF2_{n+1}-P(=O)-R where R can be a carbon chain, a hydrogen, a halogen, a hydroxyl group, etc.

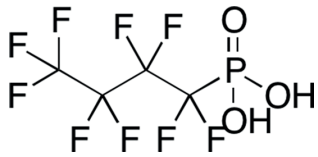


FIGURE 9: Perfluorobutylphosphonic acid (52299-24-8)

This sub-category also includes phosphonic and phosphinic acids. It contains at least 23 substances according to the OECD classification.

4.1.4 Fluorotelomer-related compounds

According to the OECD, this category contains compounds considered as fluorotelomers and related compounds. These compounds do not necessarily comply with a strict rule concerning their chemical structures; however they are substances produced by the telomerisation of fluorinated oligomers.

They are named using an "n: x" prefix where "n" indicates the number of fully fluorinated carbon atoms and "x" indicates the number of carbon atoms that are not fully fluorinated.

Therefore, the following molecule **(Figure 10)** has 8 perfluorinated carbon atoms and 2 non-fluorinated carbon atoms as well as a hydroxyl group (OH); it is therefore named 8:2 fluorotelomer alcohol or 8:2 FTOH for short.

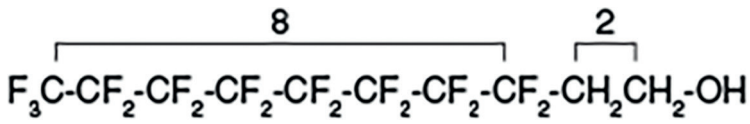


FIGURE 10: 8:2 FTOH (678-39-7)

This sub-category includes a large number of fluorotelomer groups such as fluorotelomer-based non-polymer PFAS **(Figure 11)**, n:2 fluorotelomer alcohols **(Figure 12)**, phosphate esters **(Figure 13)** and n:2 fluorotelomer-based (meth)acrylate polymers **(Figure 14)**.

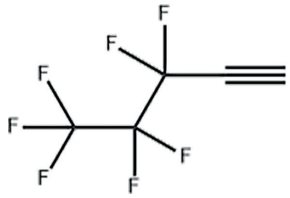


FIGURE 11: 3,3,4,4,5,5,5-heptafluoropentyne (CAS No.: 80337-25-3)

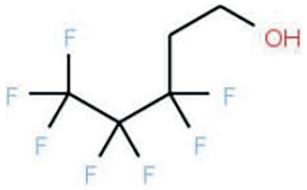


FIGURE 12: 1-Pentanol, 3,3,4,4,5,5,5-heptafluoro- (CAS No.: 755-40-8)

FIGURE 13: Bis[2-(perfluorohexyl)ethyl] Phosphate (CAS No.: 57677-95-9)

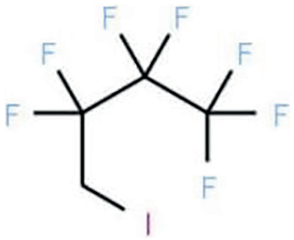


FIGURE 14: 1H, 1H-heptafluoro-1-iodobutane (CAS No.: 374-98-1)

This sub-category consists of at least 1,872 substances according to the OECD classification.

4.1.5 Per- and polyfluoroalkyl ether-based compounds

These substances are characterised by the presence of a functional ether group which fulfils the chemical structure CnF2n+1-O-CmF2m+1-R where R can be a carbon chain, an aromatic, another functional group, etc.

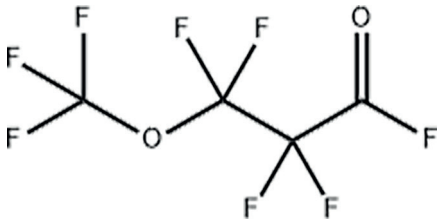


FIGURE 15: Propanoyl fluoride, 2,2,3,3-tetrafluoro-3-(trifluoromethoxy)- (CAS No.: 425-38-7)

This sub-category contains at least 365 substances according to the OECD classification. It includes perfluoromono carboxylic acids and diethers.

4.1.6 Other PFAA precursors and related compounds – perfluoroalkyl one and semifluorinated

These two subgroups include perfluoroalkyl acid precursor compounds, i.e. PFAS compounds consisting of a perfluorinated carbon chain and a charged or uncharged functional moiety, typically a carboxylate, a phosphonate or a sulfonate. Therefore, these two categories do not specifically correspond to precise chemical structures, but rather to substances which can lead to the synthesis of other PFASs.

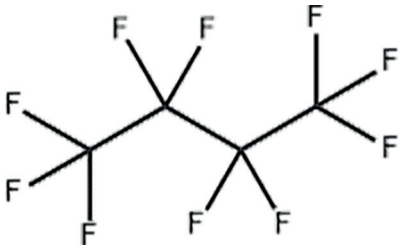


FIGURE 16: Butane, 1,1,1,2,2,3,3,4,4,4-decafluoro- (CAS No.: 355-25-9)

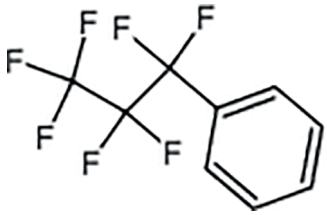


FIGURE 17: Benzene, (1,1,2,2,3,3,3-heptafluoropropyl)- (CAS No.: 378-98-3)

The perfluoroalkyl category consists of at least 314 substances **(Figure 16)** and the semi-fluorinated category, 745 substances **(Figure 17)**.

This sub-category does not have the highest number of substances, however it should be noted that in 2019, fluoropolymers represented 22% of PFAS imports into the European Union. This category also includes fluoroelastomers such as FKM, FFKM and FVMQ. These fluoroelastomers

are used in applications where the material undergoes pressure changes and/or must exhibit elastic properties, in addition to the properties of the PFASs.

4.1.7 Fluoropolymers

This sub-category includes all polymer PFASs, both functionalised (with one or more chemical functional groups) and non-functionalised. Given the multiple number of existing polymers, there is no rule as to the chemical structure of these substances.

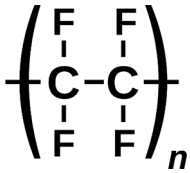


FIGURE 18: PTFE (CAS No.: 9002-84-0)

This category consists of PTFE, PVDF, FEP, PVA and PVF. This last sub-category contains at least 267 substances according to the OECD classification.

4.2 Physical and chemical properties

PFASs possess good high temperature-stability due to the presence of the fluorinated chain. This tail withstands temperature changes, acids, bases, oxidation-reduction agents as well as photolysis and microbiological degradation processes. This resistance stems from the carbon-fluorine bonds which are chemically very stable.

Most PFASs have one or more functional groups in addition to this fluorinated chain. The structure of this group varies considerably and will therefore determine the use made thereof, nevertheless the generally polar nature of PFASs allows them to have good surface-active properties and as such they are used in industry as surfactants. The presence of the apolar polyfluorinated carbon chain and the polar functional group provides PFASs with hydrophobic and lipophobic properties, respectively.

Most functional groups can separate and form ions. Different types of PFAS are obtained depending on the type of ion:

- Anionic: Contains one or more acid functional groups (carboxylic acid, sulfonic acid, sulphate, phosphate, etc.) that can release an H+ ion, and form a negatively-charged anion.
- Cationic: Contains one or more basic functional groups (amine, etc.) that can obtain a H+ ion, and form a positively charged cation.
- Zwitterionic: Contains two or more functional groups able to form an anion and a cation, resulting in, a positively and negatively charged molecule.
- Non-ionic: Does not contain any group able to form ions; the molecule is and remains neutral unless it suffers degradations or it reacts.

The ionic nature of the substance will affect its mobility in the environment, its effectiveness (acid chrome plating bath, zwitterionic surfactants) and its reactivity with other molecules.

One other criterion used to characterise PFASs is the length of the fluorinated chain. The distinction is usually made between short-chain PFASs, with 6 or less carbons, and long-chain PFASs with

7 or more carbons. Long-chain PFASs have increased toxicity for organisms, can be bioaccumulative by fauna and flora and are more persistent than short chain PFASs.

The emissions and the accumulation in the natural environment, particularly in water, are especially complex issues as they depend on the nature of the functional group, the length of the chain as well as nature of the medium, the transport processes at play and the transformations. More in-depth details are provided in the section regarding the mobility of PFASs.

5 Applications

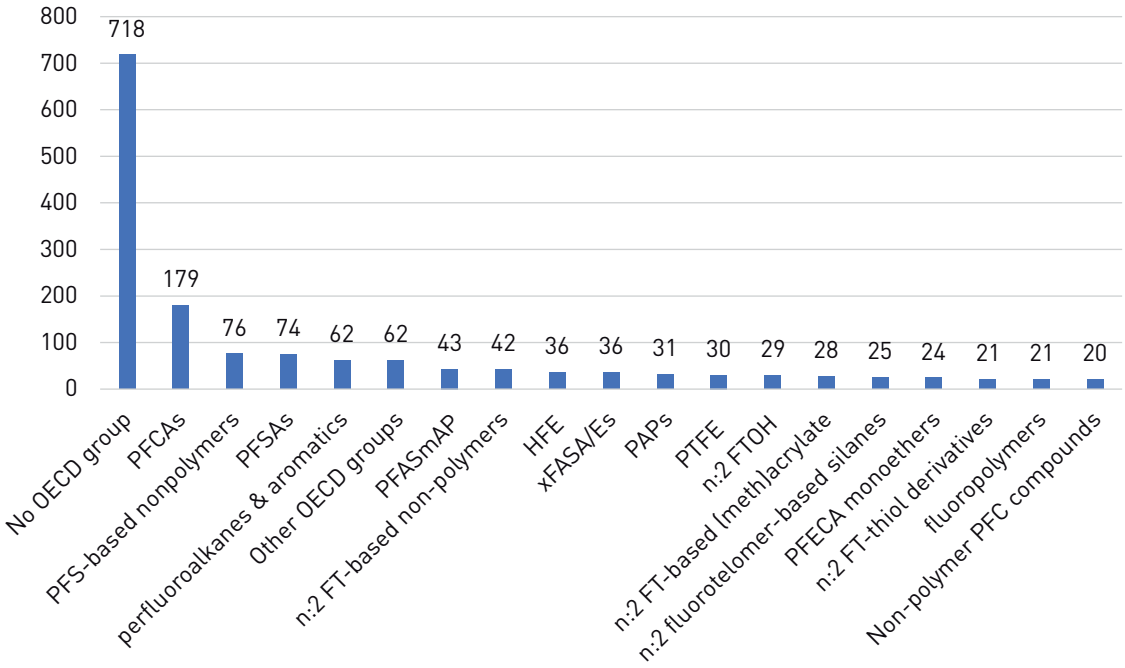
5.1 Overview

PFASs constitute a family covering a large number of molecules, as previously seen and are therefore used for many applications in industrial sectors. Since the early 2000s, there has been a significant reduction in the use and the production of PFCA in Europe, the United States and Japan, where a decrease of 95% in the production of this substance has been reported.

However, it is worth noting that PFASs are generally used in small quantities, including as surfactants or are present as production residues for certain plastics. Moreover, their use in many sectors has been continued through the replacement of long-chain PFASs with short-chain PFAS.

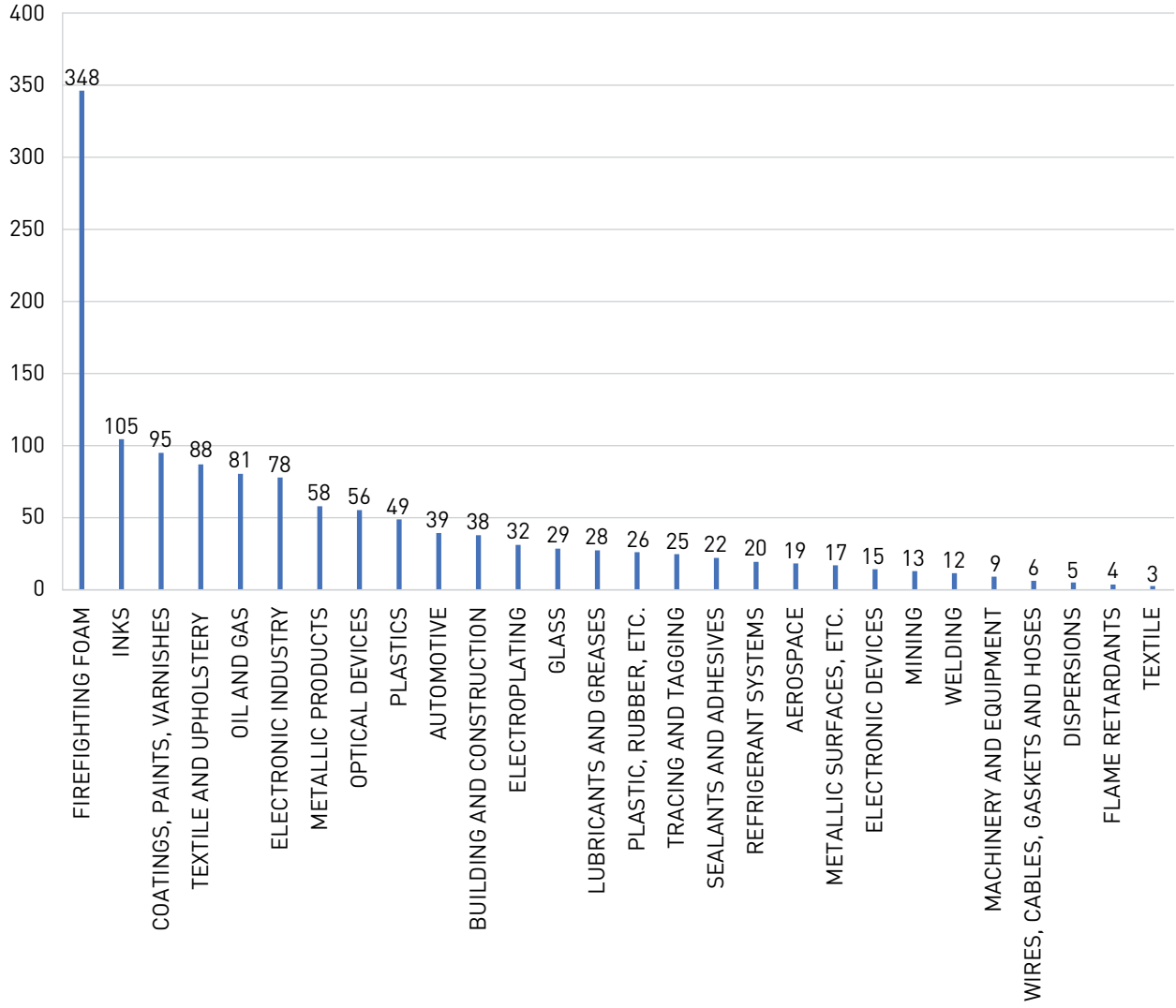
Over the past few years, given the increasing focus placed on PFASs in regulations, a lot of data and studies has been published concerning their uses. This data gives insight into the applications of PFASs in mechanical engineering.

The collected data is presented by sector of application. The sectors of use of PFASs are primarily taken from the restriction proposal, or from studies conducted on their applications in industry.



GRAPH 1: Main categories of PFASs with an identified use

Many PFASs with an identified application in industry are not included in the OECD database. This reflects how complicated it is to compile an exhaustive list of the substances considered as PFASs, as well as the difficulties involved with specifically determining the applications, uses, production tonnages and the steps to be taken to handle each substance.



GRAPH 2: Number of PFASs with an identified use per sector

The available data regarding the uses is not exhaustive; a 2020 study identifies applications for over 1,400 PFASs, via patents and other documents, while an article based on feedback from PFAS producers estimates that there are 256 fluorinated substances used in the industry, a number that is considered more reasonable by the author. As a result, there is some degree of uncertainty concerning the number of PFASs used, the specific properties required for their applications and the associated tonnages.

5.2 Firefighting foams

Firefighting foams are the most representative application for PFASs, due to their great stability at high temperature and their surface active properties. They are primarily used for liquid fires (class B), such as fires caused by oil, acetone, petroleum or alcohol.

The types of firefighting foams are broken down into several sub-categories depending on the technology used to fight the fire:

Type of foam	Subcategory of foams	Application of PFASs
Synthetic foams	Aqueous film forming foams (AFFF)	Aid the formation of the aqueous film
	Alcohol-resistant aqueous film forming foams (AR-AFFF)	Foam stabiliser
Protein foams	Fluoroprotein foam (FP)	Fuel repellent
	Film-forming fluoroprotein foam (FFFP)	Assist with the formation of the aqueous film Foam stabiliser
	Alcohol-resistant fluoroprotein foam (AR-FP)	No data
	Alcohol-resistant film-forming fluoroprotein foam (AR-FFFP)	No data

TABLE 1: Classification of the various types of firefighting foams

AFFF foams are divided into three sub-categories depending on their compositions: the former POSF-based AFFFs, the former fluorotelomer-based AFFFs, the modern fluorotelomer-based AFFFs.

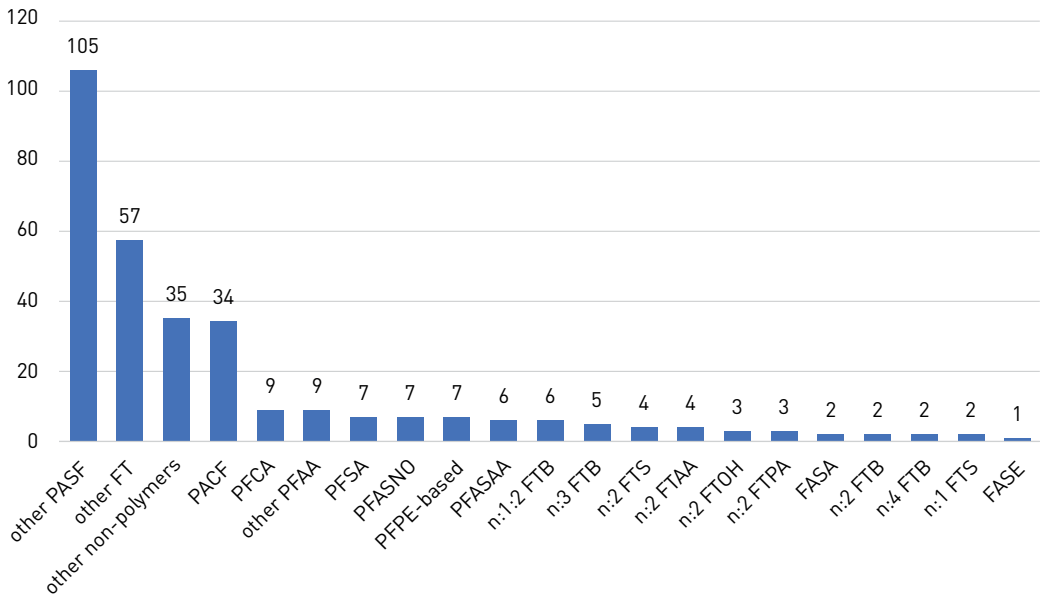
Type of foam	Date of manufacture	PFAS used and present
POSF-based AFFF	Manufactured from late 1960 to early 2002	POSF, POSF precursors, short-chain PFSA (PFHxS)
Fluorotelomer-based AFFF	Manufactured between 1970 and 2016	Short-chain (C6) PFAS (50-98% in the formulation)
Modern fluorotelomer-based AFFF	Current formulation	Short-chain (C6) PFAS exclusively

TABLE 2: Types of AFFF foams and main PFASs used in their formulations

The long-chain fraction of these foams can break down in the environment into PFOA and into other PFCAs.

Firefighting foams, particularly fluorotelomer-based foams, have a long lifetime (10 to 20 years). Accordingly, there is still a usable stock of long-chain PFAS-based firefighting foams available, and as a result, fluorinated substances are still being released on industrial sites and into the environment.

There are many PFAS used in the AFFFs and they belong to various sub-categories:



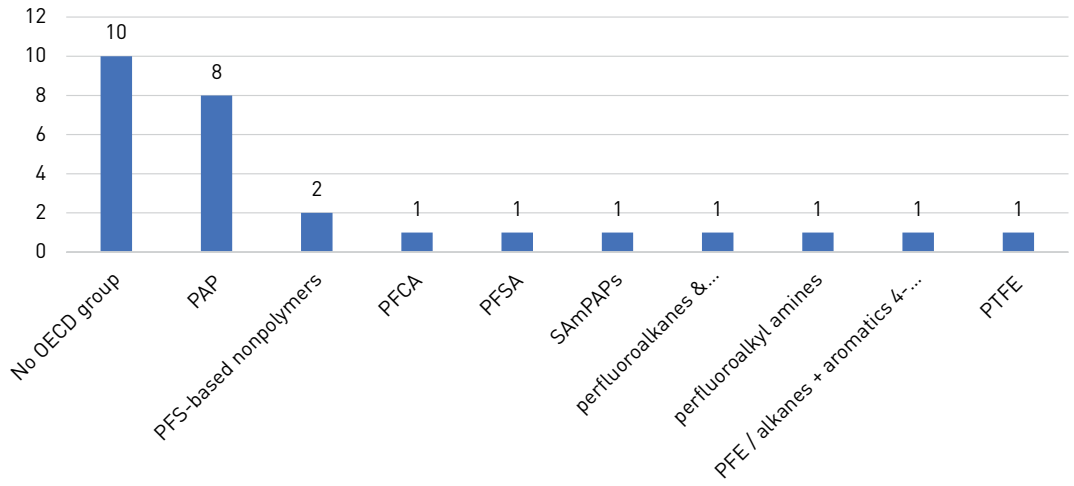
GRAPH 3: Main categories of PFASs used in AFFF foams

The firefighting foams which have PFAS in their formulations are mainly used for liquid fires on professional sites such as airports, fire stations and military sites.

A high proportion of sulfonyl (PASF) has been noted as well as many short-chain fluorotelomers. The PFASs of the PFHxA regulatory category are reportedly the most widely used in the field of firefighting foams.

5.3 Production of plastics and rubber

There is widespread use of PFASs in the plastics industry; fluoropolymers such as PTFE (CAS No.: 9002-84-0), PVDF (CAS No.: 24937-79-9), poly[tetrafluoroethylene-co-perfluoro (alkyl vinyl ether)] (CAS No.: 24937-79-9) and THV (CAS No.: 25190-89-0) are used for the production of plastic and rubber products; non-polymers can be used as additives for plastic and rubber, mould release agents (thanks to their hydrophobic and oleophobic properties) or as processing aids for non-fluorinated polymers.



GRAPH 4: Main categories of PFASs used as mould release agents for plastics

At present, worldwide, the most heavily consumed PFAS polymer in industry is PTFE. It is extensively used in many professional disciplines including aerospace, and for various applications namely coating for construction materials (e.g. greenhouses) and for plastic items (containers, tanks, hoses, valves, moulds, etc.).

PTFE is also used in consumer goods, particularly as a non-stick coating for cookware.

Fluoroelastomers are used for certain sealants, gaskets, wire and cable insulations, filters and sliding bushes. They provide, especially the FKMs, good resistance to temperature and to chemicals, better high speed wear resistance and therefore require less maintenance. They can be found in motor vehicle gearboxes and engines.

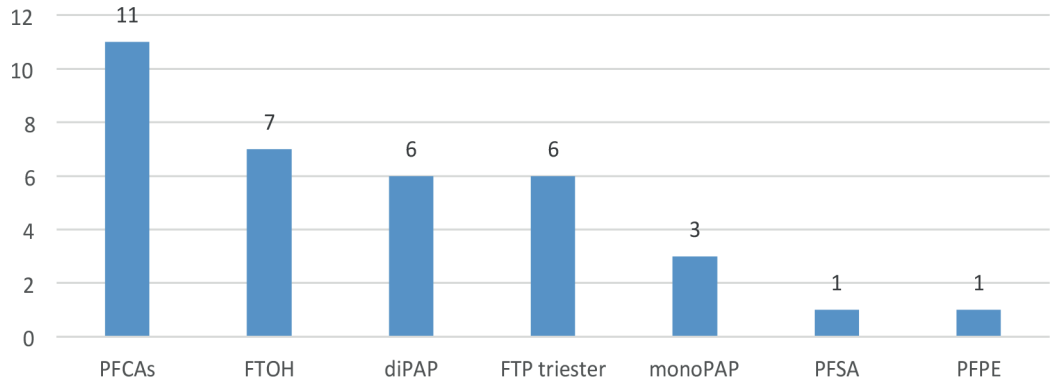
A lot of cables are covered with fluoropolymer sheaths to protect them under specific conditions: aggressive chemical products, oxidation, high or low temperature. These cables can be found in various applications – gearboxes, motor vehicles, aircraft and space equipment. Several FKMs are used: VDF-HFP, PVDF, as well as fluoropolymers such as FEP, ECTFE, ETFE, PCTFE.

5.4 Food contact and packaging materials

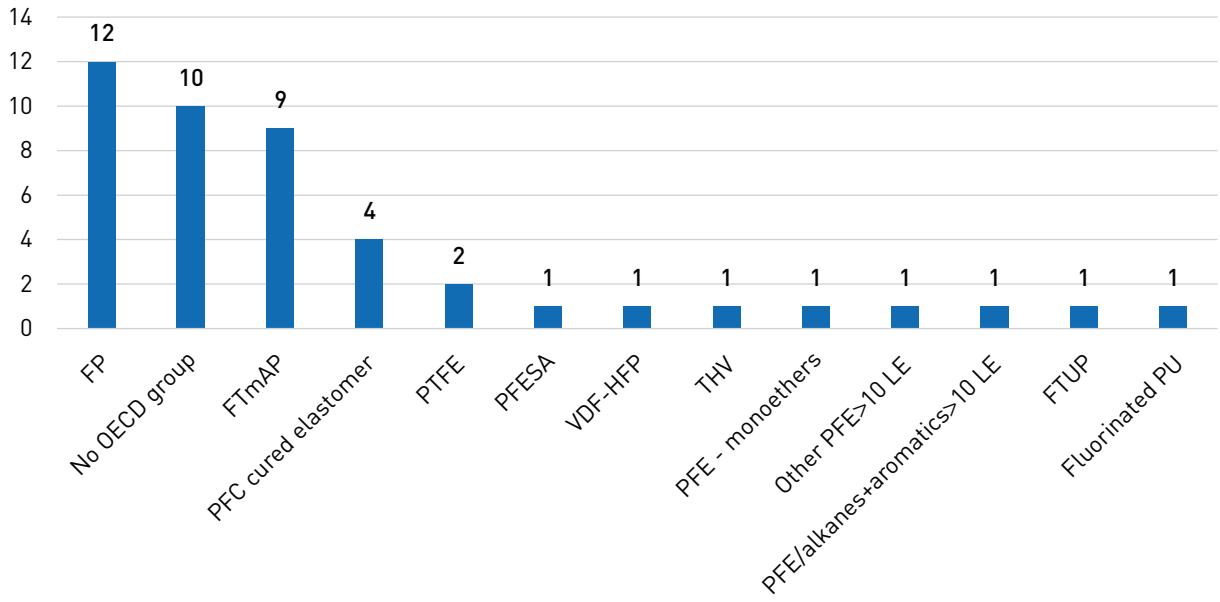
5.4.1 Food packaging

PFASs have been used for food contact materials since at least the 1960s. Their lipophobic and hydrophobic properties make PFASs excellent substances for waterproofing food packaging such as cardboard boxes, plastics, baking paper and paper plates.

Most PFASs, primarily telomers, are used in food packaging as surfactants. They can be used as-is or as fluorotelomer-based side-chain fluorinated polymers. More specifically, the following categories of PFASs can be found in food packaging:



GRAPH 5: Categories of PFASs detected in food packaging



GRAPH 6: Categories of PFASs approved for food use by the US EPA

Reference is also made to fluorosilicones and fluorosiloxanes such as fluoroelastomers used for grease-proof purposes in food packaging.

The fluoropolymers (PTFE, PFPE) and fluoroelastomers used help to prevent the retention of smells and also provide good resistance to aggressive cleaning products (hydrogen peroxide-based).

5.4.2 Cookware

PFASs are used for cooking utensils and appliances to form non-stick coatings in particular for kitchen items such as frying pans, baking dishes, pots, baking trays (for example in toasters, waffle irons, planchas, etc.). These coatings prevent food from sticking to the cookware and allow for easy cleaning.

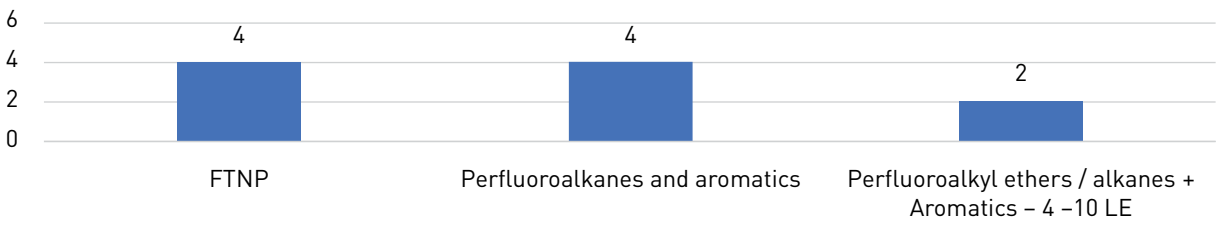
The main fluoropolymers used for this application are PTFE (CAS No.: 9002-84-0), FEP (CAS No.: 25067-11-2) and poly[tetrafluoroethylene-co-perfluoro (alkyl vinyl ether)] (CAS No.: 26655-00-5).

Other PFASs have been detected such as PFOA (CAS No.: 335-67-1) and PFBS (CAS No.: 375-73-5).

5.4.3 Food machines

Due to their lipophobic properties, PFASs are also used in the food industry as coatings for non-stick conveyor belts. They can also be found in other items such as: seals, O-rings, tubes, pipes, expansion joints, valves, conveyor belts, guiderails, rollers, funnels, hoppers, sliding plates, walls of tanks, funnels, rollers, baking trays, ovens, grills, knife and scissors blades, springs, filter membranes, sensor covers and lubricants.

The production materials made from fluoropolymers are regularly used for this purpose. The most commonly used are PTFE, FEP, PFA and ETFE. The following CAS numbers were found in a patent dating from 2019 for use in food contact materials other than papers:



GRAPH 7: Categories of PFASs used in food contact materials

This field also takes advantage of the high-temperature resistance properties of fluorinated substances, particularly for sealing and joints during industrial cooking processes.

5.5 Lubricants

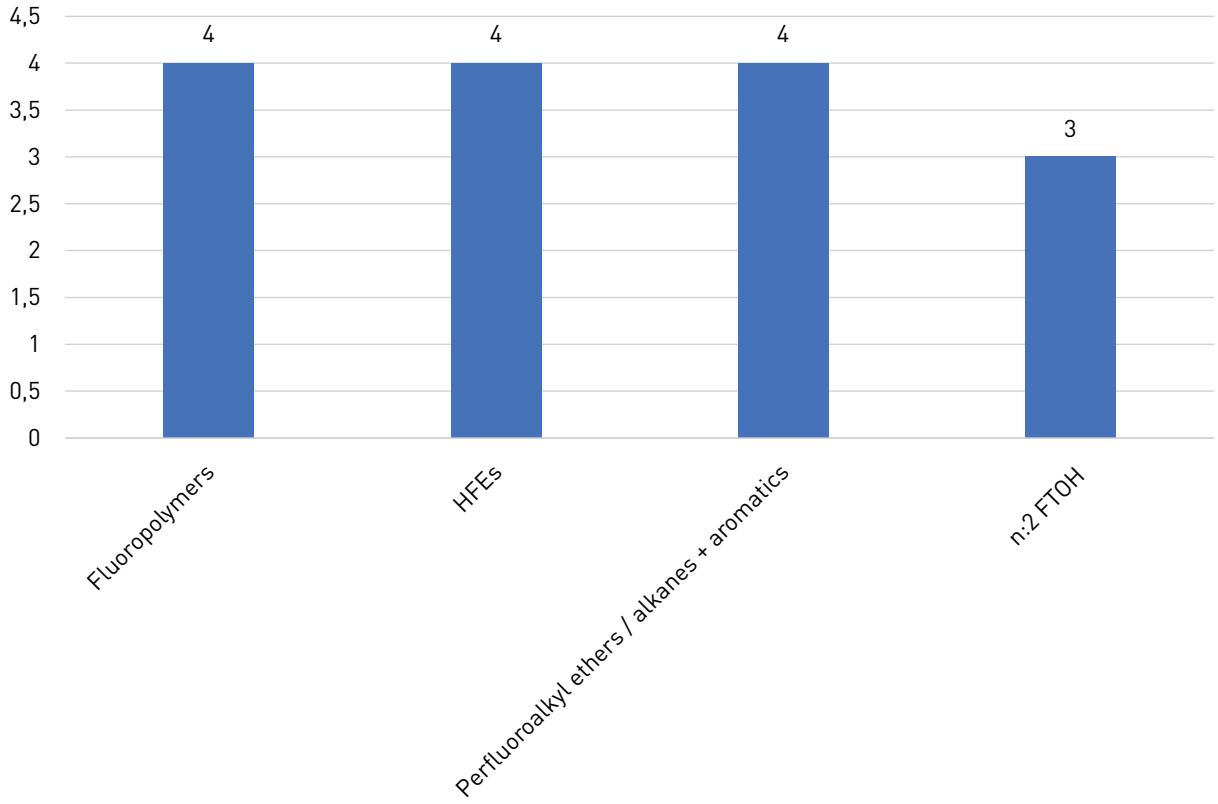
PFASs are used in lubricants as they form a thin film that decreases wear on load-bearing surfaces. Their high temperature resistance allows for their use in industrial applications with a lower risk of residue being formed on the parts. The consultation file identifies uses of PFASs in lubricants for many sectors.

Sector	Application
Food	Chains and bearings (e.g. for ovens). Lubrication on closed parts, in small quantity over the lifetime of the product, on semi-closed mobile mechanical parts, spray for occasional food contact. Additional lubrication on the inside of metal containers for food and drink – enables filling without damaging the coating.
Aerospace	Combustion engines. Hydraulic systems including control valves. Bearings, jet engine actuators, landing gears.
Automotive	Combustion engines. Reduction of the friction in many mechanical parts such as the brake system. Bearings and acceleration controls. ESP system. Electrical and auxiliary components. Sliding glass and door mechanisms. Mould release agent, assembly aid, grease (e.g.: acceleration control), seat rail, door hinge, switch actuation.
Railway	Power plant valves. Lubrication of train doors.
Nuclear	Pump bearings. Grease for laboratory glassware. Critical bearings, grease for handling nuclear waste, lubrication of equipment for the production of fuel and compaction.

Sector	Application
Electronic	Electric circuit breakers. Production of semi-conductors: plate handling mechanism, linear guide for multibeam control phase, source mirror actuator, other applications with bearings.
Medical	Oxygen breathing equipment. Medical injection instruments (syringes, pumps, etc.)
Renewable energy	Wind turbine: Lubrication of screws, bolts, magnetic anchors, nuts, bearings, etc. Fuel cell technology: assembly aid, grease for O-rings. Bearing and lubricant additive for plastic in energy storage and conversion.
Oil and gas	Lubrication of screws, nuts, magnetic anchors, bolts, etc. Bearings. Sealants for units and tubes for high definition nets made from high chromium steel.
Plastic	Polymer industry, added as lubricant additive to the polymer before processing.
Other sectors	Watchmaking. Application for hearing loss: vacuum pumps and bearings during production. Laboratory and measuring instruments: optical equipment (lubrication of mobile parts, bearings, pivots). Chemistry: production of oxidants, rupture disks and gaskets for heat exchangers, reactors and synthesis units. Diving equipment for oxygen contact. Prostheses, orthoses, wheelchairs, etc.: pistons and gears, lubricants for plastic components. Paper: roller bearings for corrugated paper machine. Chains, bearings, pivots, valves, automatic regulators. Plain bearings for hinges, reclining chairs, vibration dampers, chain tighteners, shock absorbers, pumps, suspensions for cable cars, etc. Bolted joints, screwed joints, nuts and gaskets in general. Lubricants for devices comprising a high risk of contact with high oxygen concentrations. Vacuum devices and mechanisms. Office machinery (radiators, printers). Electrical tools.

TABLE 3: Identification of applications of lubricants with per- and polyfluoroalkyl substances

There is a broad range of PFASs used in lubricants. An extract from a study highlights certain categories and specific molecules used for surfactant purposes.



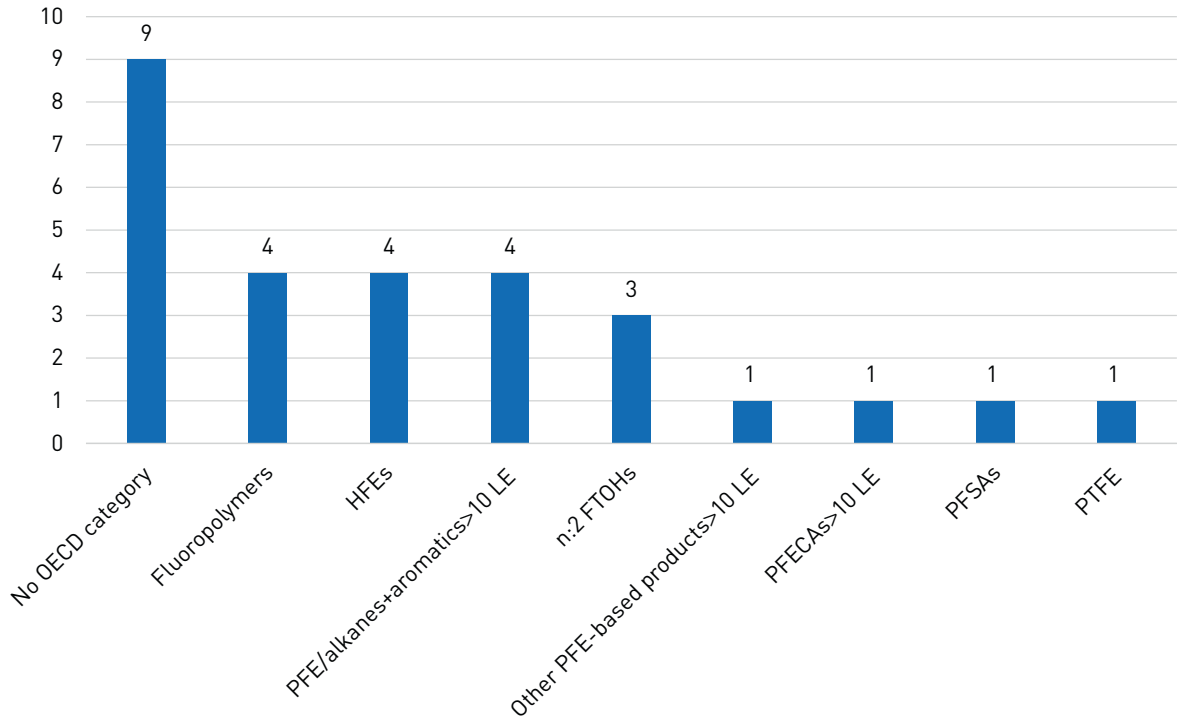
GRAPH 8: Category of PFASs used in lubricants

There are other PFASs used for the design of lubricants. Chemours uses PFPE-based lubricants for their superior performance in lubricating plastic/metal and plastic/plastic contacts. PTFE is also included as an additive for certain lubricants present in mechanical bearings, although its precise function is not known.

A study carried out in the automotive sector highlighted the presence of PFASs in engine oils, greases and hydraulic fluids. C8-C12, C4-C7 PFCAs, PFSAs as well as potential oxidation precursors of PFCA were detected. The most common PFCAs in this range of products are PFDoDA, PFunDA, PFBA, PFDA, PFPePA and PFNA, with hydraulic fluids exhibiting the largest average concentration of PFASs of the various types identified, followed by greases and lastly engine oils.

FFKM type fluoroelastomers can also be found in oils and lubricants in engines, where their high temperature resistance makes it possible to ensure smooth operation of the engine.

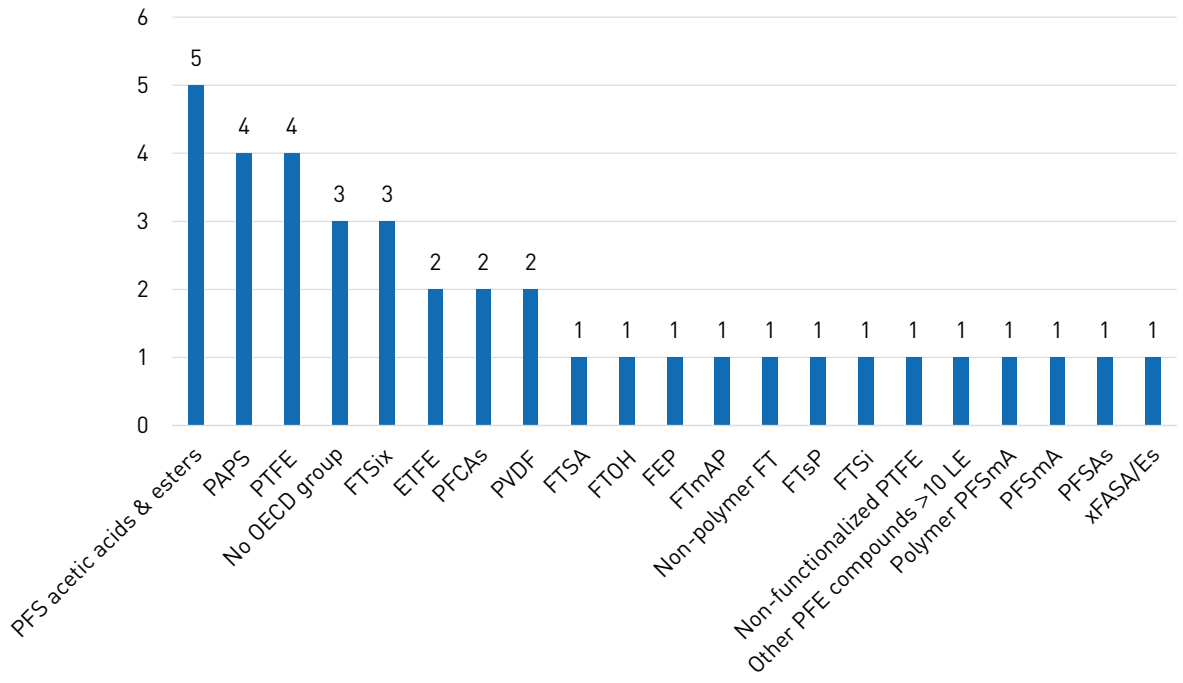
Various categories of PFASs can be highlighted in lubricants. The most represented category is perfluoroether, despite the fact that a large number of PFASs are not present in the OECD list and are therefore not related to a specific category.



GRAPH 9: Categories of PFASs identified in lubricants and greases

5.6 Building materials

PFASs are used in construction and building for a wide range of applications. They are notably used in paints and coatings, as surfactant additives, taking advantage of their oleophobic properties. They also serve to improve spreading and resistance.



GRAPH 10: Main categories of PFASs used in construction

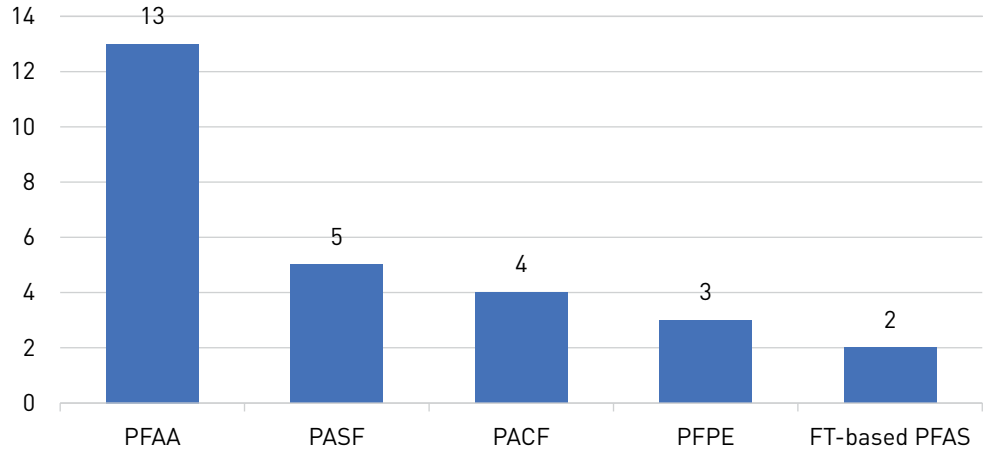
Fluoropolymers are also used for the production of waterproof membranes (for example in stadiums), or greenhouse components. The most widely used fluoropolymers are ETFE (CAS No.: 25038-71-5), PTFE (CAS No.: 9002-84-0), PVDF (CAS No.: 24937-79-7) with traces of PFCA and FTSA. PTFE is also used as a coating for some metals and plastic materials.

5.7 Metal plating and production of metal products

5.7.1 Electroplating

Some PFASs are used for their surface-active properties in metal surface treatment baths. They serve as wetting agents and fume suppressants, in particular in hard chromium plating baths. They were used in decorative chromium plating baths, however the replacement of chromium VI with chromium III has made this practice unnecessary.

The use of hard chromium plating in industry enables heightened corrosion and abrasion resistance. The hard chromium plating treatment relates to all types of parts, such as hydraulic cylinders and metal bars, railway wheel couplers and bearings, moulds and mould components for rubber and plastic industries, aircraft and motor vehicle components exposed to conditions that favour corrosion and friction.



GRAPH 11: Categories of PFASs used for hard chromium plating baths

As regards chromium plating, the PFASs used have a low surface tension so that they can act as a surfactant and must be stable in highly acidic and oxidising conditions.

Low quantities of fluorinated substances are also used in small quantities in other types of metal baths such as for electroless copper plating or electroless nickel plating. The PFASs used in electroless copper plating baths inhibit the formation of chemical mist by regulating the foam and enable a uniform deposition over the treated metal part. There is little data available; nevertheless the use of the following substances can be noted:

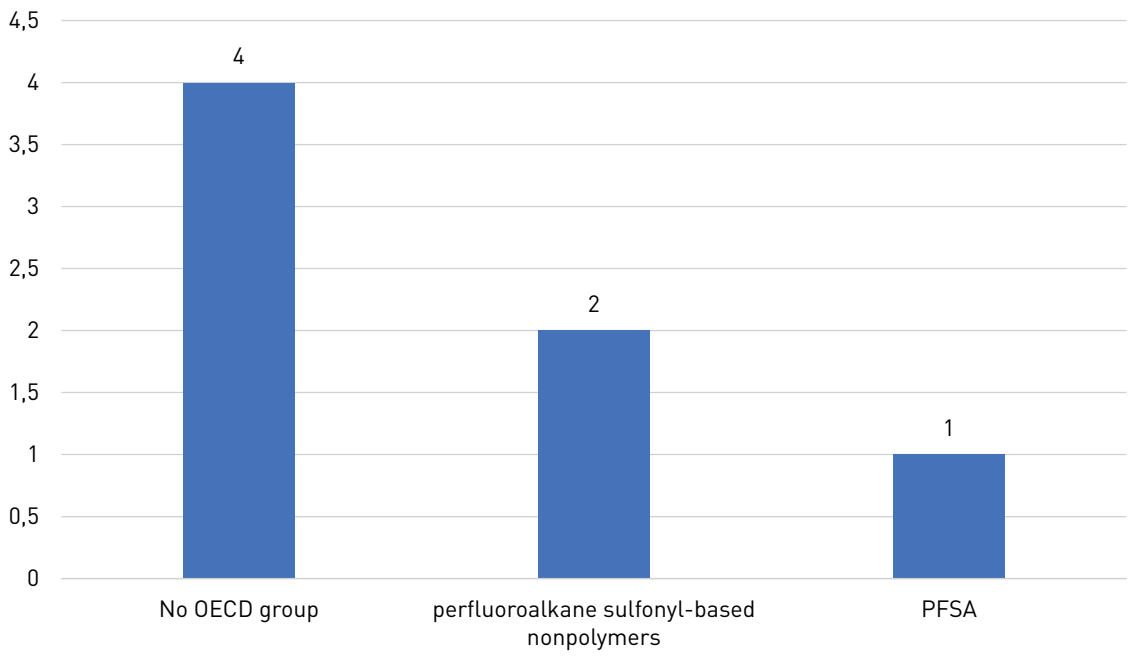
- Non-polymer PFSs (CAS Nos.: 81190-38-7, 73772-32-4);
- Not listed in the OECD base (CAS Nos.: 81190-39-8, 81190-42-3).

Similarly as for chromium plating, the PFASs used for electroless copper plating must have a low surface tension.

The restriction proposal identifies the PFASs based on C6 chemistry as the substances that are the most commonly used for metal plating, particularly PFOS and 6:2 FTS.

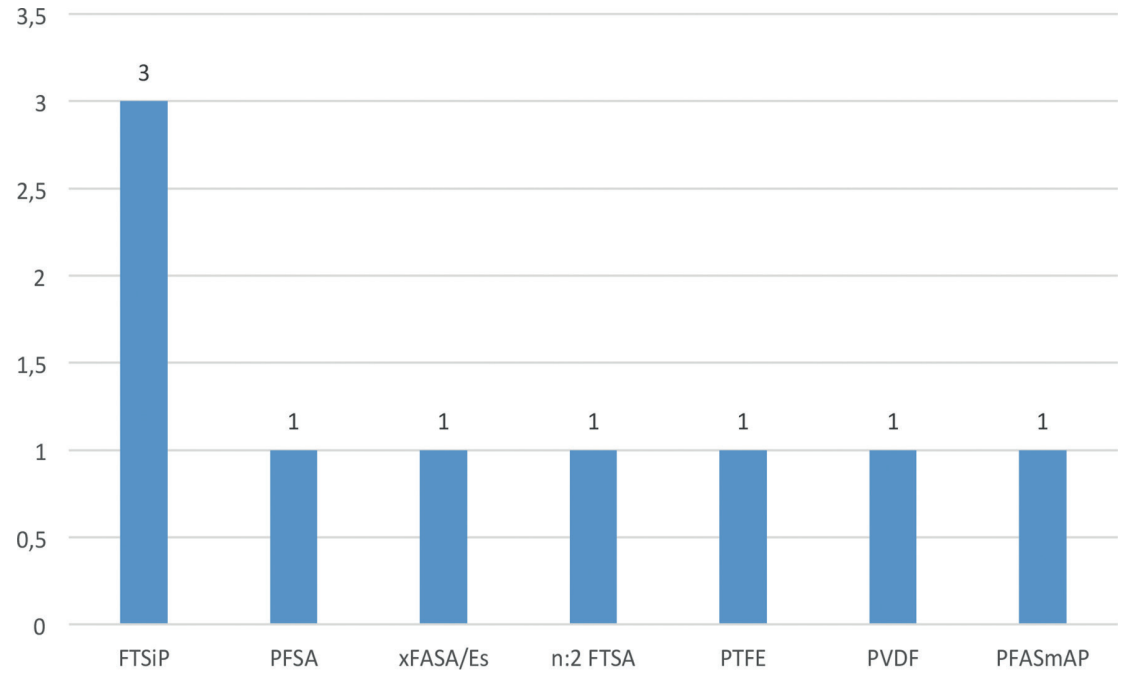
5.7.2 Manufacture of metals and metal products

Metals such as copper and nickel are manufactured from mineral ores processed by electrowinning. During this process, acid mist can be formed and promote the diffusion of highly acid electrolytes into the atmosphere. Using PFASs such as perfluoro-2-methyl-3-pentanone (CAS No.: 756-13-8) helps to limit the formation of acid mist during the process.



GRAPH 12: Categories of PFASs patented as acid mist suppressing agents for electrowinning baths

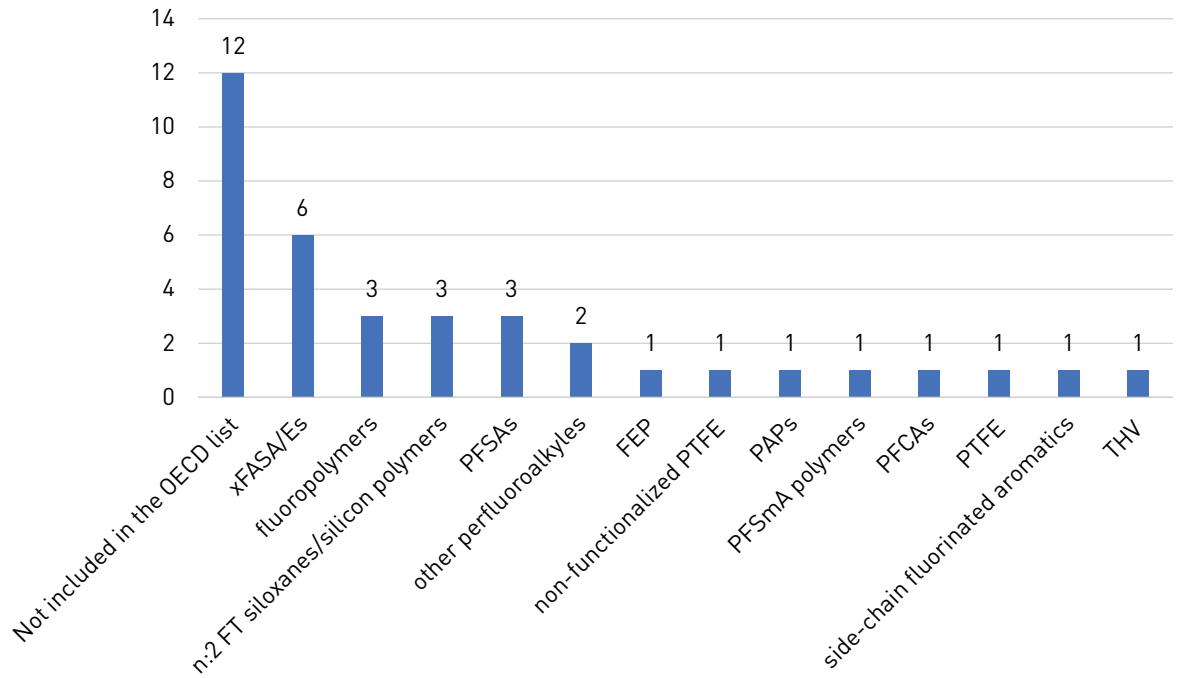
The SPIN database of Nordic countries also lists PFASs used in the manufacture of metal products, without providing clarification as to their specific use.



GRAPH 13: PFASs used for the manufacture of metal products

5.7.3 Treatment and coating of metals

Fluorinated surfactants are also used in the metal treatment processes to promote the flow of metal coatings and prevent the formation of cracks in the coating during the drying phase. Some substances can also be used as corrosion inhibitors.



GRAPH 14: Main categories of PFASs used in the treatment of metals

5.7.4 Cleaning and degreasing of metallic surfaces

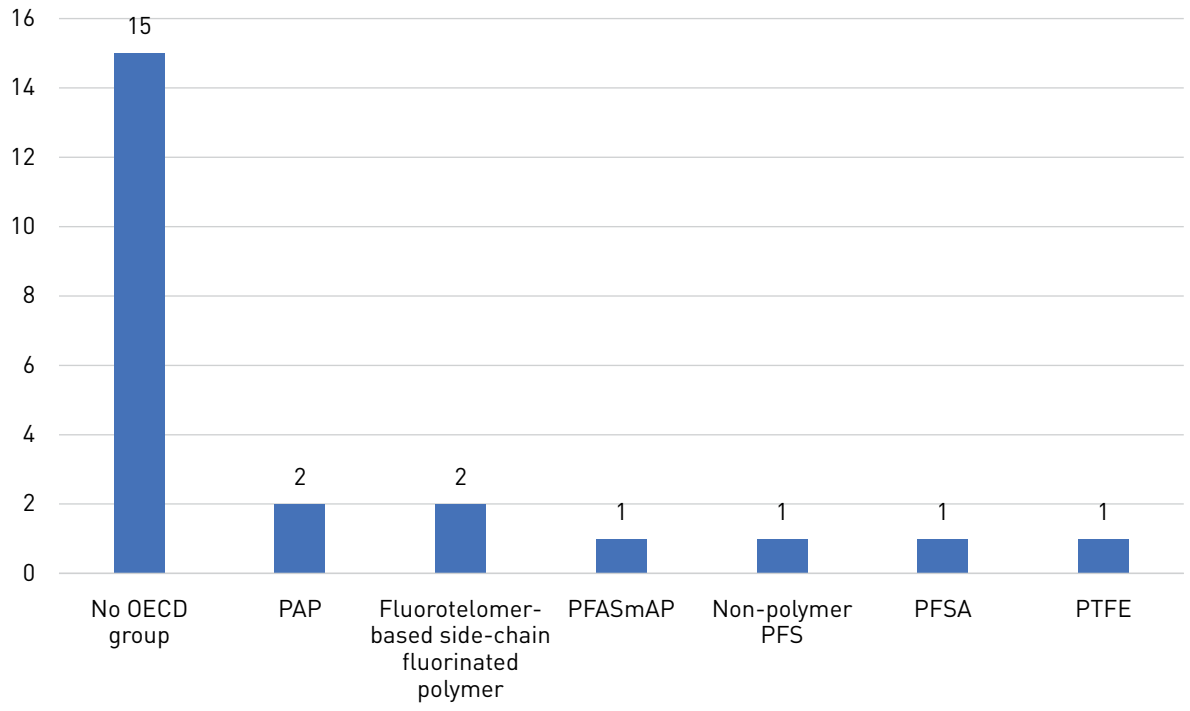
Some PFASs are also used as solvents for cleaning and degreasing metallic parts and surfaces. Only three could be identified for this use:

- Ethane, 1,1,2,2-tetrafluoro-1-(2,2,2-trifluoro ethoxy)- (CAS No.: 406-78-0);
- Pentane, 1,1,1,2,2,3,4,5,5,5-decafluoro- (CAS No.: 138495-42-8);
- Cyclopentane, 1,1,2,2,3,3,4-heptafluoro- (CAS No.: 15290-77-4).

5.8 Sealants and adhesives

The sealants and adhesives which have PFASs in their formulations are mainly used in conditions that require these substances: high temperatures and resistance to acids. PFASs are found in fluoroelastomer sealants for O-rings, V-seals, contact seals, shaft seals as well as for processed fabrics. These sealants can be found in the pumps, valves and fittings sector where there is widespread use of fluoroelastomers.

Fluorinated substances are used in adhesives as surfactants to improve levelling and spreading as well as the penetration of the adhesive between the materials. They are serve to enhance the strength of the adhesive bond or more rarely as antistatic agents.



GRAPH 15: PFASs used in sealants and adhesives

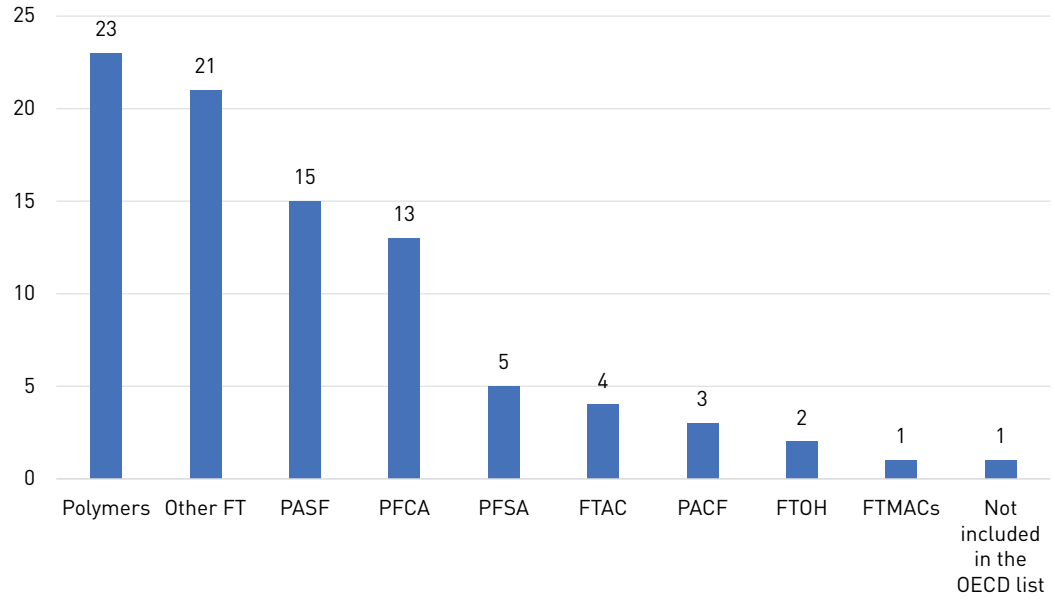
5.9 Textile, leather and upholstery

The properties of fluorinated surfactants provide water and oil repellency and therefore good stain resistance and soil release properties for textiles. These substances are very difficult to replace as few molecules possess comparable properties with a high level of efficiency and lower toxicity.

PFCAs and PFSAs can be found in blinds, seat coverings (public transport and furniture), tarpaulins, soil release upholstery materials, curtains, bed linen, textile foams and covers. Fluorinated substances can also be found in the textiles used for filtering and medical applications.

PFASs are also used for bulletproof fabrics, knapsacks, car seat coverings, ropes, sleeping bags and water repellent fabrics such as tents or umbrellas.

The PFASs used in the textile industry are mainly side-chain fluorinated polymers, with long-chain fluorotelomers and POSF derivatives which have now been replaced by less toxic short-chain equivalents. Studies are underway to find substitutes for short chain PFASs, whether it involves chemical substitutes (other molecules with oleophobic or hydrophobic properties) or physical substitutes (lotus effect, roughness).



GRAPH 16: Main categories of PFASs used in textiles and upholstery

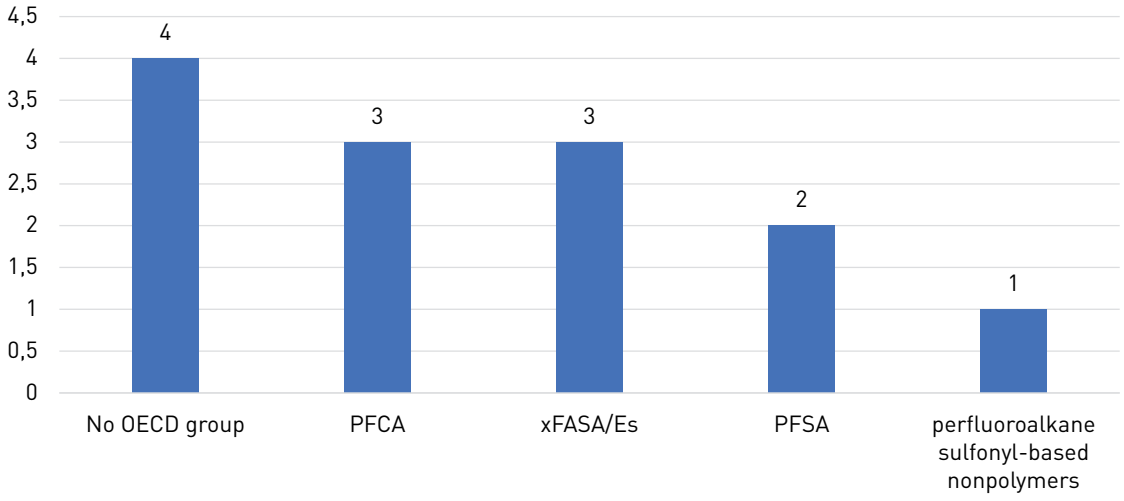
Many polymers are used for fabrics and so are short-chain fluorotelomers which primarily serve as mixing additives.

5.10 Oil and mining industry

5.10.1 Mining industry

PFASs have been used in the mining industry in order to increase wetting of the sulphuric acid or cyanide-based selections that leach the ore. They also play a similar role for surface treatment baths as acid mist supressing agents. Fluorinated surfactants are also used as foam stabilisers to separate the metal salts from soil during floatation separation.

Due to the small amount of information available, it is not possible to determine the quantities of PFASs used nor whether they are widely used in the mining industry.

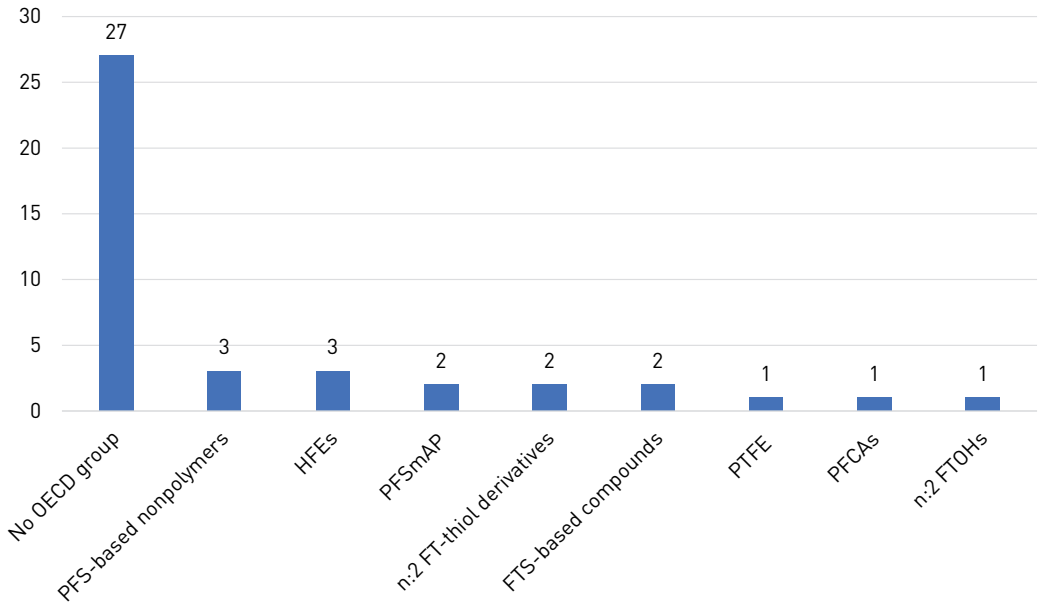


GRAPH 17: Main PFAS used in the mining industry

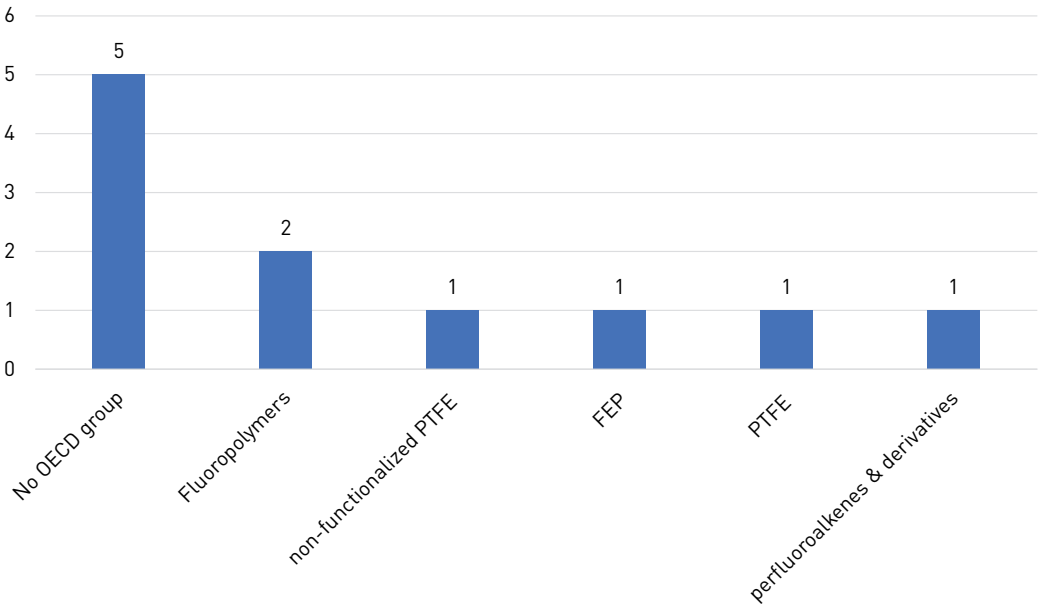
5.10.2 Oil industry

PFASs are used as surfactants in many applications:

- Drilling fluids, as anti-foaming agents;
- Tracers for oil and gas in the mapping of natural gas and petroleum reservoirs;
- Foaming agents for chemical-driven oil and gas production processes;
- Coating of metallic parts, pipelines, valves and gaskets made of fluoropolymers to prevent corrosion, simplify oil transport and handling.



GRAPH 18: Main PFASs used for the assisted recovery of oil and gas



GRAPH 19: Main PFASs used for oil and gas transport and storage

A number of fluoropolymers, particularly PTFE, PFA, FEP and ETFE, are used to insulate communication cables in drilling processes.

It should be noted that most PFASs with an identified use are not included in the OECD database.

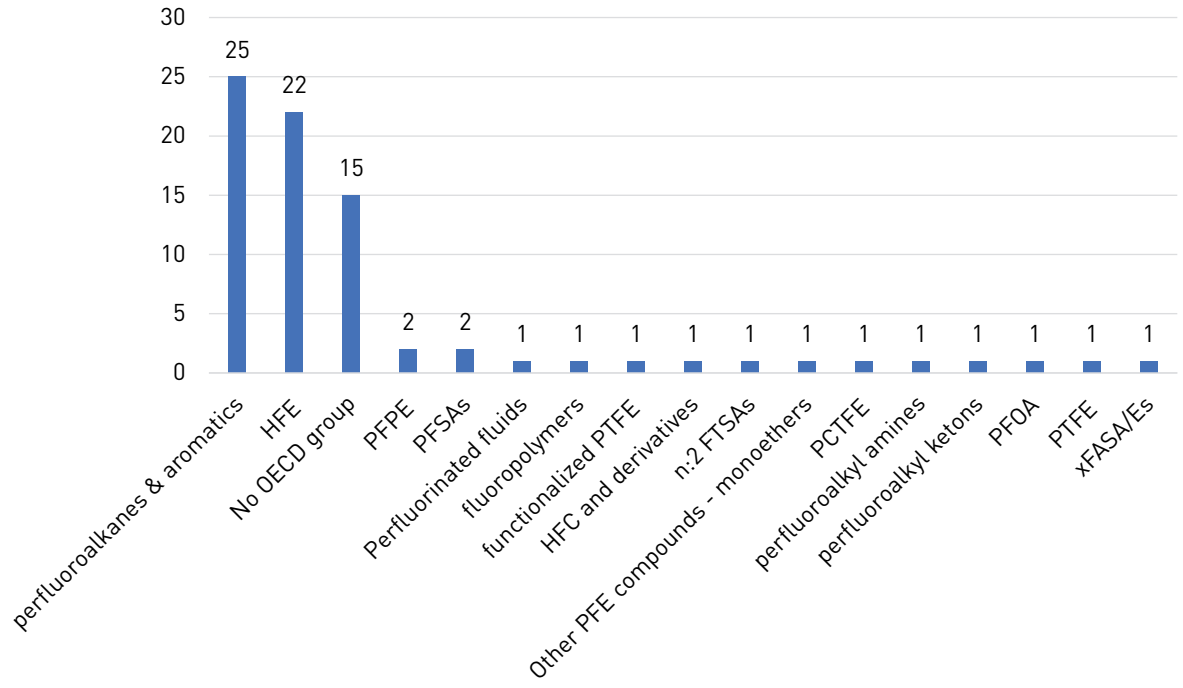
5.11 Electronics and energy

5.11.1 Electronics industry

PFASs have many applications in the electronics industry due to their hydrophobic properties, low surface tension and high dielectric breakdown strength. They are used in the production of printed circuit boards and semiconductors, loudspeakers, digital cameras, mobile phones, printers, scanners and transistors.

They also serve in photolithography processes to ensure specific properties such as a low refractive index, surface tension, resistance to temperature and chemical products.

PFAS are also used as functional fluids in closed circuits, surfactants and surface treatment agents.



GRAPH 20: PFASs used in the electronics industry

PFAS are also used during aging tests, particularly thermal tests, on electronic equipment, such as in heat transfer fluids to cool electronic devices (power supplies, memory cards, logic circuits, processors, lasers, etc.).

Lastly, perfluorinated substances can be applied in cleaning solutions when mixed with alcohol to ensure heat transfer, form a non-flammable vapour layer and rinse solvent residues.

Fluoroalkylsilanes can be found in non-stick coatings for micro-electromechanical (MEM) systems, such as sensor chips.

5.11.2 Energy sector

Perfluorinated substances are also used to produce and store electrical power. Fluoropolymers such as PVDF, FEP and ETFE are used in films in photovoltaic cells and solar panels.

PFASs can also found in fuel cells, electrolytic cells, in water repellent and breathable membranes, proton conductor materials (PTFE, PFSA) and gas diffusion lasers (FEP). Fluoropolymer seals also serve in fuel cells to prevent any gas leakage while withstanding the applied chemical products. PFASs may also be used as additives for certain lithium-air and lithium-sulphur battery electrolytes, to improve the oxygen transport as well as in materials for electrodes (PVDF, PTFE as binders) and cooling pipes to guarantee optimal operation in an extreme electrochemical environment.

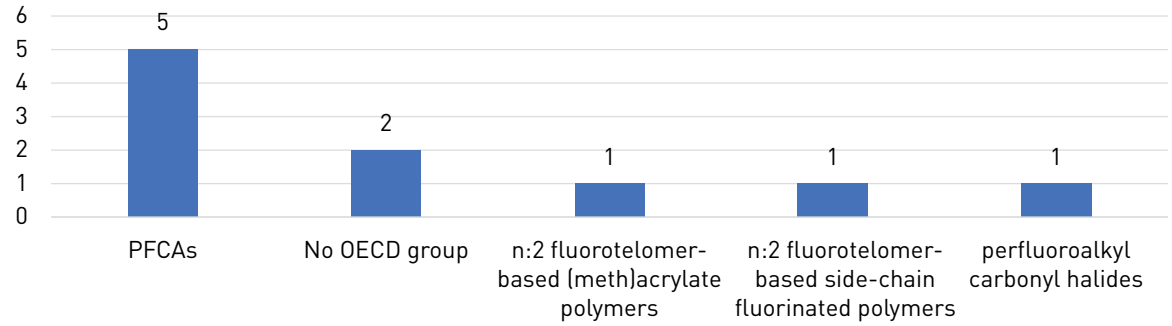
Applications have also been noted in coal-fired power plants where fluoropolymers are present in the combustion gas tubing of heat exchangers. The polymers used are PFECA, PFESA and PFS-based compounds.

5.12 Transport

PFASs are widely used in means of transport and mobility. The applications of fluoropolymers include the construction of structures for motor vehicles as well as coatings and gaskets for aerospace and maritime transport. Non-polymer PFASs can be used in treatments or in mixtures such as cooling fluids, lubricants and brake fluids.

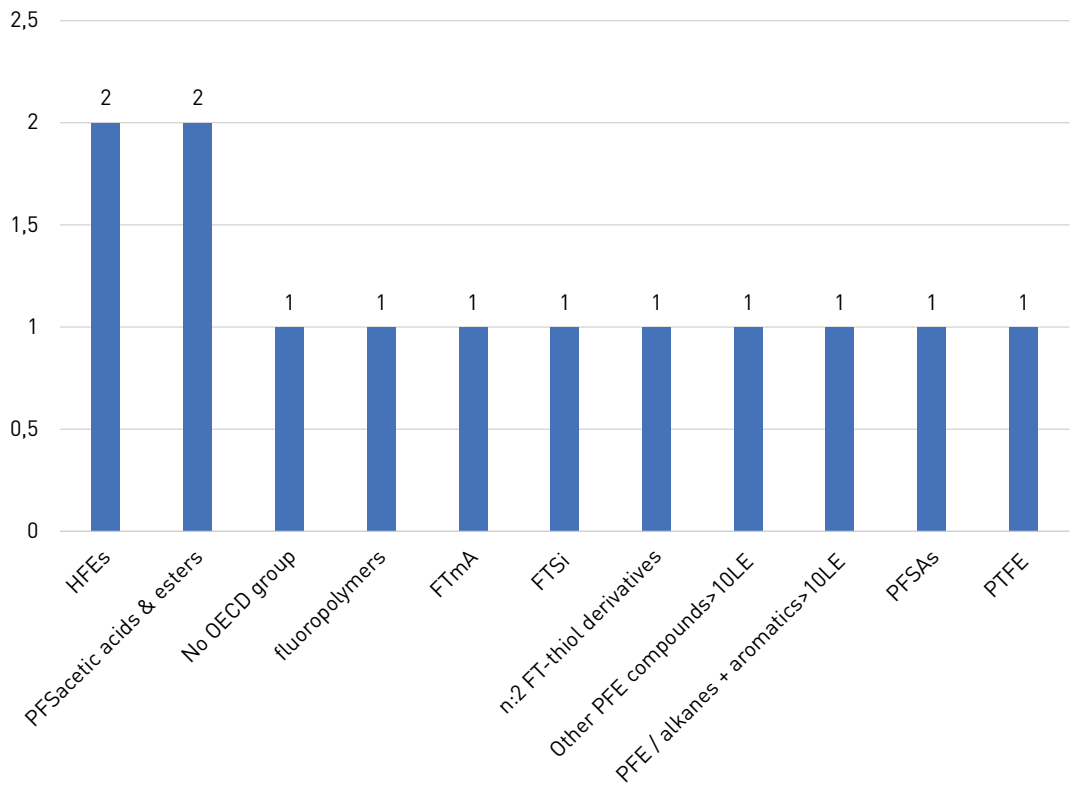
5.12.1 Automotive

PFASs are found in many applications in the automotive sector. Some fluorinated substances are used in car parts, however no specific details as to their functions are available.



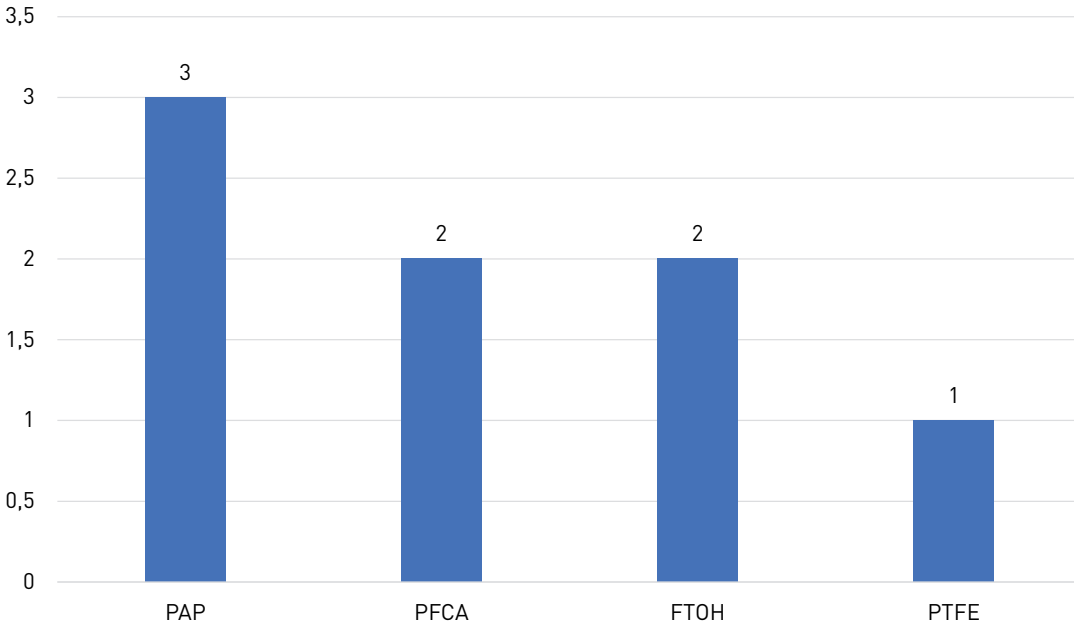
GRAPH 21: Categories of PFASs used in car parts

The SPIN database also specifies the use of PFASs for the maintenance and repair of motor vehicles, but here again, there are no specific details as to their functions.



GRAPH 22: PFASs used for maintenance and repair of motor vehicles

PFASs also serve as surfactants in automotive waxes, polishes and varnishes, to aid spreading and improve the resistance to water and oil.



GRAPH 23: PFASs used in automotive waxes and varnishes

Category	Application
Car body	Raw material to build the body (polymer, plastics) Mould release agent of plastic materials (ETFE, PTFE)
Sealing	O-rings, valve seals, ring seals, rotating shaft seals, piston seals, seals for electronic components (NOX/O2 sensors), seals for battery electrodes
Engine	Coating and sealing
Lubricants	Fluoroelastomer-based lubricants used to reduce friction: bearing box, chain guide, ring, clutch system, thermal and electrical protection for the connectors of the electronic systems, gaskets, sunroof rail
Hydraulic fluids	Braking, steering systems
Electrical systems	Manufacturing processes of semiconductors for control systems, safety systems, data transmission (fluoropolymer optical fibres), electric motors, batteries (fluoroelastomer for sealing, fluorinated gases to regulate the temperature of propulsion batteries for electric vehicles, fluoroelastomer to coat the separation wall in Li-ion batteries), proton conductors in the catalytic layer of batteries.
Coatings	PTFE, ETFE, PFA, FEVE Coatings for cables in the selective catalytic reduction system for diesel fuel vehicles, coatings for particle filter tubes in gasoline / diesel vehicles Gloss improvement films Coating of insulating materials Stain resistant treatments of fluoroalkylsilane glass surfaces Abrasion resistance for windshield wipers
Heating, ventilation and air-conditioning system	Fluorinated gases: heat transfer fluid for electronic equipment, processing aids for the production of fluoropolymers, cleaning fluids, blowing agents
Other	Reflective and protective coatings for panels and roads Gyroscope flotation fluid (navigation and control systems)

TABLE 4: Use of PFASs in the automotive sector

Other uses of PFASs are covered by different subsections, particularly the textile and upholstery present in the vehicle interior, metallic surfaces subjected to surface treatment or plastic materials.

5.12.2 Aerospace

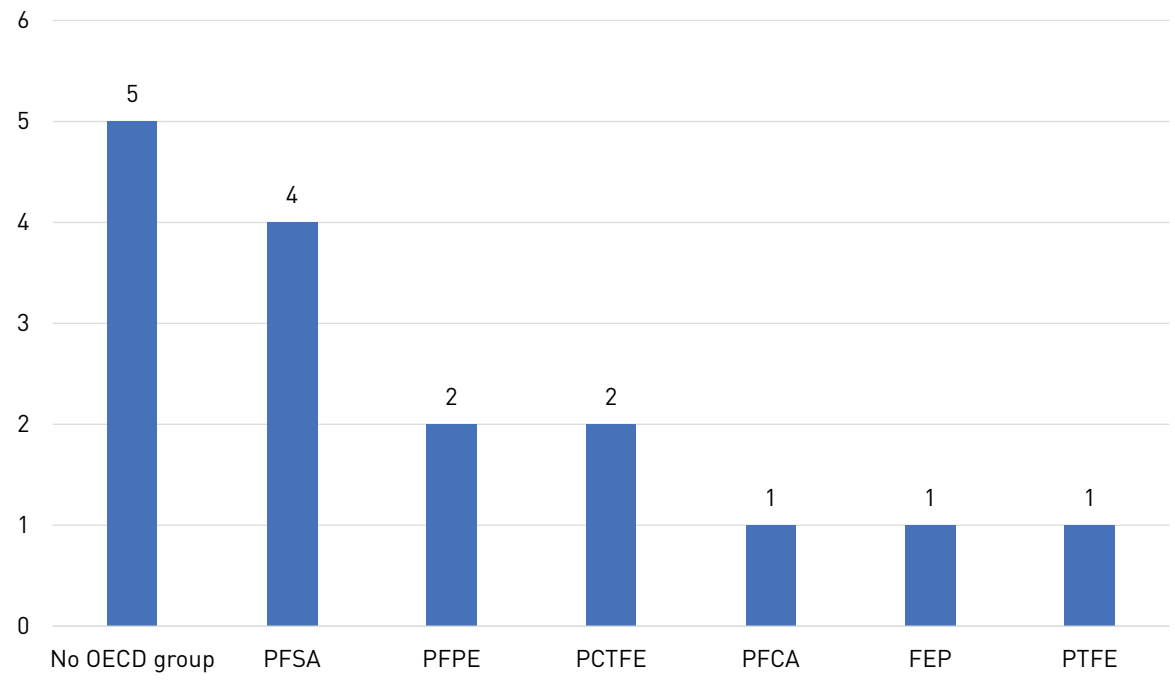
The use of PFASs in the aerospace industry is similar to that of land-based applications with applications over a wide operating temperature range, significant friction, good resistance to chemical substances and dielectric properties.

Fluorinated substances can be found in metal treatment baths, particularly for hard chromium plating processes **(refer to 5.7)**, to improve corrosion resistance and resistance to extreme conditions.

PFASs are also used in the hydraulic fluids of mobile aircraft components such as flaps, ailerons, control surfaces and landing gears. There are three types of hydraulic fluids:

- Mineral oil based;
- Poly-alpha-olefine based;
- Phosphate ester based.

Phosphate ester-based fluids are the most widely used in the aerospace sector with fluorinated surfactants being included in their formulations as corrosion inhibitors. By altering the electrical potential of the metal surfaces in contact with the fluids, these surfactants help to protect the metal surfaces from severe corrosion. In addition, their high temperature stability serves to prevent fires, and the evaporation of hydraulic fluids.



GRAPH 24: Categories of PFASs used in the aerospace industry

Fluorinated substances are also used for aerospace applications, especially for the thermal control of spacecraft having to withstand temperatures ranging from –80 to + 150°C. FEP and PTFE are the main fluoropolymers used to obtain radiating surfaces with the desired properties.

5.13 Applications of fluorinated gases

Fluorinated gases are mostly fluorinated compounds which are known as powerful greenhouse gases, with much more significant global warming potential than CO2.

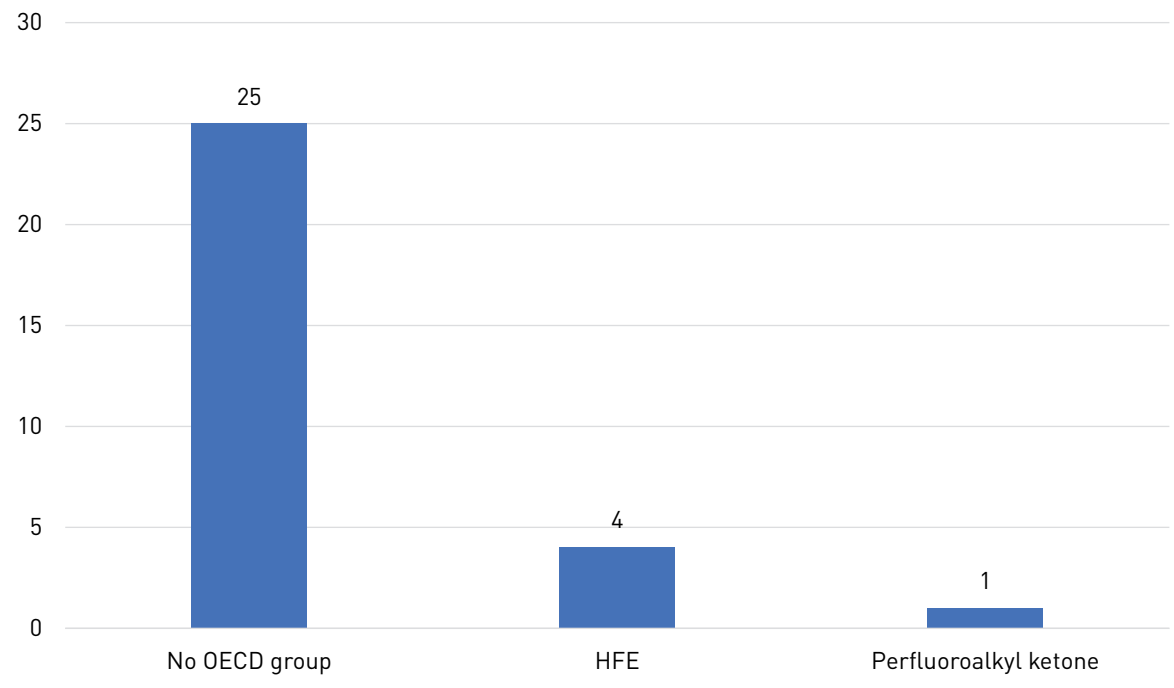
Similarly as with PFASs, there are different types of fluorinated gases:

- Hydrofluorocarbons, with hydrogen atoms in the molecule. They are mainly used in cooling systems, for firefighting, aerosols, as foam expansion agents or in the manufacture of semi-conductors.
- Perfluorocarbons, which are only composed of carbon and fluorine atoms. They can be found in the semiconductor manufacturing processes or in heat transfer fluids.

The new definition used for the restriction proposal includes some fluorinated gases in the characterisation of PFASs, a restriction which therefore could impact sectors such as the electronics industry, as well as the uses made thereof in the ventilation, heating and cooling machines industry.

They are mainly used for heating, ventilation and cooling devices. They can also be found as blowing agents for foams, where their production gives rise to high emissions, in fire protection systems upon the triggering of devices, as well as in some aerosols and insulating foams.

The emissions of fluorinated gases mainly occur during the use, particularly the triggering of fire extinguishing devices, during the production of fluids themselves, as well as during the lifecycle of products, although this later phase is not generally the most significant cause of emissions.

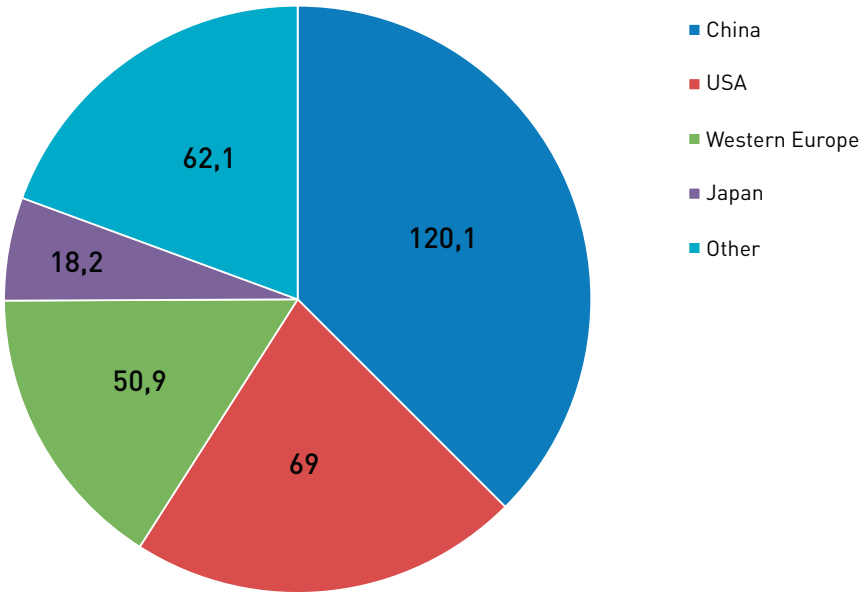


GRAPH 25: Fluorinated gases used in cooling systems

6 Production and emissions of PFASs

6.1 Production of fluoropolymers

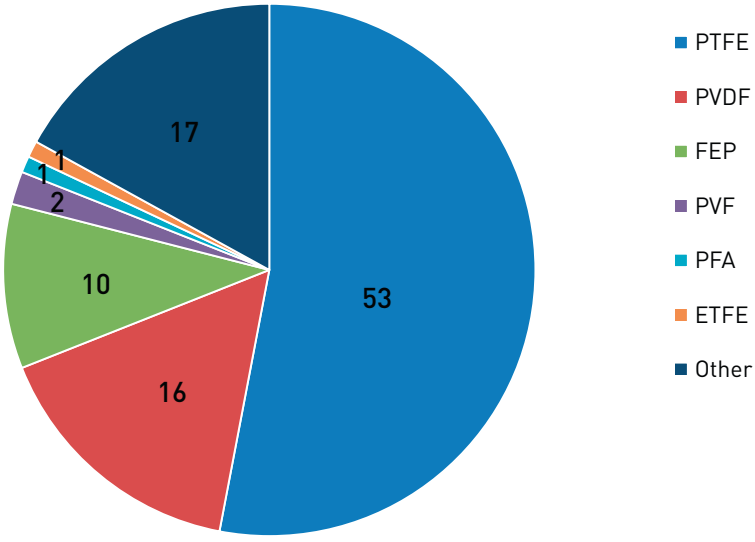
320,000 tons of fluorinated polymers were consumed worldwide in 2018, with PTFE being the most consumed fluoropolymer.



GRAPH 26: Global consumption of fluoroplastics per country, 2018 (ktons)

In comparison, in 2015, the global consumption of fluoropolymers was 270,000 tons, i.e. an increase of 18.7% in 3 years.

As regards the types of fluoropolymers produced, PTFE accounts for the largest production tonnage.



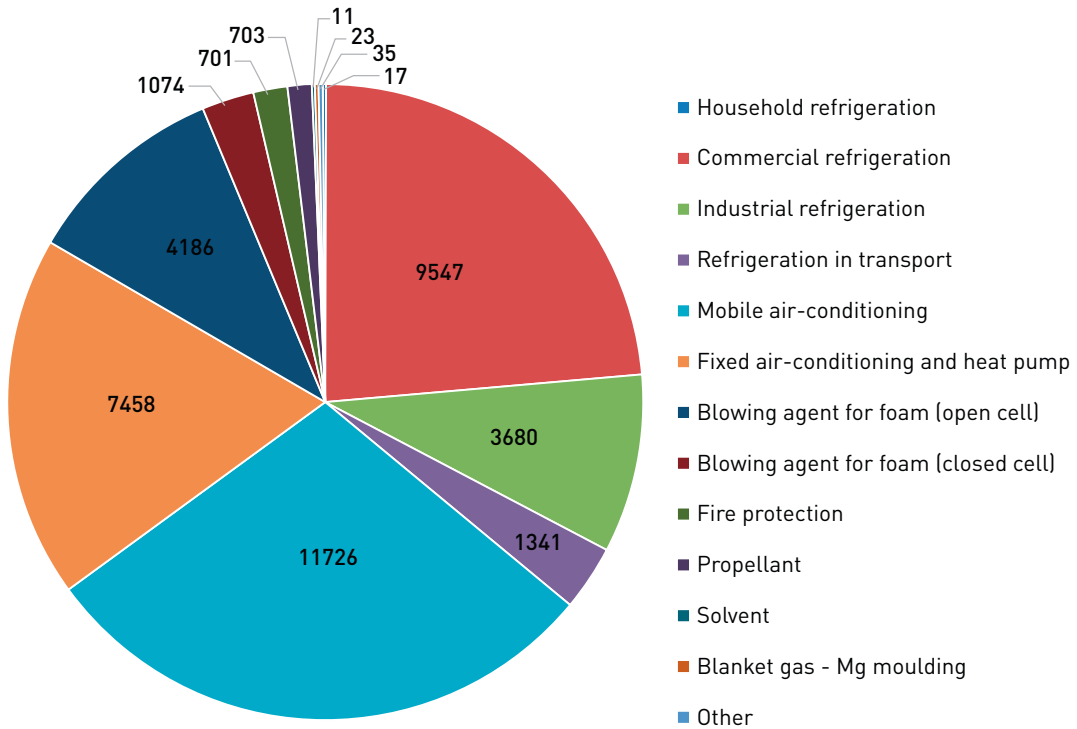
GRAPH 27: Global consumption of fluoropolymers per type, 2018 (percentage)

Apparently, fluoropolymers are released in the environment only via soil and water, particularly through plastic waste accumulated in landfills and in water. Fluoropolymers are also the source by which non-polymer PFASs are emitted into the air through the incineration of fluoroplastic waste.

6.2 Production of fluorinated gases

As for fluorinated gases, 30,671 tons of all types of fluorinated gases were loaded into devices and produced during their manufacturing processes, while 492,173 tons were already present in operational products. Lastly, 19,724 tons of fluorinated gases were present in declassified products. These figures only refer to European Union countries in addition to the United Kingdom, Norway and Iceland.

In terms of emissions into the environment in 2018, 40,502 tons of fluorinated gases were emitted, 96% of which took place during the life cycle of the product, whereas the remaining 4% were emitted during the production of the products and equipment (including during the production of fluorinated gases).



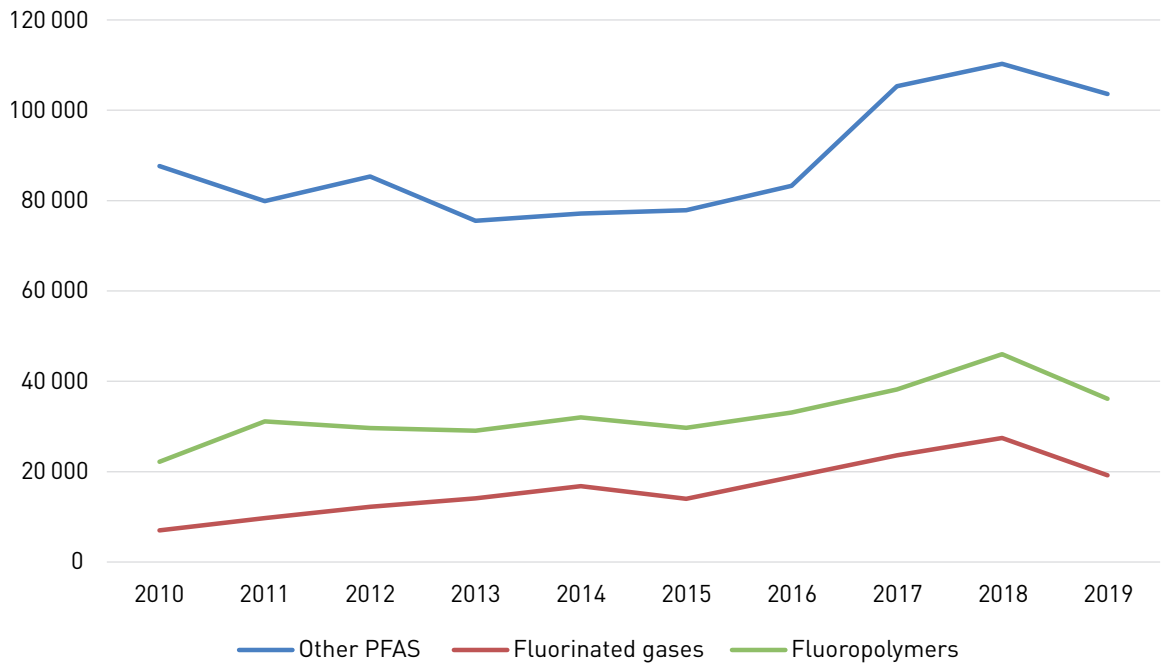
GRAPH 28: Tonnage of fluorinated gases emitted in the EU in 2018 by use (tons)

All these emissions are air emissions, with most stemming from air-conditioning and refrigeration devices.

6.3 Production of other fluorinated substances

There is little information about the production of other fluorinated substances. For example, the Norwegian environment agency estimates that between 2011 and 2016, the global production of PFHxS was between 1,000 and 1,500 kg per year with a consumption on the decline since then.

Most fluorinated substances used in the European Union are imported from non-EU countries. Although there is little data available about the production of these substances, we have relatively accurate estimations concerning imports into the European Union.



GRAPH 29: Imports of PFASs into the European Union (tons)

6.4 Sources of PFAS emission into the environment

The use of PFASs in industry causes the release of many fluorinated substances into the environment. These include liquid effluents, laden with fluorinated surfactants, which represent a significant source of release in the environment. The high stability of PFASs furthermore promotes their mobility in the various compartments (water, soil, air) until they are absorbed by living organisms.

6.4.1 Metal surface treatment effluents

When it comes to metal surface treatment processes, PFASs are mainly emitted during the rinsing steps as well as during replacement of used electrolytic solutions. According to the German association for electroplating and surface treatment industrial companies, 20% of the surfactants used are lost during the surface treatment operations.

These emissions may take place via wastewater as well as in solid form in metallic hydroxide sludge and waste ion exchange resins, and to a lesser extent via the air. The surfactant PFASs used in the treatment baths are subsequently found in the effluents treated by the public networks. The identified pathways for fluorinated surfactants are as follows:

- 50-85%: liquid effluents;
- 0.1-24%: filter sludge;
- < 0.1%: exhaust air.

Chromium plating baths also use fluorinated surfactants. These baths have a limited lifetime and must be regularly changed. Effluents are processed as chemical waste with isolation of the chromium residues. However, surfactant PFASs are not isolated and may cause contamination of soil and water.

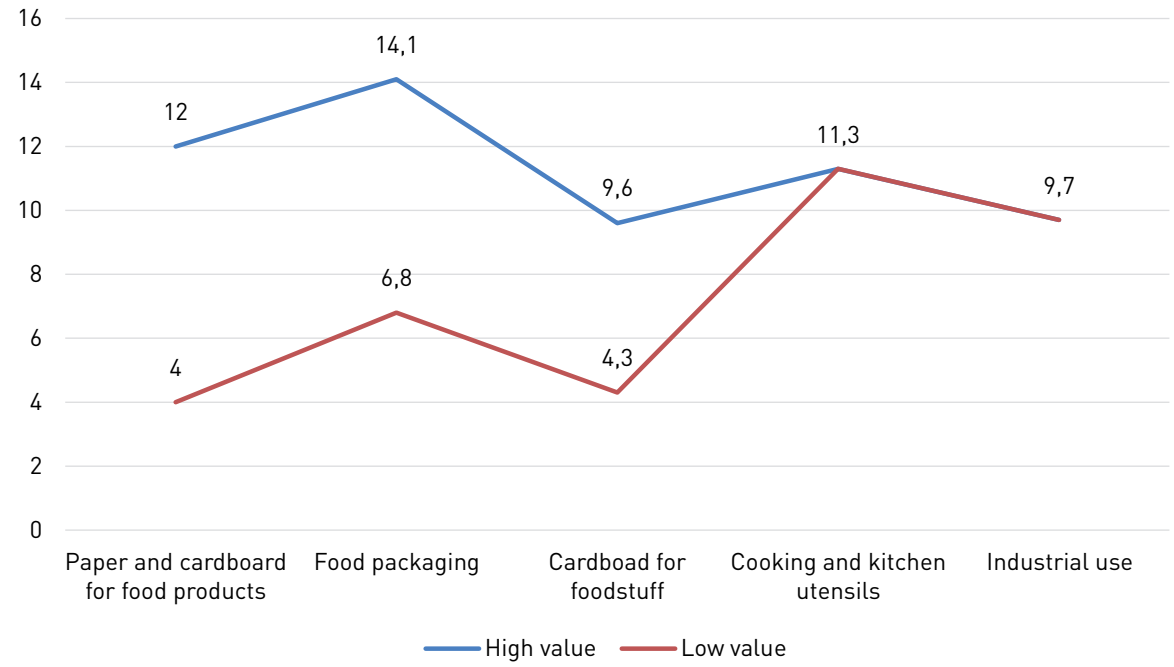
The short-chain PFASs generally used, such as PFOS or 6:2 FTS, have a low adsorption potential, are hard to eliminate from water using conventional treatment processes and may be released in the environment.

Based on information about PFHxA included in the restriction proposal, approximately 0.5 to 11 tons per year of 6:2 FTS are released in the environment in Europe each year with a central accepted value of 6 tons/year.

6.4.2 PFASs in food contact materials

The PFASs used in food contact materials may be released in food, whether during production, packaging or during the lifetime of the products. The exact quantity of emissions is not known and only estimations are available regarding the releases from items processed with PFAS.

In 2017, it was estimated that 3,000 tons of fluoropolymers are used in food contact materials for industrial applications per year, however this estimate does not seem to differentiate between food uses and pharmaceutical uses and as such should best be taken as a guide value.



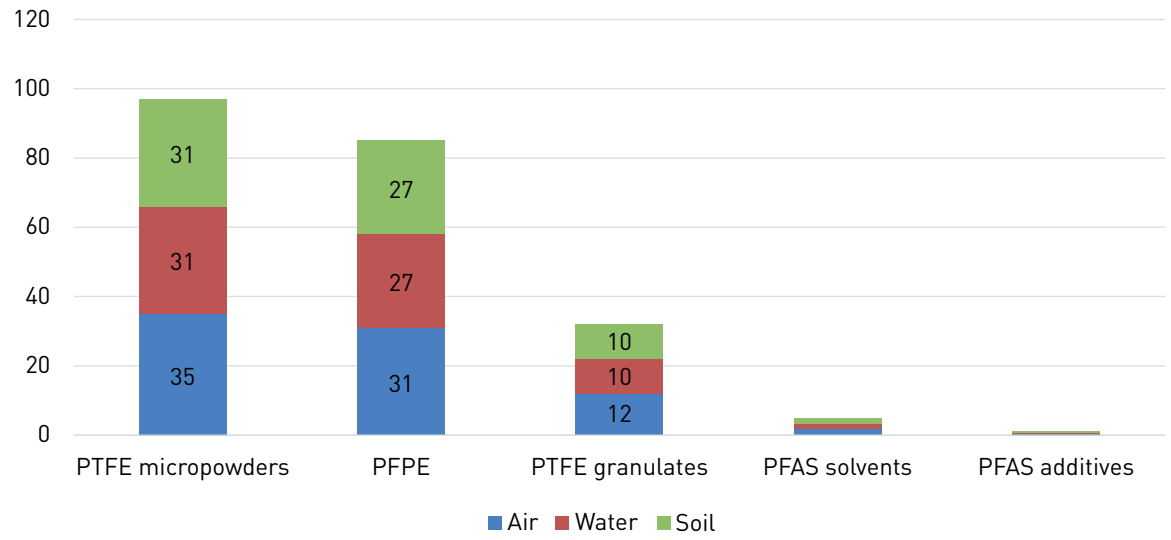
GRAPH 30: Estimated outdoor PFAS emissions from food contact materials during their use (tons)

As regards indoor emissions, estimates set the level to 0.2 tons per year on average for the same categories. This data only relates to the emissions during the useful life of the items processed with PFASs.

The main emission source is the manufacturing of paper and cardboard for food packaging, which, although an estimate, represents between 113.1 and 825.7 tons per year with respect to the fluorinated substances deliberately added during the manufacturing processes.

6.4.3 Greases and lubricants

PFAS emissions from greases and lubricants take place in the same way as for food packaging, either during the manufacturing of greases and lubricants or during their use within an industrial framework.



GRAPH 31: PFAS emissions from greases and lubricants in 2020 (tons)

The formulation of lubricant products accounts for 22-23% of the total emissions of PTFE granulates and micropowders, as well as PFPE. The remaining emissions occur during the effective life of the items, whether in relation to lubricants and greases contained in closed systems or for applications in open systems.

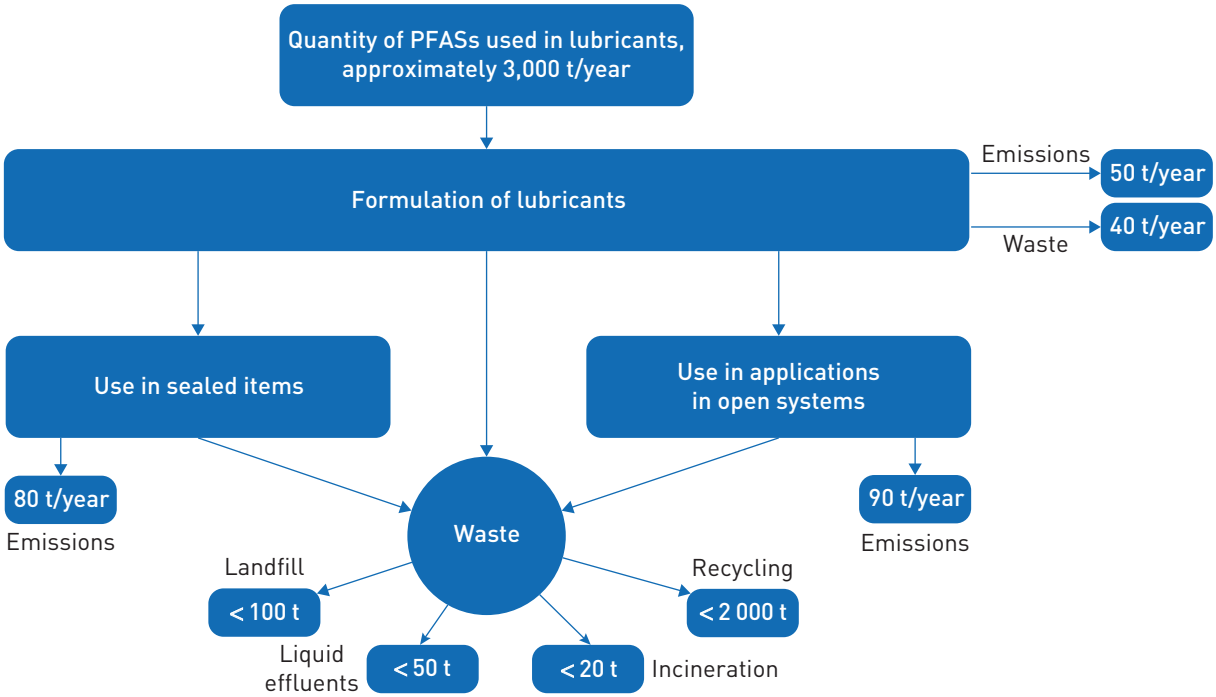


FIGURE 19: Mapping of PFAS emissions from lubricants and greases

Most PFASs used in the lubricant industry are therefore recycled for the formulation of new products, through the reprocessing of items containing PFASs. An appreciable number of tons are also emitted into the environment, particularly via landfills which may then promote the migration of PFASs into the soil and water.

7 Mobility of fluorinated substances

PFASs make up categories of highly persistent substances, particularly due to the strength of the carbon-fluorine bond. This persistence allows the substances to accumulate in the environment further to emissions, and thereby subsequently be assimilated by living organisms.

Although it is not possible to generalise on the properties of PFASs due to the very high number of substances and the diverse nature of molecular functional groups, the migration and mobility of fluorinated substances are still matters of priority if we are to determine their toxicity potential for humans as well as the environment. Knowledge of this mobility is rendered more complex by the existence, in the case of many PFASs, of degradation routes that can form toxic fluorinated compounds from other substances that are considered less dangerous, such as polyfluorinated dialkyl phosphate esters which can be biotransformed into PFOA.

Several mechanisms are taken into account in the mobility of PFASs in the environment:

- Partitioning: This is the sharing of a chemical substance between various solvents or media. In the case of PFASs, this partitioning is especially important as many substances have an apolar fluorinated body and a polar head. Important PFAS partitioning mechanisms in the various compartments of the environment include hydrophobic effects of substances, electrostatic interactions and interfacial behaviours.
- Media-specific migration processes: These are processes such as diffusion into low-permeability matrices, atmospheric transport and leaching from soil to water. Unlike partitioning, these processes are specific to the media.
- Transformations: A number of PFASs can be partially degraded via biological, physical or chemical mechanisms. These transformations have a significant influence on the PFASs found during analyses of a medium but can also influence how a fluorinated substance will bioaccumulate in the living species.
- Uptake into biota and plants: This phenomenon can potentially concentrate PFASs in organisms which are later consumed by fauna and humans.

PFAS emission into the environment is a matter of vital concern that must be taken into consideration by industrial companies, in order to minimise initial concentrations and the number of PFASs which may later migrate between the various compartments and accumulate in living organisms. As previously seen, these emissions occur:

- During the synthesis of fluorinated substances;
- During the production of items and products containing PFASs;
- During the effective life of these items and products (air-conditioning, grease, etc.);
- Upon land filling and processing of waste.

7.1 Partitioning

7.1.1 Water

The mobility of PFASs in liquid phases is promoted by their surfactant properties, as well as the presence of a polar functional group, even though they do not all share these properties. The fluorinated compounds found in water generally stem from mixtures of several substances, although they can theoretically exist in the form of salts, particularly PFCA derivatives.

When the concentrations of fluorinated surfactants are high enough (for example close to the release sites), these may also form micelles; aggregates of molecules where the hydrophilic heads interact with each other.

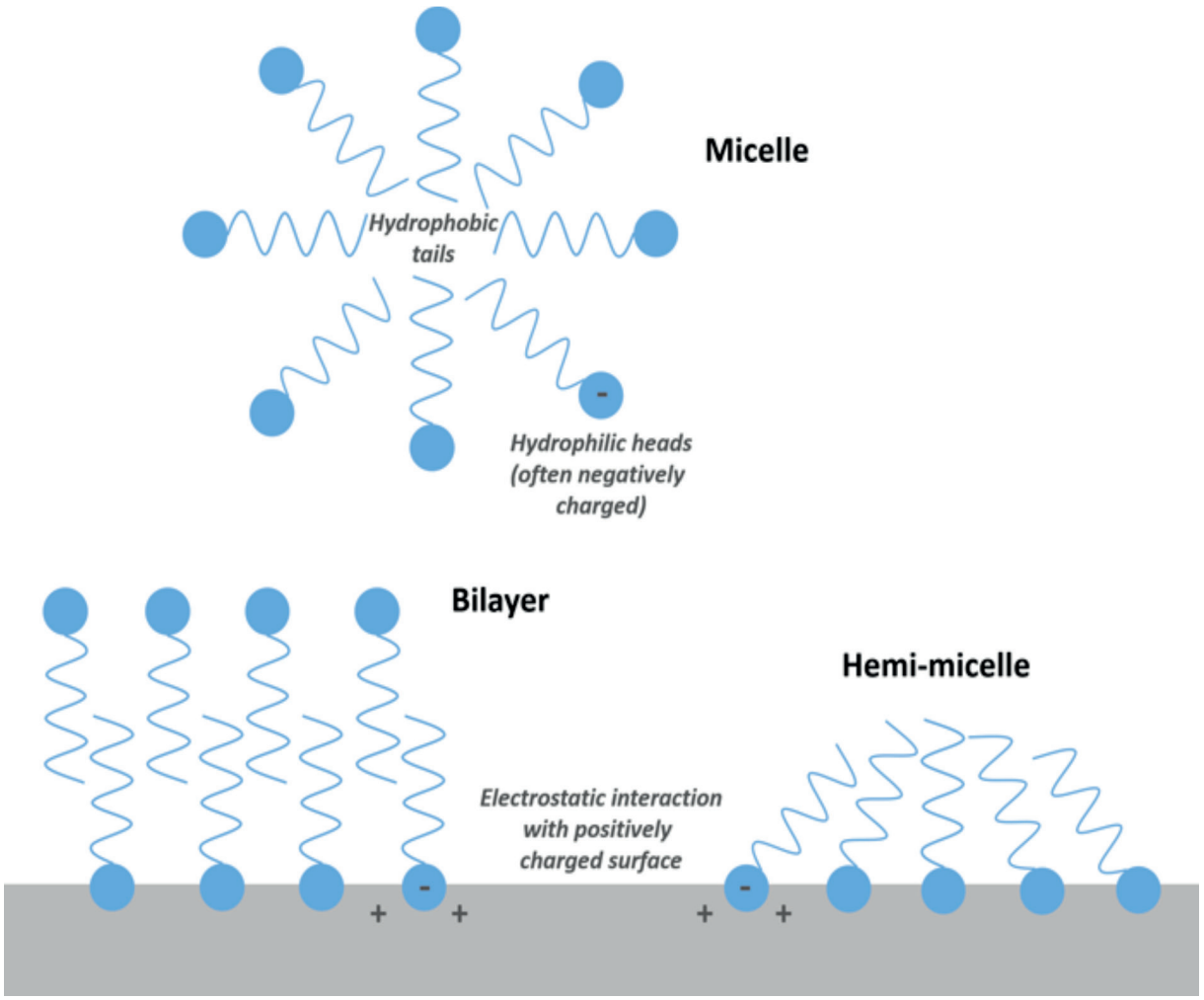


FIGURE 20: Illustration of different types of micelles

The formation of micelles alters the mobility of the PFASs; for example they can promote their adsorption in minerals and soil in the environment, with the formation of a layer of molecules on positively charged surfaces, leading to different concentrations at the core of the solution and at the solid-liquid interface.

These micelles can also contribute to the formation of foam with high concentrations of PFASs at the air-water interface, or even promote the release into the air of certain molecules from the liquid phase.

In the case of the PFOS, the concentration cited for formation of micelles varies from 500 to 5,000 mg/l, although hemi-micelle formation has been observed for concentrations sometimes 1,000 times lower. The concentrations leading to the formation of such aggregates is greatly determined by the presence of co-contaminants and the nature of the medium.

7.1.2 Soil

PFAS mobility in soil is thought to occur through two processes:

- Adsorption to organic carbon via hydrophobic interactions;
- Electrostatic interactions.

Studies of PFSA and PFCA behaviour in soil have determined that chain length plays a significant role in the adsorption on carbon organic materials. Therefore, short-chain PFSAs and PFCAs are less retarded than their long-chain counterparts, and are therefore more mobile and less accumulable.

In addition, PFSAs tend to adsorb more strongly than PFCAs of equal length, and branched isomers are less sorptive than linear isomers.

Lab-based study of PFAS migration has established several characteristics of their mobility in soil and between water and soil:

- There seems to exist a kinetic equilibrium between concentrations in water and soil which is achieved after several days to several weeks of transfer. However, although the achievement of this equilibrium seems possible in controlled conditions, field surveys suggest that PFASs would also be highly subject to mass transfer between water and soil; an abrupt change in the conditions of the medium (precipitation, release of polluted materials, construction, etc.) will affect the establishment of this equilibrium and promote or work against the migration of fluorinated substances.
- The adsorption of PFASs in soil is reversible; a molecule that is able to physically bond to a solid material can also disbond and be mobile in the environment. There is evidence that in real conditions, the desorption process is disadvantaged and occurs more slowly than adsorption, meaning that fluorinated substances are therefore less subject to migration and less bioavailable once fixed in the soil, while being more persistent on polluted sites.
- Electrostatic interactions depend on the soil type in which the PFASs migrate and evolve; most PFAS species can have a charge that is influenced by the pH, and the presence of such a charge may subsequently improve mobility (in the case of a charge of the same nature as the medium), or on the contrary slow down migration (in the case of a charge that is different from that of the medium). Low pH values may improve the sorption of PFASs such as PFOS and perfluorinated acids, making them slower and more persistent.

Despite the extensive information available, additional research is needed to further evaluate if any of the parameters influencing the mobility of PFASs in soil can be used predictively to anticipate the migration of waste and enable better management.

PFASs in soil can be subject to leaching, especially during precipitation, and thereby increase the proportion of PFASs in ground water, with respect to soil. However, this phenomenon seems to be more significant for short-chain PFASs which are more mobile whereas long-chain PFASs are more likely to be retained by the soil.

7.1.3 Air

Partitioning to air is undoubtedly the least known type, with a lack of data about vapour pressure or Henry's law constants of the various PFASs, used to establish if a substance is more or less volatile.

Available data suggests that FTOHs have a functional group that help to impart greater volatility. For that matter, they are found in gas phases even in regions that are far from industrial sites.

During industrial emissions, particularly combustion and incineration, PFASs may be released into the air as witnessed during emission processes, particularly via the presence of airborne aerosols with which some anionic PFASs will associate in order to become volatile. For example, PFOAs and PFOSs have been detected in airborne particulate matter in urban and semi-rural areas, with PFOAs detected in ultrafine particles and PFOSs in larger, coarser particles.

PFASs can also be transported in the atmosphere via suspended droplets, a transport mechanism which will influence the PFAS concentrations in soil and water around industrial sites. PFASs contained in suspended droplets will not partition to the air, but rather to water and the ground via these droplets.

In addition, PFASs seem to accumulate at air-water interfaces due to their surfactant properties. This accumulation is further aided by the fact that PFAS concentrations in water are lower and this phenomenon retards the transfer of fluorinated substances to the soil. This retarded transfer could make it possible to consider different treatments for PFAS polluted sites, even if this phenomenon depends on the type of soil in which it occurs.

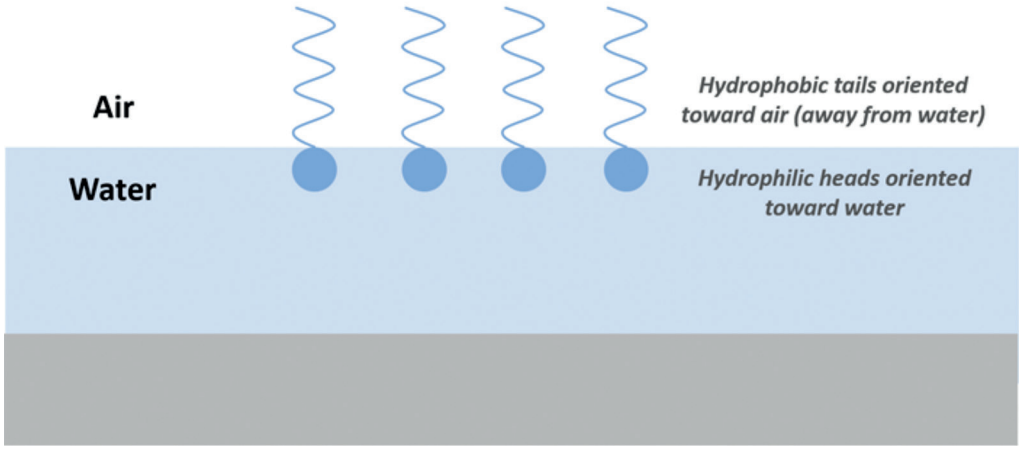


FIGURE 21: Illustration of PFAS accumulation at air/water interfaces

It is through the air that fluorinated substances may be the most mobile, either directly in gaseous phase or via suspended droplets or particles. Once emitted, fluorinated substances may migrate over long distances and be deposited in the soil and water thereby impacting the level of pollution over areas that are wider than the soil and water.

7.2 Transformations of PFASs in the environment

Polyfluorinated substances are the most likely to undergo transformation processes in natural environments. Indeed, it is the presence, location and number of carbon-hydrogen (C-H) bonds and potentially carbon-oxygen (C-O) bonds in the molecules which explain their higher transformation potentials with respect to perfluorinated substances without hydrogen.

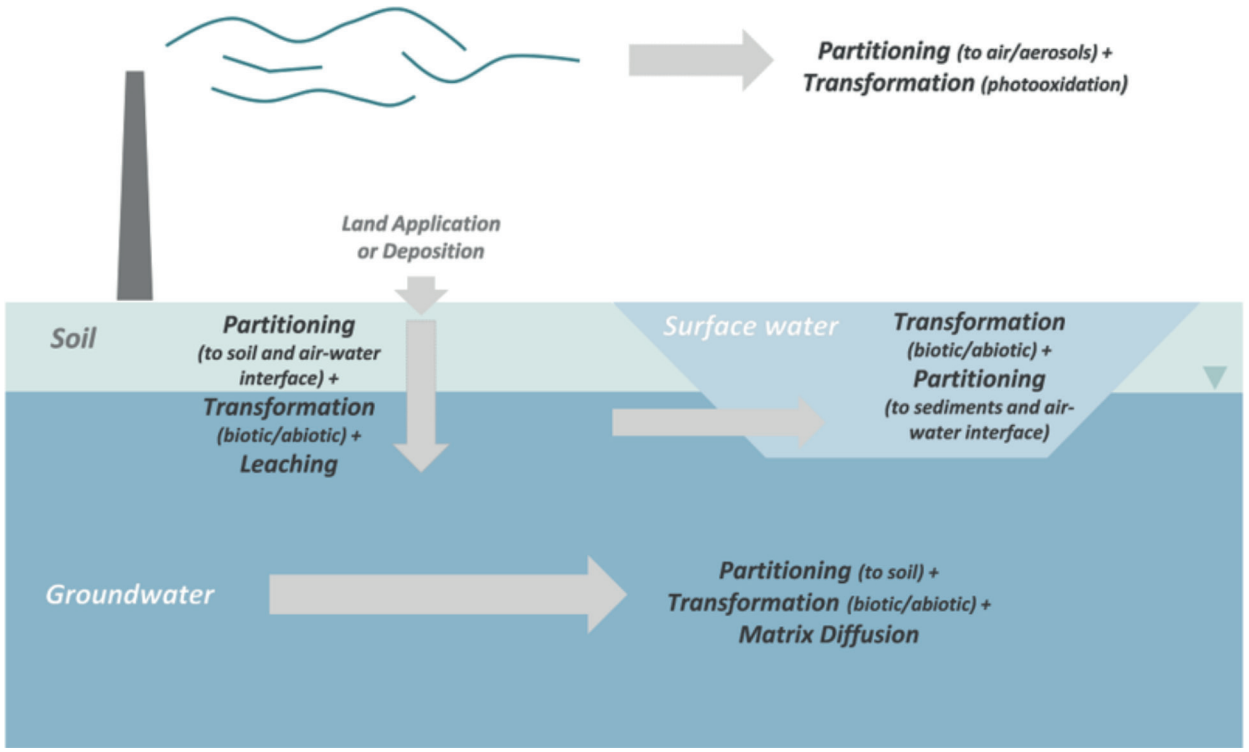


FIGURE 22: Illustration of PFAS partitioning and transformation processes in the various compartments

The products that stem from transformation of the various PFASs are primarily perfluoroalkyl acids as these compounds are more stable and then persist in the various media. The transformations occur in all compartments, air, water and soil, each with its own specific characteristics.

Although PFCA emissions have declined, atmospheric emission of PFCA precursors, such as FTOH, have increased. Similarly, emission rates for PFSA precursors have also increased. The main mechanisms are thought to be indirect photolysis, for example compounds such as 8:2, 6:2 and 4:2 FTOH are degraded via hydroxyl and chlorine radicals. These transformations highly depend on other molecules and radicals present in the atmosphere (NOx, peroxides, etc.), and thus the degradation of PFASs into long-chain PFCA is lowered by the presence of NOx and is therefore more significant in non-urban atmospheric environments that are far from industrial sites.

Transformations in soil and water may occur via abiotic or biological pathways. In the first case, PFAS transformations result from environmental conditions that are independent of living organisms, such as hydrolysis, photolysis and oxidation processes which are generally followed by biological degradation.

Biological degradation may occur via aerobic or anaerobic pathways. Numerous aerobic biotransformation pathways exist with relatively rapid reaction kinetics. They enable the production of perfluorinated acids such PFCA, including from fluorotelomer-derived compounds.

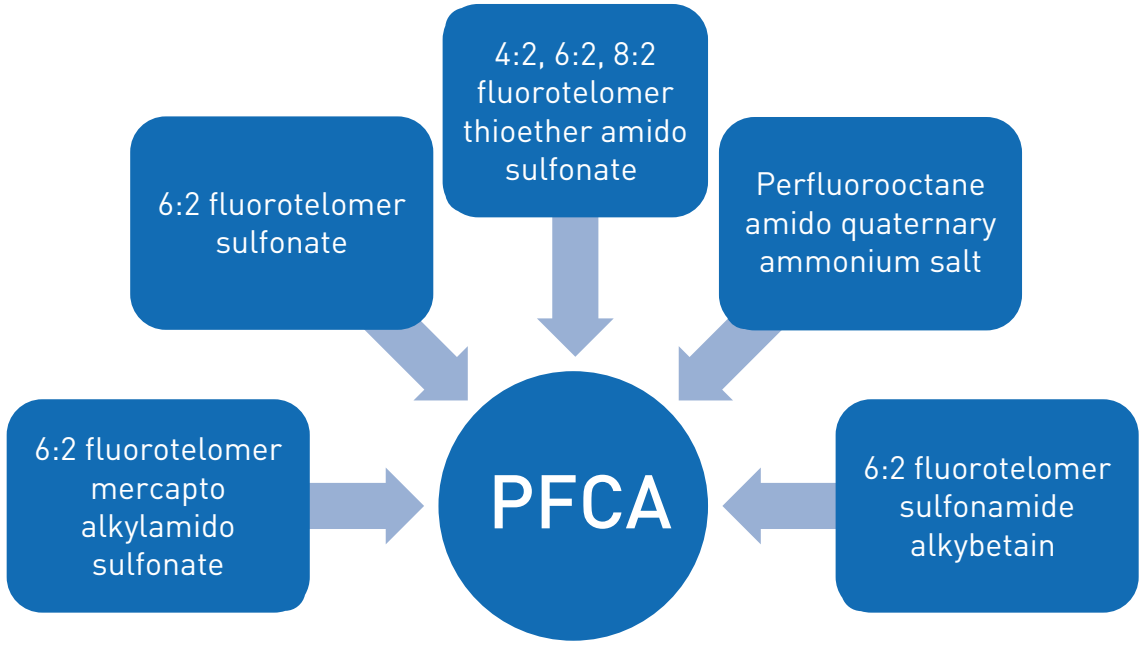


FIGURE 23: Examples of PFAS transformations into PFCA via aerobic biological pathways

Lastly, there is little information about the anaerobic biological pathway, it seems that FTOHs can degrade into stable perfluorinated acids via this pathway, however with much lower kinetics relative to aerobic biotransformation. The relevance of anaerobic biotransformation is uncertain as this may be marginal relative to aerobic biotransformations.

8 Summary

The entire family of PFASs represents several thousand substances each with its own chemical properties and benefits for industrial sectors. Although some properties such as high temperature resistance and surfactant properties can be easily generalised, PFASs must be divided into sub-categories for more efficient management.

The categories of PFASs with the most widely reported uses are PFCA, PFSA and PFS-based non-polymers; nevertheless, a large majority of PFASs with an identified use are not classified by the OECD.

Among those generally used, we have seen a general decrease in the use of long-chain PFASs (> 7 carbons) to the benefit of short-chain counterparts, since the high toxicity of long-chain PFASs has been demonstrated. Nevertheless, the restriction proposal relates to all PFASs. Although short-chain substances are less toxic, they can also be more mobile in various compartments and can potentially accumulate more easily in living organisms.

In terms of the applications, firefighting foams are amongst the main uses of PFASs where their high temperature stability makes them effective substances for the formulation. PFASs are also used as surfactants in a large number of industrial sectors, particularly metal surface treatment industries where they serve to reduce emissions of gas phase toxic compounds.

Of the various fluorinated polymers, PTFE is the most widely used both in Europe and the rest of the world for multiple applications such as non-stick coatings, bearings, plastic or rubber parts and membranes, as well as gaskets and insulations. Despite the fact that fluorinated polymers do not account for a large number of substances, they represent 22% of the PFAS tonnage imported

into the EU in 2019, and their uses as plastic materials which withstand temperature and chemical degradation make them difficult to replace, similar to fluoroelastomers.

Fluorinated gases are primarily used as heat transfer and cooling fluids and as blowing agents for foams. They can be found in many cooling and air-conditioning systems.

Lastly, many applications were found for other substances classified as PFASs, but there are often very few specifics about their role. For the most part, they seem to be used as surfactants, for which, the properties of PFASs are highly appreciated. They are also used as additives for certain mechanical fluids due to their high temperature and fire resistance.

Despite broad research, there is still a lack of knowledge regarding the fluorinated substances used in industry; there is little data available about their specific uses. In terms of the tonnages produced, used and released, there is a lack of available data or the data available only relates to estimations. There is also a lack of data as to the fate of PFASs as well as available means for recycling fluorinated substances.

Despite the substitution of long-chain PFASs, these may still have applications, while short chain PFASs represent most of the current uses. In light of future regulations, substitutions need to be found for industrial uses, especially firefighting foams, greases, lubricants and textiles.

9 References

- [1] INSERM, "Composés perfluorés", 2011. [Online]. Available: https://www.ipubli. inserm.fr/bitstream/handle/10608/222/Intro_Partie_8.html.

- [2] National institute for public health and environment – NL, BAUA – DE, KEMI – SE, Norwegian Environment Agency – NO, Ministry of Environment and Food of Denmark Envi- ronmental Protection Agency –, "Second Stakeholder Consultation on a Restriction for PFAS", October 2021. [Online]. Available: https://www.reach-clp-biozid-helpdesk.de/SharedDocs/Downloads/DE/REACH/Verfahren/Beschr%C3%A4nkung/Consultation-PFAS.pdf?__blob=publicationFile&v=3. [Accessed on 8 November 2021].

- [3] OCDE, "Portal on Per and Poly Fluorinated Chemicals", [Online]. Available: https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/. [Accessed on 8 November 2021].

- [4] OCDE, "Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, Series on Risk Management, No. 61, OECD", OECD Publishing, Paris, 2021.

- [5] US EPA, "Our Current Understanding of the Human Health and Environmental Risks of PFAS", US EPA, [Online]. Available: https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas. [Accessed on 8 November 2021].

- [6] J. W. D. R. D. M. J. A. P. R. Shruti V.Kabadi, "Characterizing biopersistence potential of the metabolite 5:3 fluorotelomer carboxylic acid after repeated oral exposure to the 6:2 fluorotelomer alcohol", *Toxicology and Applied Pharmacology*, 2020.

- [7] J. A. J. C. O. B. S. V. Penelope A.Rice, "Comparative analysis of the toxicological databases for 6:2 fluorotelomer alcohol (6:2 FTOH) and perfluorohexanoic acid (PFHxA)", *Food and Chemical Toxicology,* vol. 138, 2020.

- [8] OECD, *Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances* (PFASs), Paris: OECD Publishing, 2018.

- [9] OECD, "WORKING TOWARDS A GLOBAL EMISSION INVENTORY OF PFASs: FOCUS ON PFCAS – STATUS QUO AND THE WAY FORWARD", Paris, 2015.

- [10] M. S. I. T. C. J. C. D. G. G. D. H. R. L. C. A. N. X. T. Z. W. Juliane Glüge, "An overview of the uses of per- and polyfluoroalkyl substances (PFAS) – Electronic supplementary information 1", *The Royal Society of Chemistry – Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts*, 2020.

- [11] J. F. U. B. J. M. C. I. T. C. P. d. V. A. A. J. K. K. S. A. M. a. S. P. v. L. Robert C. Buck, "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins", *Integrated Environmental Assessment and Management*, vol. 7, n° 14, p. 513-541, 2011.

- [12] K. K. Hongkai Zhu, "A pilot study of per- and polyfluoroalkyl substances in automotive lubricant oils from the United States", *Environmental Technology & Innovation* – Elsevier, vol. 19, 2020.

- [13] B. Améduri, "The promising Future of Fluoropolymer", *Macromolecular chemistry and physics*, 2020.

- [14] G. o. D. H. M. M. C. A. N. S. P. M. S. X. T. L. V. Z. W. J. C. D. Iant T. Cousin, "The concept of essential use for determining when uses of PFASs can be phased out", *Environmental science Processes & Impacts*, 2019.

- [15] B. A. Frédéric Boschet, "(Co)polymers of chlorotrifluoroethylene: Synthesis, properties and applications", *ACS Publication*, 2011.

- [16] G. P. K.-W. S. Stefan Fiedler, "Poly and perfluorinated compounds in household consumer products", *Toxicological and environmental chemistry*, 2010.

- [17] G. S. M. Raveena Dhore, "Per/polyfluoroalkyl substances production, applications and environmental impacts", *Bioresource technologue* – Elsevier, 2021.

- [18] Y. C. Jia Lv, "Fluoropolymers in biomedical applications: state-of-the-art and future perspectives", *Chem Soc Rev*, 2021.

- [19] Interstate Technology Regulatory Council, "Per- and polyfluoroalkyl substances (PFAS)", 2020.

- [20] C. D. X. Z. P. G. P. W. G. M. W. F. N. E. M. S. Xindi C. Hu, "Can profiles of poly- and Perfluoroalkyl substances (PFASs) in human serum provide information on major exposure sources", *Environmental Health*, 2018.

- [21] X. T. &. K. G. &. J. H. Christensen, "Polyfluorinated surfactants (PFS) in paper and board", *Environmental science and pollution research international*, 2011.

- [22] C.-P. Keller, "AGC Fluoroplastics", [Online]. Available: https://www.agcce.com/fluoroplastics/. [Accessed on 17 December 2021].

- [23] N. A. K. G. W. K. C. C. M. L. B. Dandan Huang, "The Co-Transport of PFAS and Cr(VI) in porous media", *Chemosphere*, vol. 286, 2021.

- [24] N. Y. M. L. B. B. G. X. Z. M. D. H. L. a. X. L. Yifan Ji, "Impact of a Hydrocarbon Surfactant on the Retention and Transport of Perfluorooctanoic Acid in Saturated and Unsaturated Porous Media", *Environmental Science & Technology*, vol. 55, 2021.

- [25] US EPA, "CompTox Chemicals DashBoard", [Online]. Available: https://comptox.epa.gov/dashboard/. [Accessed on 16 December 2021].

[26] S. H. K. E. l. F. A. Robert C. Bück, "Identification and Classification of Commercially Relevant Per- and Poly-fluoroalkyl Substances (PFAS)", *Integrated Environmental Assessment and Management*, 2021.

[27] NRDC, "New EPA Data: Huge Amounts of PFAS Underreported and Burned", [Online]. Available: https://www.nrdc.org/experts/yiliqi/new-epa-data-huge-amounts-pfas-underreported-and-burned-0. [Accessed on 5 January 2022].

Study of PFASs applied to mechanical engineering
FIM/Cetim study

Per- and polyfluoroalkyl substances (PFAS), are a broad family of fluorinated molecules made up of oligomers, polymers and non-polymers. However, their industrial uses and their structures are still poorly identified. Although these substances have definite advantages - high thermal, chemical and biological stability - they all contain carbon-fluorine bonds which do not decompose after use, making them dangerous for the environment and humans. As a result of changes to regulations on the use of PFAS intended to reduce said use, particularly through the REACh regulation, work has been undertaken over the past few years to improve our understanding of these uses. Nevertheless, these studies are still far too few and lack data, including as regards the production tonnages as well as possible or already available substitution products. The French association of mechanical industries (FIM) therefore asked Cetim to carry out a documentary study on PFASs in the mechanical engineering sector. Accordingly, their classification, physical and chemical properties, applications, production and emissions, mobility of fluorinated substances have been closely examined and illustrated by many graphs, tables and figures.

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