

# Per- and Poly-Fluorinated Alkyl Substances Chemical Action Plan (PFAS CAP) – 2019 Updates

## Chemistry Chapter

In 2017, the Washington State departments of Ecology and Health shared draft PFAS CAP chapters with external parties for review and comment. Comments received are available [online](#). This document a new 'chapter.' Ecology and Health are sharing chapters with interested parties prior to the **May 15, 2019 PFAS CAP webinar** (*previously planned for March*). Chapter updates will be discussed during the May webinar. We expect to publish the entire Draft PFAS CAP around July 2019 followed by a 60-day comment period.

On **May 15, 2019**, Ecology and Health will host a PFAS CAP webinar to:

- Briefly review activities underway: firefighting foam, food packaging, drinking water.
- Review updated/new chapters – comments will be accepted on the updated chapters. Responses will be provided after the 2019 public comment period (summer 2019).
- Discuss preliminary recommendations – requesting comments and suggestions from interested parties – due June 3, 2019.
- Submit comments [online](#).

### Quick summary of PFAS CAP efforts:

- PFAS CAP Advisory Committee and interested parties met in 2016, 2017 and 2018.
- September 2017 Draft PFAS CAP chapters posted:

Intro/Scope	Environment
Biosolids	Health
Chemistry	Regulations
Ecological Toxicology	Uses/Sources

- March of 2018, Ecology and Health published the Interim PFAS CAP.
- The 2019 updated PFAS CAP “chapters” to be posted (in the order we expect to post on the PFAS CAP website):

Biosolids	<i>Fate and Transport (new)</i>
Ecological Toxicology	<i>Analytical methods (new)</i>
Environment	Chemistry
Regulations	<i>Economic analysis (new)</i>
Uses/Sources	<i>Preliminary</i>
Health	<i>Recommendations (new)</i>

Questions - contact Kara Steward at [kara.steward@ecy.wa.gov](mailto:kara.steward@ecy.wa.gov).

This document is posted on the PFAS CAP Website - <https://www.ezview.wa.gov/?alias=1962&pageid=37105>

## General Chemical Information

### Summary

Per- and polyfluorinated alkyl substances (PFAS) are a class of fluorine-containing chemicals with broad application in commercial products. Fluorosurfactants are prized for their effectiveness in reducing surface energy (of solids) and surface tension (of liquids). Side-chain fluorinated polymers and polyether products help impart oil and grease resistance or soil resistance to food packaging or other substrates. The unique properties of PFAS arise from the strength of the carbon-fluorine bond.

Fluorosurfactants and side-chain polymer PFAS are manufactured from raw materials made by either electrochemical fluorination (ECF) or the telomerization process. Both processes produce end-mixtures of variable composition. The ECF process gives mixtures of various structural shapes (branched chains) and lengths (odd and even) while telomerization produces a homologous mixture of even chain lengths. Per- and polyfluorinated ethers can be manufactured by several diverse processes, however, comparatively little has been published on their by-products or the composition on polyether technical mixtures.

Global PFAS production includes both newer short-chain chemistries and ongoing production of long-chain chemistries in developing countries. The rapid transition from legacy products to new chemistries has led to a concurrent increase in what was an already large number of PFAS substances. The OECD has estimated that there are over 4,700 PFAS substances. This large number of substances together with the fact that products may contain mixtures of target substances, residuals, and contaminants complicates efforts to understand and characterize PFAS uses, emissions, and impacts.

### What are Per- and Polyfluorinated Alkyl Substances (PFAS)?

*[The discussion here is based largely on Buck et al., 2011 and Knepper & Lange, 2012. Other references are provided inline as needed.]*

Table 1 provides a classification hierarchy of environmentally relevant perfluoroalkyl and polyfluoroalkyl substances (PFAS).<sup>1</sup> These include both polymers and non-polymer substances. The table shows typical PFAS families, substance types within the family, and example uses.

This chapter primarily addresses non-polymers and side-chain fluorinated polymers. Non-polymer PFAS are often used as additives to industrial or commercial formulated products, such as cleaners, polishes, paints, and sealers. Other common uses include surfactants in PFAS fire-fighting foams and polymerization aids in fluoropolymer production (Hu et al. 2016; Prevedouros et al. 2006; Ye et al. 2015).

Side-chain fluorinated polymers and perfluoropolyethers are used for surface treatments of paper and packaging, textiles, upholstery, and carpeting (Buck et al. 2011). The structure and function

---

<sup>1</sup> Source: adapted from Buck et al. 2011.

of fluorinated surfactants, side-chain fluorinated polymers and perfluoropolyethers are further described later in this chapter.

Fluoropolymers are often used as linings for fluid pipes, wire and cable, and as layers in laminated fabrics. High molecular weight fluoropolymers are stable at high temperature and in extreme environments. Table 1 provides some specific examples of the most common PFAS.

**Table 1 Typical PFAS families with example substances and common uses. Uses include legacy applications that are relevant for understanding emissions from ongoing uses of legacy products and end-of-life emissions such as those from landfills.**

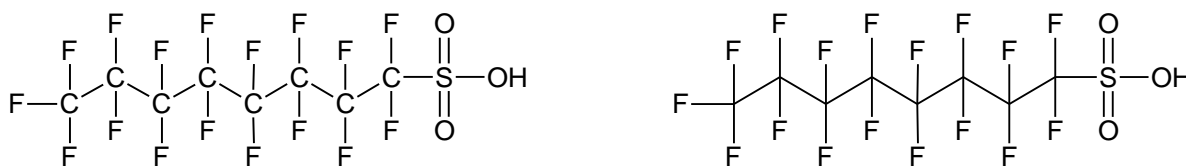
<b><u>Non-Polymers</u></b>	<b><u>Polymers</u></b>
<p data-bbox="217 636 561 667"><b><u>Perfluoroalkyl Substances</u></b></p> <p data-bbox="217 674 756 810"><i>Compounds for which all hydrogen atoms on all carbon atoms (except for carbon atoms associated with functional groups) have been replaced by fluorine atoms, such as:</i></p> <ul data-bbox="266 821 724 1031" style="list-style-type: none"><li>• (Aliphatic) perfluorocarbons.</li><li>• Perfluoroalkyl acids.</li><li>• Perfluoroalkane sulfonyl fluorides.</li><li>• Perfluoroalkane sulfonamides.</li><li>• Perfluoroalkyl iodides.</li><li>• Perfluoroalkyl aldehydes.</li></ul> <p data-bbox="217 1041 716 1104">Example uses: surfactants, manufacturing intermediates.</p> <p data-bbox="217 1167 574 1199"><b><u>Polyfluoroalkyl Substances</u></b></p> <p data-bbox="217 1205 781 1304"><i>Compounds for which all hydrogen atoms on at least one (but not all) carbon atoms have been replaced by fluorine atoms, such as:</i></p> <ul data-bbox="266 1314 781 1451" style="list-style-type: none"><li>• Perfluoroalkane sulfonamido derivatives.</li><li>• Fluorotelomer-based compounds.</li><li>• Semifluorinated <i>n</i>-alkanes and alkenes.</li></ul> <p data-bbox="217 1461 729 1560">Example uses: ski wax, water, oil, and stain repellency for textiles, leather, and food contact paper.</p>	<p data-bbox="841 636 1268 667"><b><u>Side-chain Fluorinated Polymers</u></b></p> <p data-bbox="841 674 1391 737"><i>Variable composition non-fluorinated polymer backbone with fluorinated side chains, such as:</i></p> <ul data-bbox="889 747 1391 884" style="list-style-type: none"><li>• Fluorinated acrylate and methacrylate polymers.</li><li>• Fluorinated urethane polymers.</li><li>• Fluorinated oxetane polymers.</li></ul> <p data-bbox="841 905 1378 968">Example uses: water, oil, and stain repellency for textiles, leather, and food contact paper.</p> <p data-bbox="841 999 1049 1031"><b><u>Fluoropolymers</u></b></p> <p data-bbox="841 1041 1365 1104"><i>Carbon-only polymer backbone with fluorine atoms directly attached, such as:</i></p> <ul data-bbox="889 1115 1235 1220" style="list-style-type: none"><li>• Polytetrafluoroethylene.</li><li>• Polyvinylidene fluoride.</li><li>• Polyvinyl fluoride.</li></ul> <p data-bbox="841 1230 1276 1293">Example uses: wire and cable linings, cookware, lubricants.</p> <p data-bbox="841 1335 1105 1367"><b><u>Perfluoropolyethers</u></b></p> <p data-bbox="841 1377 1349 1472"><i>Carbon and oxygen polymer backbone with fluorine atoms directly attached to carbon atoms, such as:</i></p> <ul data-bbox="889 1482 1179 1514" style="list-style-type: none"><li>• Perfluoropolyethers.</li></ul> <p data-bbox="841 1524 1349 1619">Example uses: functional fluids and surface protection products for stone, metal, glass, plastics, leather, and paper.</p>

The Washington Administrative Code (WAC) 173-333-310 identifies five persistent, bioaccumulative, and toxic (PBT) substances in a perfluorooctane sulfonic acid (PFSA) chemical group, Table 2(Washington State Legislature, n.d.).<sup>2</sup>

**Table 2 Perfluorooctane sulfonic acid and selected salts identified in Washington Administrative Code(Washington State Legislature, n.d.) 173-333-310.**

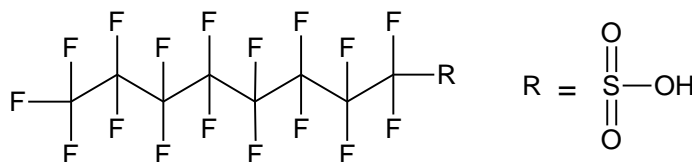
CAS Number	Substance	Formula	R-Group
1763-23-1	Perfluorooctane sulfonic acid (PFOS)	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> H	SO <sub>3</sub> H
29081-56-9	Perfluorooctane sulfonic acid, ammonium salt	C <sub>8</sub> H <sub>4</sub> F <sub>17</sub> NO <sub>3</sub> S	SO <sub>3</sub> NH <sub>4</sub>
70225-14-8	Perfluorooctane sulfonic acid, diethanolamine salt	C <sub>12</sub> H <sub>12</sub> F <sub>17</sub> NO <sub>5</sub> S	C <sub>4</sub> H <sub>12</sub> NO <sub>5</sub> S
29457-72-5	Perfluorooctane sulfonic acid, lithium salt	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> Li	SO <sub>3</sub> Li
2795-39-3	Perfluorooctane sulfonic acid, potassium salt	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> K	SO <sub>3</sub> K

Figure 1 illustrates the first of these substances, perfluorooctane sulfonic acid (1), also designated as PFOS. The structure on the left shows all the individual atoms, while the structure on the right shows a simplified version where each carbon atom (C) is indicated only by the intersection of the straight lines (which represent bonds between the atoms). The style on the right will be used throughout this chapter.



**Figure 1 Perfluorooctane sulfonic acid (PFOS) shown with carbon atoms visible (left) and with carbons represented only by bond intersections (right).**

For convenience, structure illustrations often use R to represent a “functional group” add-on to the main carbon chain. R may represent a single atom or a group of atoms. In Figure 2, R



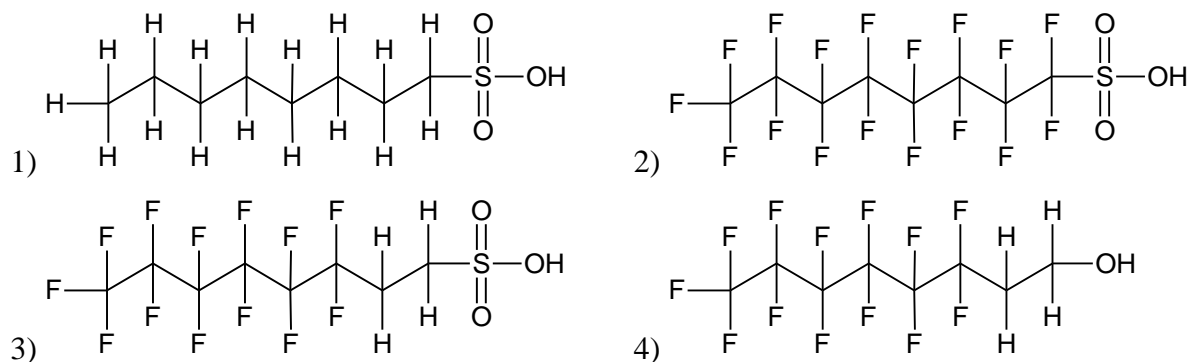
**Figure 2 PFOS in which the SO<sub>3</sub>H functional group is represented by R.**

<sup>2</sup> “Sulfonates” referred to in the WAC are identified here as “sulfonic acids.” This chapter uses the widely-adopted terminology for PFASs described in Buck et al., 2011. Chemical names cited in sources, such as the WAC in this case, are modified without further reference.

represents the SO<sub>3</sub>H sulfonic acid group. Manufacturers may alter the R-group to achieve desired properties, for example, solubility in a formulation solvent.

Each substance in Table 1 can be represented by an appropriate definition of the R-group. For example, perfluorooctane sulfonic acid, potassium salt is represented as C<sub>8</sub>H<sub>17</sub>SO<sub>3</sub>K, or by C<sub>8</sub>H<sub>17</sub>R, where R = SO<sub>3</sub>K. When the H associated with the sulfonic acid group is replaced by any of several single atoms, for example, potassium, the name reflects this substitution:  
*perfluorooctane sulfonic acid, potassium salt.*

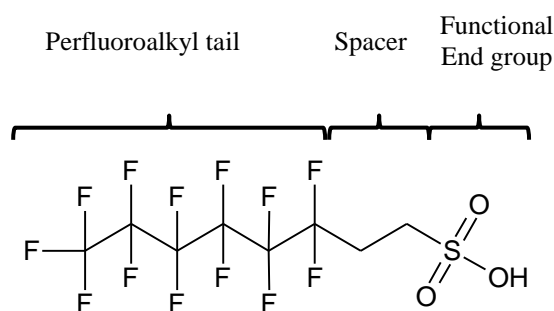
Ordinary *hydrocarbons* contain mostly hydrogen (H) and carbon (C) atoms, however, when the H are totally replaced by fluorine (F) atoms, the substance is described as *perfluorinated*. Figure 3 includes a non-fluorinated hydrocarbon, octane sulfonic acid (1), and its perfluorinated cousin, PFOS (2). The third and fourth structures in Figure 3 are *poly*-fluorinated substances, where the C atoms have a mix of both F and H atoms attached. The end-group is also different in (4), with the SO<sub>3</sub>H replaced by an OH, indicating an alcohol.



**Figure 3** Four example structures: 1) the non-fluorinated octane sulfonic acid (a hydrocarbon with no fluorine), 2) its perfluorinated cousin PFOS, 3) the polyfluorinated 6:2 fluorotelomer sulfonic acid (with hydrogen and fluorine on the backbone carbon chain) and 4) the polyfluorinated 6:2 fluorotelomer alcohol.

This chapter focuses primarily on *alkyl* substances, referring to the single-bonded perfluoroalkyl chain of carbons bearing fluorine atoms in three of the four structures of Figure 3. Structures (1), (2), and (3) are *acids* defined by the sulfonic acid end-group, SO<sub>3</sub>H. While (1), (2) and (3) are *alkyl acids*, (2) is a *perfluorinated alkyl acid* (PFAA). Substances like (2), (3), and (4), but also many others of varying lengths and types of substituent R-groups are together referred to as per- and polyfluoroalkyl substances (PFAS).

Perfluoroalkyl chains are often represented in a shorthand form as C<sub>n</sub>F<sub>2n+1</sub>. In Figure 4, the 6 perfluorinated carbons, n = 6 could be represented as C<sub>6</sub>F<sub>13</sub>, the hydrocarbon spacer as C<sub>2</sub>H<sub>4</sub>, and the end group as SO<sub>3</sub>H. This mix of a perfluoroalkyl chain and a hydrocarbon spacer results in a *polyfluorinated* carbon chain. The polyfluoroalkyl structures have a numerical prefix based on these structural elements to indicate the number of *perfluorinated* versus *non-fluorinated* C atoms. Figure 4 illustrates the 6:2 fluorotelomer sulfonic acid.



**Figure 4. Schematic structure of a polyfluorinated surfactant, the 6:2 fluorotelomer sulfonic acid. In this naming convention, there are six perfluorinated carbons and two hydrogenated carbons (Hs not shown except for those in the functional end-group). Generally, the hydrocarbon (H) atoms are not shown on the carbon backbone. The hydrocarbon portion of the carbon backbone is sometimes described as a spacer.**

## Select Physical and Chemical Properties of PFAS

### Essential Characteristics of PFAS

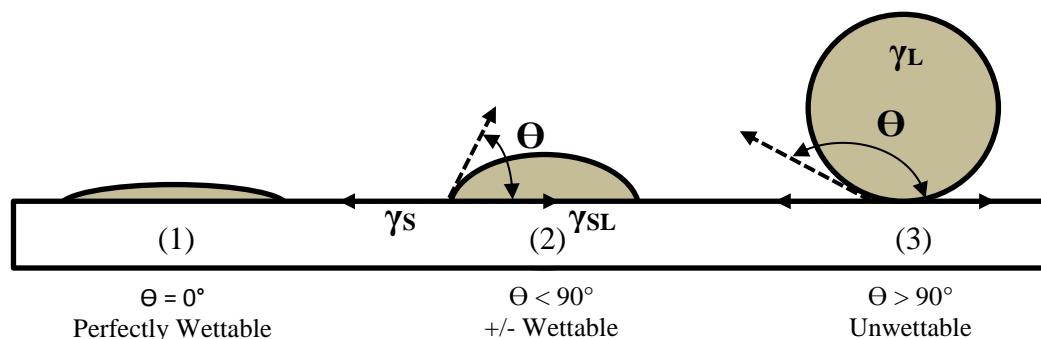
PFAS have some unique and valuable properties when compared with non-fluorinated hydrocarbon chemicals of similar structure (Krafft & Riess, 2015). Fluorine forms an extraordinarily strong bond with carbon, and when fluorine completely replaces hydrogen in an alkyl chain of carbons, the resulting substance is much more resistant to thermal or chemical attack than a similar fluorine-free hydrocarbon. As a result, PFAS are often preferred for use in extreme environments (high temperatures, strongly reactive conditions, etc.).<sup>3</sup>

PFAS treatments or polymer coatings are often used to create *low surface energy* materials. Fluoropolymers, such as polytetrafluoroethylene (PTFE), are un-wettable in that both oil and water will “bead-up” on PTFE surfaces. Common applications include thin fluoropolymer linings in hydraulic tubing, linings for chemical and pharmaceutical processing equipment, and breathable membranes for garments. Side-chain polymers or perfluoropolyethers derived from PFAS can be used to coat surfaces on a molecular scale, imparting oil and water (i.e., stain) resistance at the individual fiber level in textiles, fabrics, or carpets. Other PFAS are added to liquid formulations and function mostly as surface-active agents or emulsifiers.

Surface-active agents (surfactants) are commonly used to affect wetting and spreading of liquids (Chemistry, Properties and Uses of Commercial Fluorinated Surfactants in Knepper and Lange 2012). Wetting is controlled by the interplay of solid surface energy and liquid surface tension, Figure 5. Droplets of water, which normally has high surface tension, will bead-up on low energy hydrocarbon surfaces like polyethylene plastic, reflecting the *hydrophobic* (water-hating) nature of many hydrocarbons. On the other hand, oil, itself a hydrocarbon, has a much lower surface tension. Oil droplets will spread on polyethylene, Figure 5-2, and polyethylene is described as *oleophilic* or oil-loving.

<sup>3</sup> These same characteristics are responsible for the extreme environmental persistence of perfluorinated substances as they are completely resistant to naturally occurring breakdown mechanisms; see the CAP chapter on Fate.

When a surfactant is added to water, the normally high surface tension is reduced and droplets behave more like oil droplets, spreading on the polyethylene surface. Fluorinated surfactants are effective at reducing surface tension in both oil- and water-based products to promote wetting and spreading.



**Figure 5 Contact angle and spreading.** The three cases illustrate (left) complete wetting, (middle) partial wetting and, (right) no wetting.  $\Theta$  represents the contact angle and  $\gamma$  the surface energy or tension (see Equation 1 below). Water will bead-up on many hydrophobic plastics (3), but oil will more likely wet and spread (2). Both oil and water behave like (3) when the solid is a fluorinated-polymer surface.

Wetting and spreading are critical for a great many commercial processes: paints must cover surfaces uniformly and completely, with tolerance for surface defects like roughness or sporadic contamination; inks need to achieve full coverage on printing plates; etc. A spreading formula is often used to describe this behavior:

**Equation 1** 
$$S = \gamma_S - \gamma_L - \gamma_{SL}$$

where  $S$  is termed the *spreading coefficient*. In simplest terms,  $S$  must be positive for good wetting and spreading, and is favored when the solid surface energy,  $\gamma_S$ , is high, and the liquid surface tension,  $\gamma_L$ , is low. [The interfacial tension,  $\gamma_{SL}$ , a property of the interface between the liquid and the solid, is ignored here.] Table 3 contains some typical values for surface energy and surface tension of various solids and liquids. While the spreading formula provides some *qualitative* understanding, dynamic spreading is far more complex and depends on many properties beyond surface energy and surface tension (Kovalchuk et al., 2014).

The principle uses of PFAS surfactants (fluorosurfactants) reflect their unique surface energy properties and their ability to modify wetting and spreading behavior. When these requirements are combined with a need for chemical inertness or resistance to high temperature, PFAS can have distinct advantages over traditional hydrocarbon surfactants or materials. Krafft & Riess, 2015 contains an excellent discussion of the physical chemistry behind these properties and other unique characteristics of fluorinated substances.

**Table 3 Adapted from Posner in Knepper & Lange, 2012. Due to water's high surface tension, water-based coatings will not readily spread onto low-energy hydrocarbon or fluorocarbon polymers. Surface-active additives (surfactants) can reduce the liquid coating's surface tension, facilitate spreading, and improve the final coated surface evenness.**

Solid	Surface energy, $\gamma_s$ (mN/m)	Liquid	Surface tension, $\gamma_L$ (mN/m)
-CF <sub>3</sub>	6	Water	72
-CF <sub>2</sub> H	15	n-Octane	22
-CF <sub>2</sub> -	18	Olive oil	32
-CH <sub>3</sub>	22		
-CH <sub>2</sub> -	31		
Polyester	42		

## Modifications for PFAS Chemical Function

Hydrocarbon surfactants are often described as having a *head* and a *tail*. The tail is often a long alkyl chain and relatively insoluble in water (hydrophobic). In contrast to the tail, the head is typically more compact, and often hydrophilic, or water-loving. Most surfactants for water-based applications orient at the surface of the liquid, with the tail portion extending out and over the surface at the molecular level and the head-only immersed in liquid. The head is equivalent to the R-group described in the previous section.

Many fluorosurfactants have a similar design, but the fluorocarbon tail is *insoluble in both oil and water* (oleophobic *and* hydrophobic). Most often, the tail is a long perfluorinated carbon chain. The head varies more widely and is chosen so that surfactants will perform certain functions in each product application. For example, a fluorinated surfactant for a water-based paint application usually has an R-group that is hydrophilic (water-loving). Sulfonic acid or carboxylic acid R-groups work well in these applications, so both PFOS and PFOA were used for water-based applications.

Formulating a product from a mixture of chemical ingredients and solvents is a complex art. A surfactant may play multiple roles and need to meet other functional requirements (color, temperature stability, etc.). In a floor polish, the surfactant improves wetting and spreading, but also helps achieve a smooth, glossy finish through its effect on surface tension as the polish dries. Several surfactants may be used in a single product, with hydrocarbon surfactants used to keep ingredients dispersed and fluorinated surfactants used to promote wetting. The individual constituents must work well together in the complete system of ingredients for the product to function as intended.

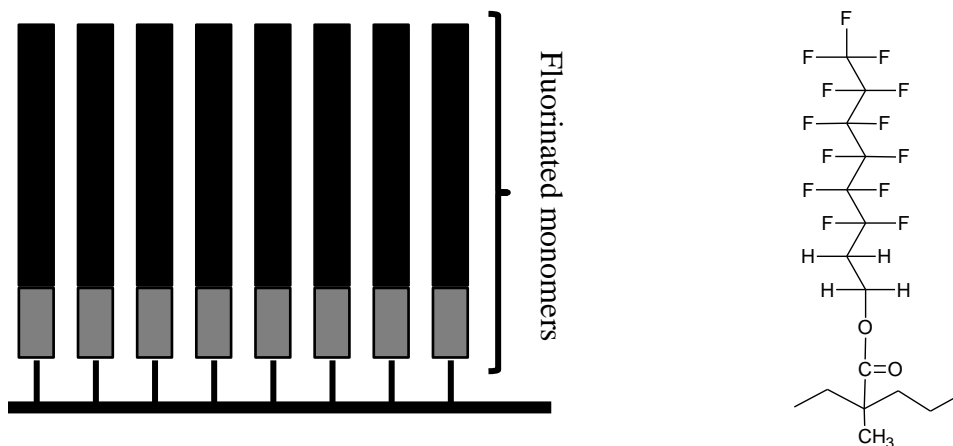


The basic head/tail concept is a bit different in polyfluorinated surfactant design, Figure 6. Manufacturers have introduced a hydrocarbon spacer between the perfluorinated tail and the head-group. The hydrocarbon “spacer,” often a two-carbon group extends the combined surfactant tail length. Figure 4 above shows a specific example: the 6:2 fluorotelomer sulfonic acid. Some reports suggest that the use of a spacer helps to balance function and toxicity as manufacturers have moved to shorter perfluorinated chains, Figure 6 (Renner, 2006).



**Figure 6 Schematic of a fluorinated surfactant. The perfluorinated chain is represented by the black bar (left), the non-fluorinated hydrocarbon spacer by the gray portion (center), and the functional R-group (right) by the white portion. The R-group is selected to ensure solubility in the solvent of interest or to confer other functional properties.**

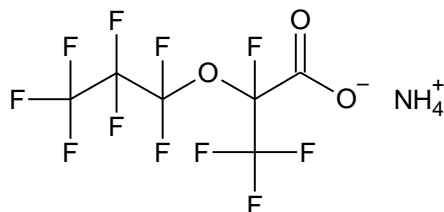
Very similar surfactant-like structures are used in the production of polymeric surface-treatment or impregnation products for textiles and paper. R-groups such as acrylate or methacrylate form fluoroalkyl acrylate and methacrylate monomers. These may be combined with non-fluorinated monomers. The monomers are polymerized to form a non-fluorinated hydrocarbon backbone with fluorinated side-chains, like teeth on a comb. These are commonly called “side-chain polymers,” Figure 7. Side-chain polymers are often sold as aqueous dispersions and used for surface treatment or impregnation of textiles, carpets, and paper products, among other uses. Side-chain polymers are not themselves considered surfactants.



**Figure 7 Fluorinated “side-chain polymer” typical of stain-resistant surface treatments for textiles. In the schematic (left), the solid line at the base represents the main, non-fluorinated polymer backbone. Fluorinated side-chains (black bars) are bonded to the backbone through reactions with the hydrocarbon spacer group (gray bar). The treated surface is at the bottom of the figure with the air interface at the top. The structure on the right is a typical example of one “tooth” of the comb.**

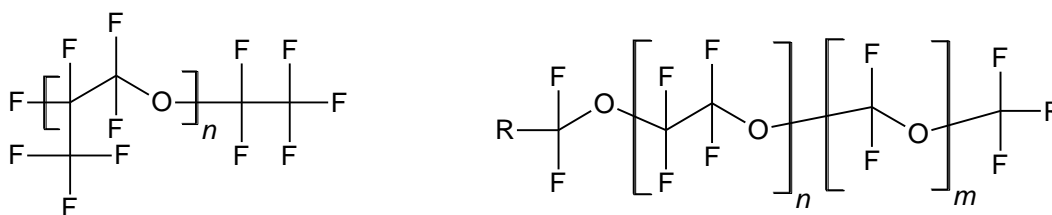
In some applications, heteroatoms, like oxygen (O), may be introduced into the fluorinated tail. The resulting perfluoroalkyl ether surfactants are currently used as processing aids in emulsion polymerization, where they replace legacy processing aids like ammonium perfluorooctanoate (APFO), the ammonium salt of PFOA. One example is the ammonium salt of perfluoro-2-propoxypropanoic acid (PFPrOPrA), Figure 8. Perfluoroalkyl ether carboxylic acids (PFECAs)

contain ether O-atoms interspersed among (typically) short perfluorinated chains (Sun et al., 2016).



**Figure 8** The ammonium salt of PFPPrA is a processing aid used in the manufacture of fluorinated polymer resins like PTFE. It has been used to replace APFO, which readily dissociates in the environment to highly persistent PFOA.

Perfluoropolyether (PFPE) substances include repeating structural ether units (indicated by the bracketed structures with subscripts in Figure 9). Depending on the number of repeating ether-units these will vary in molecular weight and in their physicochemical properties. PFPEs are used as surfactants, functional fluids, and to modify properties of other polymers such as polyurethane (Solvay Company, 2015).



**Figure 9** Left: Perfluoropolyether characteristic of lubricants and other functional fluids offered by several manufacturers. The subscript “n” is the number of times the structure in brackets is repeated. One manufacturer reports that “n” can vary from 10 to 60 (Chemours Company, n.d.). Right: this PFPE includes different length ether units that repeat (“n” or “m” times) and variable “R” groups that can be tailored by application requirements (Solvay Company, 2015).

The expertise to fine-tune these surfactant, side-chain fluoroalkyl polymer, and perfluoropolyether structures is highly valued intellectual property and may be one reason why the details of these structures are often not publicly disclosed. The first chapter in Knepper & Lange 2012 contains many examples of fluorinated chemicals, their associated applications, and relevant literature citations.

## Manufacturing

*[The material in this section is based on two recent publications that review PFAS manufacturing processes: Buck et al., 2011 and Knepper & Lange, 2012. Statements supported by other references are noted inline.]*

Complex chemicals like PFAS generally require several sequential manufacturing steps and utilize multiple chemical raw materials, catalysts, and other additives too numerous to detail here. However, the principle perfluoroalkyl building blocks used for making fluorosurfactants

and side-chain fluorinated polymers are manufactured using two main processes: 1) electrochemical fluorination (ECF) and 2) telomerization.

## Electrochemical Fluorination (ECF)

When a hydrocarbon raw material is combined with hydrofluoric acid (HF), application of a strong electric current can break the H – F bond and create reactive fluoride species. These reactive species replace the hydrogens in the hydrocarbon one-by-one with fluorine resulting in a perfluorinated molecule. ECF was the dominant global method of production (principally by the 3M Company) for both PFOS and PFOA from the late 1940s until their phase-out beginning around the year 2000 (De Voogt, 2010). ECF is still used in both the U.S. and abroad, especially in China, India and Russia (OECD, 2015).

Perfluorooctane sulfonyl fluoride (POSF), Figure 10, from the ECF process was the basic building block for a wide variety of surfactant and polymer products, including PFOS.

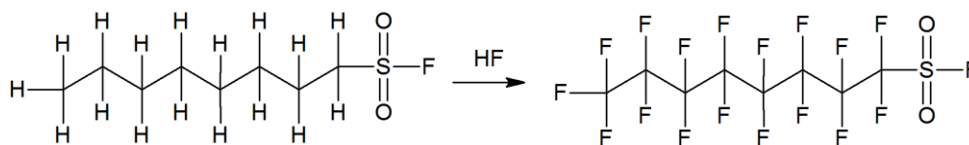


Figure 10 A schematic of the ECF reaction that forms POSF.

## Telomerization

Following the phase-out of PFOS and PFOA production by ECF, telomerization has become a dominant process for producing perfluorinated alkyl chain raw materials. Telomerization is a polymerization reaction that results in products with even-numbered carbon chain lengths and a terminal iodide (I) functional group, Figure 11 (1). Insertion of the *hydrocarbon* ethylene instead of *fluorocarbon* reactants, converts a *per*-fluorinated molecule to a linear *poly*-fluorinated alkyl chain, such as the 8:2 fluorotelomer iodide (8:2 FTI), Figure 11 (2).

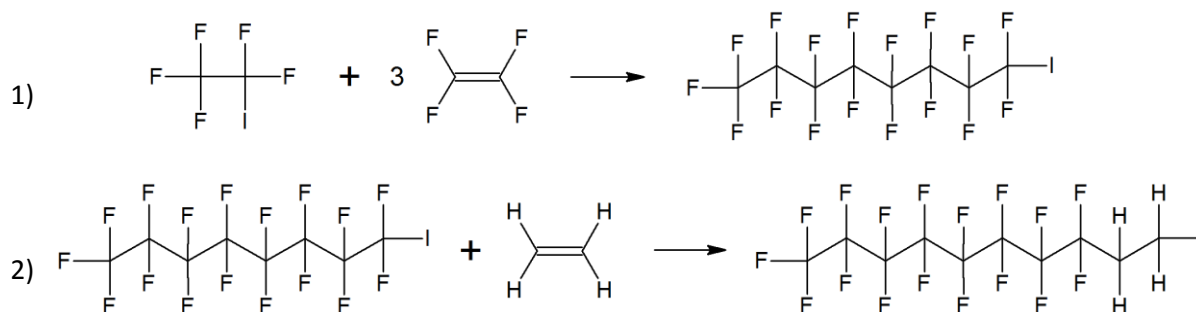
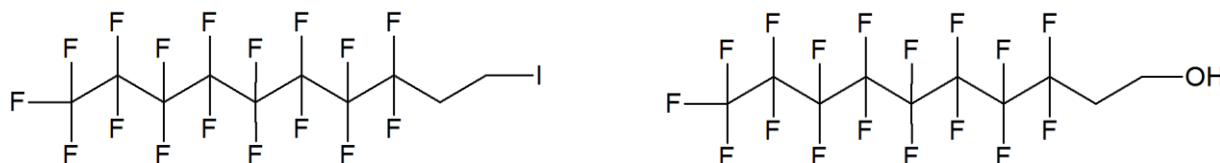


Figure 11 Reaction 1 shows the telogen (perfluoroethyl iodide) reacting with three taxogen units (tetrafluoroethene) to form a perfluorinated product, perfluorooctyl iodide (PFI). PFI can be further reacted (reaction 2) with the hydrocarbon ethene to form the polyfluorinated 8:2 fluorotelomer iodide (FTI).

PFOA can be made by oxidizing PFI [Figure 11 (1)] with sulfur trioxide. FTI [Figure 11 (2)] can be converted to alcohols (FTOHs) and further functionalized for use as fluorotelomer surfactants, Figure 12. A significant share of the fluorotelomer market is for side-chain fluorinated polymers (USEPA 2009) made from monomers like the fluorotelomer acrylates (FTACs).



**Figure 12 An 8:2 fluorotelomer iodide (left) can be converted to an 8:2 fluorotelomer alcohol (right). The “8” refers to the eight perfluorinated carbons. The “2” refers to the two hydrogenated carbons (Hs not shown) adjacent to the end group.**

## Other Processes

The per- and polyfluoroalkyl substances described in the previous section are raw materials or intermediates for commercial products. Some of the main manufacturing processes used to modify these intermediates, for example, to add functional groups, are well described in Knepper & Lange 2012.

Since the 1970s, several manufacturers have developed independent production paths to produce the many per- and polyfluorinated ether surfactants and perfluoropolyether products available on the market today. The environmental literature has only recently begun to identify and assess these substances (Sun et al., 2016; Wang et al., 2013). Some of the known manufacturing processes are briefly reviewed in Knepper & Lange 2012, or in more detail in a recent review by Ameduri & Sawada 2016.

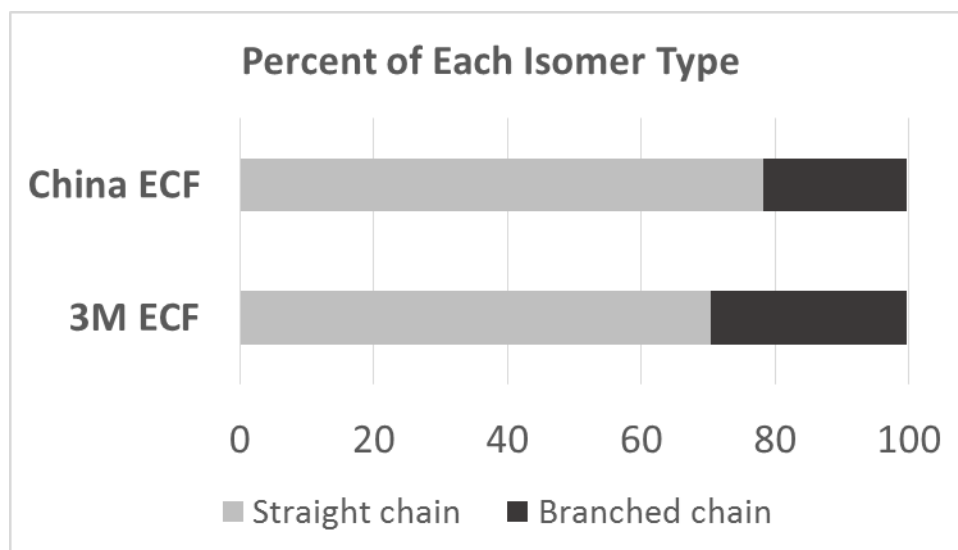
## Technical Quality and Implications for Environmental Impacts

While we often describe discrete substances, like PFOS or PFOA, the ECF and telomerization processes produce a complex *mixture* of substances rather than pure one-component products. For example, the harsh conditions of the ECF process lead to a variety of unwanted side-reactions. The resulting product mixture may contain both linear and branched chains with both odd and even chain lengths. ECF production targeting PFOA (C8) includes 70-80% linear substances (of differing carbon chain lengths) with 20-30% branched substances, including even cyclic compounds (De Voogt, 2010).

While ECF mixtures randomly vary, they are sufficiently consistent for forensic application. PFAS environmental contaminants collected in China matched the chain-length profile expected for ECF products, suggesting that nearby manufacturing facilities employ the ECF process, Figure 13 (Jiang, 2015).

The telomerization process also produces a mixture of substances, typically a series of straight chains varying in length by even numbers. For example, production targeting the 6:2 FTI may include minor quantities of 8:2 and 4:2 chain lengths. The two-carbon tetrafluoroethene taxogen (shown in Figure 11, reaction 1) adds about 100 g/mol in each addition step. As FTIs are

relatively volatile, the change in properties between the  $C_n$  to  $C_{n+2}$  homologue<sup>4</sup> allows for purification by distillation (Krafft & Riess, 2015). The extent to which manufacturers purify their products or otherwise control for by-product content is not well understood.



**Figure 13** The bars represent the isomer composition of two ECF products (adapted from Jiang 2015). The majority of these ECF products are “normal” or straight-chain isomers, but may contain 20 to 30% of various branched isomers. The top bar represents Chinese ECF production (Defu PFOSK, China). The bottom bar is typical of a 2000-era 3M PFOS.

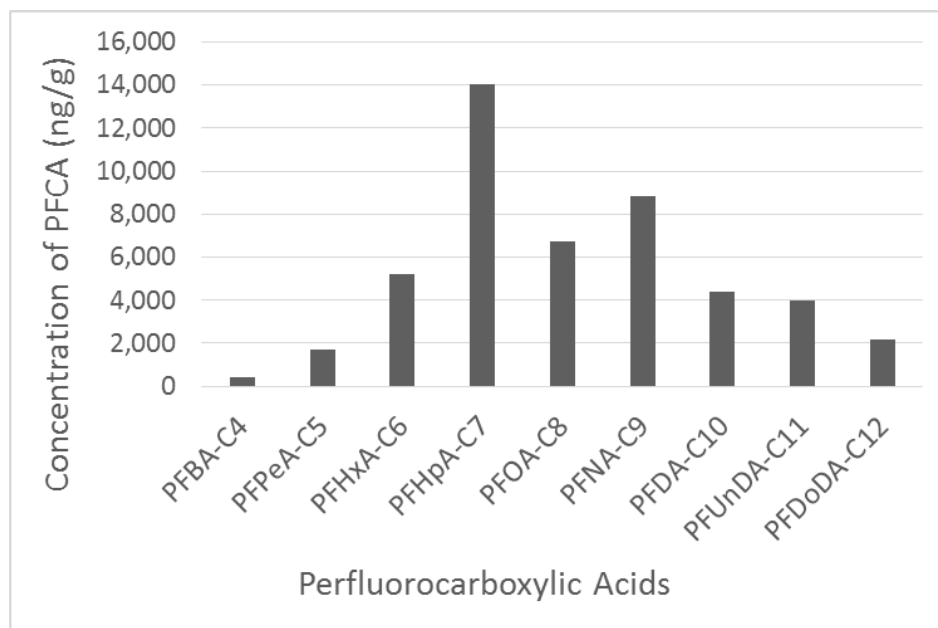
Products have been marketed as mixtures of PFAS isomers or homologues (KEMI, 2015). Surfion® S-111, a surfactant produced by telomerization and presumably discontinued, contained primarily 9-C perfluorononanoic acid (PFNA), but also significant quantities of linear homologues, the 11-C perfluoroundecanoic acid (PFUnDA) (20%) and the 13-C perfluorotridecanoic acid (PFTrDA) (5%) (Prevedouros, 2006). Chemical analysis of “articles of commerce” shows that many formulated products have been composed of complex PFAS mixtures, Figure 14 (Liu et al., 2012).

Products may also be contaminated with residual raw materials, polymerization aids and unintended by-products. PFOA, higher homologues, and PFOA precursors have been found in fluorotelomer and fluoropolymer products. Similarly, FTOHs and fluorotelomer olefins (FTOs) have been identified in fluorotelomer acrylate and methacrylate products (Lassen et al., 2013).

As Figures 13 and 14 illustrate, the manufacture and use of PFAS products can lead to the emission of a multitude of PFAS substances. As polyfluorinated chemicals transform in the environment via multiple biotic and abiotic pathways, the number and variety of unique PFAS contaminants will increase. Many or most of these substances cannot be detected by EPA approved analytical methods. These issues will be further addressed in the Fate and Analytical Chemistry chapters.

---

<sup>4</sup> A compound belonging to a series of compounds that differ only by a repeating unit.



**Figure 14 Analytical chemistry data for the PFCA content (C4-C12) of a U.S. carpet/upholstery protector concentrate (designated B-1) (Liu, 2012). The sample, purchased in 2007, contains a wide-distribution of chain lengths.**

As mentioned earlier, the perfluoroether and perfluoropolyether substances have received little attention in the environmental literature. Some very recent publications have begun to address their environmental occurrence primarily associated with manufacturing facilities (Heydebreck et al., 2015; Hopkins et al., 2018; Pan et al., 2018; Sun et al., 2016). These highlight the fact that while many polymer products may not be bioavailable, their manufacture and use can lead to emissions of bioavailable PFAS processing aids.

## PFAS Chemical Families

*[The discussion in this section is based on Buck et al., 2011, Knepper & Lange, 2012, OECD, 2015 and Poulsen, 2005. Other references are provided inline.]*

The following discussion of PFAS chemical classes describes a very few “characteristic” substances. In most cases, final products or treated articles will contain a mixture of related structures, impurities, residual raw materials, and other contaminants. Some of these substances are known and well-characterized, but many are unknown. While much of the discussion of PFAS chemicals focuses on well-known substances like PFOA, PFOS, and perfluorohexanoic acid (PFHxA), the potential environmental and human health impacts of the many other known and unknown constituents of PFAS products still needs much further work.

Given the endless variety of possible R-groups, heteroatoms, and alkyl chain lengths, manufacturers have a large chemical-design space available for innovation. A recent survey by the Organization for Economic Co-operation and Development (OECD) suggests that there may be more than 4,700 PFAS in existence (OECD 2018). Table 5 highlights some important PFAS families, the associated R-groups that define each sub-family, sub-family abbreviations, and representative substances. Figure 15 contains a simplified PFAS classification map for most of these families.

Appendix #: Chemistry

**Table 4 Partial list of PFAS families, sub-families, abbreviations, functional R-groups that define each sub-family, and example substances.**

<b>Family</b>	<b>Sub-family</b>	<b>Abbreviation</b>	<b>Functional group <math>C_nF_{2n+1}R</math>, where R =</b>	<b>Examples</b>
Perfluoroalkyl acids (PFAAs)	Perfluoroalkyl carboxylic acids	PFCAs	-COOH	Perfluorooctanoic acid (PFOA) Perfluorononanoic acid (PFNA) Perfluorohexanoic acid (PFHxA)
	Perfluoroalkyl carboxylates	PFCAs	-COO <sup>-</sup>	Sodium perfluorooctanoate (Na-PFOA) Ammonium perfluorooctanoate (APFO) Ammonium perfluorononanoate (APFN)
	Perfluoroalkane sulfonic acids	PFSAs	-SO <sub>3</sub> H	Perfluorooctane sulfonic acid (PFOS) Perfluorohexane sulfonic acid (PFHxS) Perfluorobutane sulfonic acid (PFBS)
	Perfluoroalkane sulfonates	PFSAs	-SO <sub>3</sub> <sup>-</sup>	Tetraethylammonium perfluorooctane sulfonate (NEt <sub>4</sub> -PFOS)
	Perfluoroalkyl phosphonic acids	PFPAAs	-P(=O)(OH) <sub>2</sub>	Perfluorooctyl phosphonic acid (C8-PFPA)
	Perfluoroalkyl phosphinic acids	PFPIAs	P(=O)(OH) (C <sub>m</sub> F <sub>2m+1</sub> )	Bis(perfluorohexyl) phosphinic acid (C6/C6-PFPIA)
Perfluoroalkane sulfonyl fluorides		PASFs	-SO <sub>2</sub> F	Perfluorooctane sulfonyl fluoride (POSF) Perfluorobutane sulfonyl fluoride (PBSF)
Perfluoroalkane sulfonamides		FASAs	-SO <sub>2</sub> NH <sub>2</sub>	Perfluorooctane sulfonamide (FOSA)

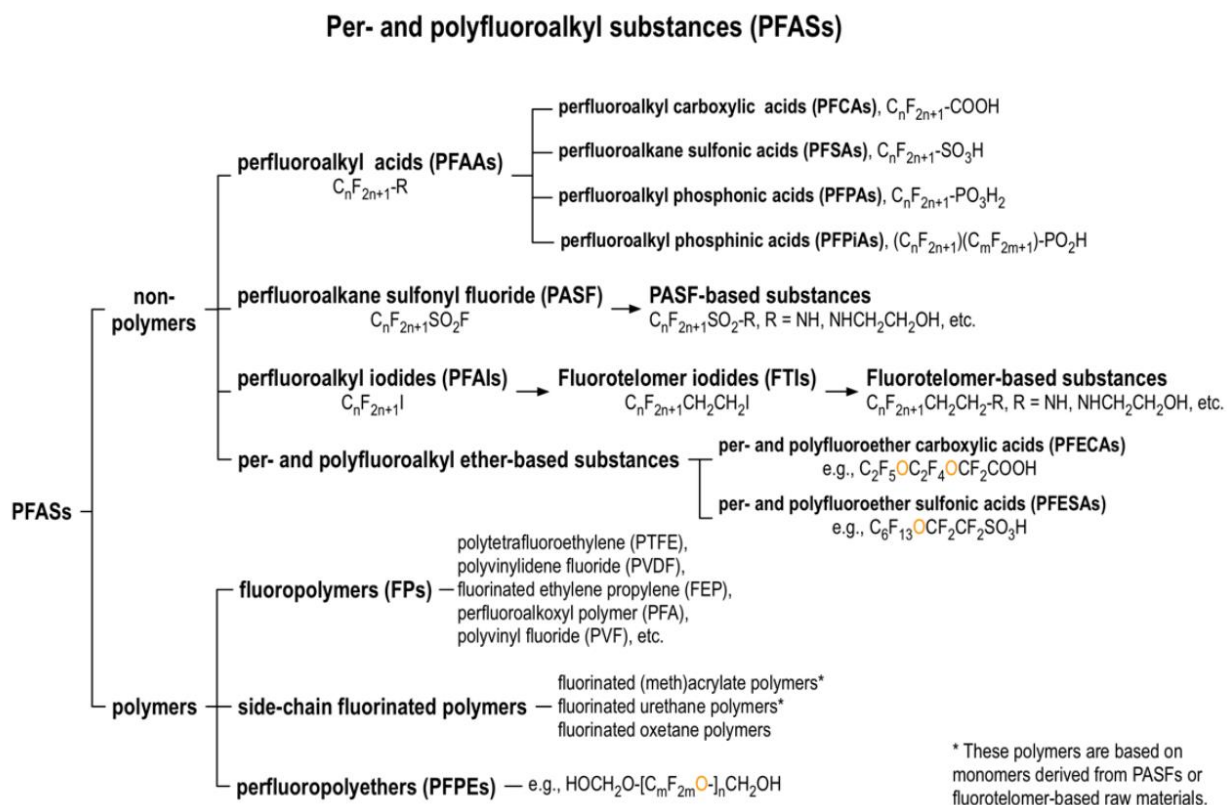
## Appendix #: Chemistry

Family	Sub-family	Abbreviation	Functional group $C_nF_{2n+1}R$ , where R =	Examples
Perfluoroalkanoyl fluorides		PAFs	-COF	Perfluorooctanoyl fluoride (POF)
Perfluoroalkyl iodides (Telomer A)		PFAIs	-I	Perfluorohexyl iodide (PFHxI) Perfluorooctyl iodide (PFOI)
Perfluoroalkane sulfonamido substances	N-Alkyl perfluoroalkane sulfonamides	MeFASA, EtFASAs, BuFASAs	$-SO_2NH(R')$ where $R' = C_mH_{2m+1}$ (m = 1,2,4)	N-Methyl perfluorooctane sulfonamidoethanol (MeFOSE), N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE)
	Perfluoroalkane sulfonamidoethanols and N-alkylperfluoroalkane sulfon- amidoethanols	FASEs, MeASEs, EtFASEs, BuFASEs,	$-SO_2N(R')CH_2CH_2OH$ where $R' = C_mH_{2m+1}$ (m = 1,2,4)	N-Ethyl perfluorobutane sulfonamidoethanol (EtFBSE) Perfluorooctane sulfonamidoethanol (FOSE)
	N-Alkyl perfluoroalkane sulfonamidoethyl acrylates and methacrylates	MeFAS(M)ACs, EtFAS(M)ACs, BuFAS(M)ACs	$-SO_2N(R')CH_2CH_2OC-(O)CH=CH_2$ and $SO_2N(R')CH_2CH_2OC-(O)C(CH_3)=CH_2$ where $R' = C_mH_{2m+1}$ (m=1,2,4)	N-Ethyl perfluorooctane sulfonamidoethyl acrylate (EtFOSAC)
Fluorotelomer substances	Semifluorinated n-alkanes and alkenes	SFAs SFAenes	$-(CH_2)_mH$ and $-CH=CH(CH_2)_{m-2}H$ , with m = 2–16 and n = 6–16	(Perfluorooctyl)ethane ( $F_8H_2$ )
	n:2 Fluorotelomer iodides	n:2 FTIs	$-CH_2CH_2I$	8:2 Fluorotelomer iodide (8:2 FTI)
	n:2 Fluorotelomer olefins	n:2 FTOs	$-CH=CH_2$	6:2 Fluorotelomer olefin (6:2 FTO)



**Appendix #: Chemistry**

<b>Family</b>	<b>Sub-family</b>	<b>Abbreviation</b>	<b>Functional group</b> $C_nF_{2n+1}R$ , where $R =$	<b>Examples</b>
	n:2 Fluorotelomer alcohols	n:2 FTOHs	$-CH_2CH_2OH$	4:2 Fluorotelomer alcohol (4:2 FTOH)
	n:2 Fluorotelomer acrylates and methacrylates	n:2 FTACs  n:2 FTMACs	- $H_2CH_2OC(O)CH=CH_2$ and  - $CH_2CH_2OC(O)C(CH_3)=CH_2$	6:2 Fluorotelomer acrylate (6:2 FTAC) 6:2 Fluorotelomer methacrylate (6:2 FTMAC)
	n:2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates	PAPs	$(-CH_2CH_2O)_x-$ $P(=O)(OH)_{3-x}$ where $x = 1$ or $2$	10:2 Fluorotelomer phosphate monoester (10:2 monoPAP)
	n:2 Fluorotelomer sulfonic acids	n:2 FTSAAs	$-CH_2CH_2SO_3H$	6:2 Fluorotelomer sulfonic acid (6:2 FTSA)
	n:2 Fluorotelomer sulfonic acid chloride	n:2 FTSAAs	$-CH_2CH_2SO_2Cl$	6:2 Fluorotelomer sulfonyl chloride
Miscellaneous	Polyfluoroalkyl ether carboxylic acids & others		e.g., $-O(C_mF_{2m})-OCHF(C_pF_{2p})COOH$	4,8-Dioxa-3H-perfluorononanoic acid (parent of the structure in Fig. 23, left)
	Perfluoropolyethers		e.g., $-O(C_mF_{2m}O)_nCF_3$	Perfluoropolyether oils and lubricants



**Figure 15 Families of per- and polyfluoroalkyl substances (PFAS) based on the terminology found in Buck et al. 2011. Figure reproduced from “Working towards a Global Emission Inventory of PFASs: Focus on PFCAs - Status Quo and the Way Forward,” © OECD, 2015, p. 3.**

## Trends in Per- and Polyfluorinated Substance Design

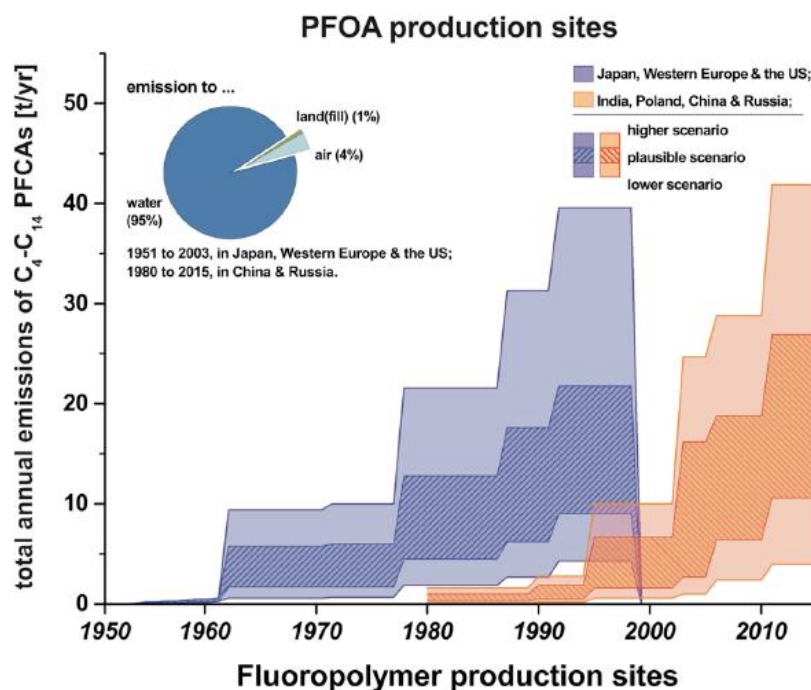
PFOS and PFOA, both with relatively long perfluorinated alkyl chains, dominate the literature on PFAS due to their well-established PBT properties. These substances are associated with workhorse technologies of the first decades of PFAS development and use. PFOS is both a directly manufactured product and a highly stable degradation product of many legacy POSF-based surfactants. PFOS can also occur as an impurity in derivative products. PFOA was widely used as a polymerization aid in fluoropolymer manufacture. PFOA emissions have historically been linked to releases from these manufacturing operations (Prevedouros et al., 2006), but also occur as breakdown products of PFOA-precursors like the fluorotelomer alcohols. Production of PFOS and PFOA-associated chemistries has continued in China, India and Russia, Figure 16. Articles treated with long-chain PFAS are still imported from these countries to the U.S.

Due to regulatory restrictions and voluntary withdrawal campaigns, manufacturers in the US, Western Europe and Japan have shifted manufacture primarily to shorter-chain PFAS products. Alternatives include (OECD, 2013):

- Perfluorobutane sulfonyl fluoride (PBSF)-based derivatives.
- Shorter-chain (i.e., 6:2) fluorotelomer-based chemicals.

- Mono- and polyfluorinated-ether compounds.
- Fluorinated oxetanes.
- Other fluorinated polymers.

Both *legacy* products, which are responsible for much of current-day emissions, but also the newer chemistries of so-called *alternative* products are included in the discussion of classes below. It is important to remember that PFOA may be present as a manufacturing impurity in shorter-chain products made by telomerization. If non-target isomers and homologues are not removed by further processing, they will end up in the final product formulation or treated articles.



**Figure 16 Manufacturing emissions estimates from the OECD. While most developed economies eliminated PFOA and PFOS production, production has moved to developing and transitional economies in recent years. Figure reproduced from “Working towards a Global Emission Inventory of PFASs: Focus on PFCAs - Status Quo and the Way Forward,” © OECD, 2015, p. 39 (OECD/UNEP 2015).**

## Characteristic Product Uses of PFAS

[Poulsen, 2005 has a good discussion of legacy product designs. Information on both legacy and current-use products is taken from OECD, 2013, Buck et al., 2011, and Knepper & Lange, 2012.]

There is little data available on the relative size of the various markets for PFAS. This section will focus on better known product types and substances more commonly discussed in the environmental literature. While fluoropolymers dominate the market for fluorinated materials,

this section will limit the polymer discussion primarily to side-chain polymers and perfluoropolyethers used as surface treatments.

Example substances for both legacy and current-use PFAS products in some selected use categories are presented in Table 6. While the term “legacy” suggests an old or outdated use, the terminology is used loosely here:

- Some of the identified legacy substances may still be manufactured in foreign markets and imported to the U.S. (as discussed above in the “Trends...” section).
- Some legacy substances have only recently been withdrawn from the U.S. market and may still be in-use or stockpiled, for example, long-chain PFAS in treated carpets or firefighting foams.
- Some otherwise widely banned substances have permitted (exempt) uses, such as long-chain PFAS in mist suppressants for chrome-plating operations.

The list of uses, products, and example substances identified here is not exhaustive. The Uses chapter includes some information on the relative market size for some PFAS applications.

**Table 6 Typical examples of legacy and current-use products for selected use categories. See Table 5 for definitions of abbreviations.**

Use Category	Example Legacy Products	Example Current-Use Product
Carpet, Textile, Leather, Stone & Tile, Paints & Coating Additives and Treatments	N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE)-based acrylate, FTOH-based acrylate, methacrylate and urethane side-chain polymers	FTI/FTOH- and PBSF-based acrylate, methacrylate and urethane side-chain polymers
Paper and Packaging Treatment	EtFFOSE phosphate esters, N-Methyl perfluorooctane sulfonamido-ethanol (MeFOSE) acrylate polymers	FTOH-based PAPs, Perfluoropolyethers, Side-chain fluorinated polymers
Specialty Chemicals	potassium salt of glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] (PFOS-based surfactant)	FTOH- and PBSF-based surfactants, Perfluoropolyethers
Fire-Fighting Chemicals	perfluoroalkyl sulfonamido amine derivatives and other PFOS-based products	6:2 FTAB (FTalkyl iodide-based surfactant) and 6:2 thiol derivatives (6:2-SH)
Polymer Processing Aids	PFOA, PFNA	Ammonium salt of perfluoro-2-propoxypropanoic acid (see Figure 23, right)

## Carpet and Textile Surface Treatment

Surface treatment for carpets, upholstery, leather, apparel and other textiles are the largest market for fluorinated side-chain polymers. Carpeting and upholstery involve large treated areas and

stain-resistance treatment is a frequent specification among institutional purchasers (DTSC, 2017).

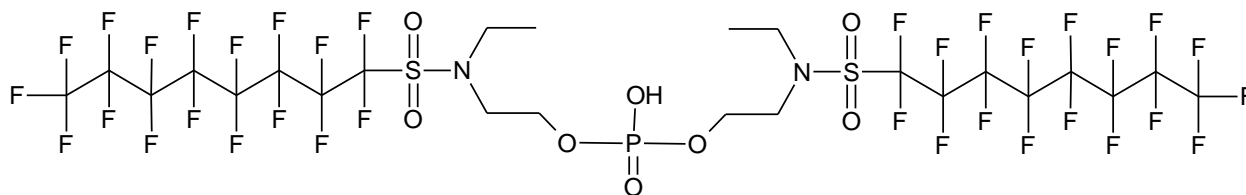
POSF is a manufacturing precursor for the perfluoroalkane sulfonamido alcohols. These alcohols are converted to acrylates and methacrylates used as monomers in the production of polymeric surface protection products. Acrylates of N-methyl or N-ethyl perfluorooctane sulfonamido ethanol (MeFOSE and EtFOSE) and related precursors have been phased-out among U.S., EU, and Japanese manufacturers over the last decade. A single MeFOSE-derived side-chain “tooth” is shown in Figure 17. These products were no longer produced in the U.S. after the early 2000s.

Similarly, fluorotelomer alcohols and ethyl iodides are the basis for acrylate, methacrylate or urethane substances that are polymerized to form fluorinated side-chain polymers as illustrated previously in Figure 7. Early versions of these telomer-based products contained broad ranges of chain lengths (e.g., recall Figure 14 analytical results) (Dinglasan-Panlilio & Mabury, 2006). 4:2 or 6:2 fluorotelomer products have replaced the longer chain legacy products in the U.S.

## Paper and Packaging Treatment

Surface treatment and impregnation products provide water, oil, and grease resistance and non-stick performance for paper and packaging. These include both food-contact materials like popcorn bags, pizza boxes, and fast-food wrappers, but also non-food applications, such as, masking papers and folding cartons.

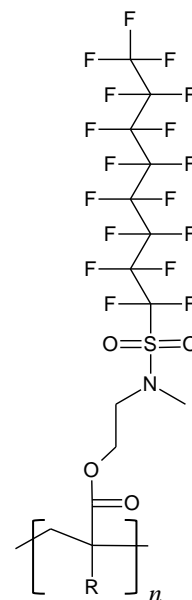
Legacy products include variants of perfluorooctane sulfonamido alcohols (like EtFOSE) in perfluoroalkyl phosphoric acid products also called SAMPAPs (D’eon et al., 2009; Geueke, 2016). The MeFOSE-based acrylate polymers similar to those used in textiles were also used for paper protection. PFOS-based and other long-chain chemistries are still used for food-contact materials in Thailand and China (Benskin et al., 2012; Geueke, 2016; Yuan et al., 2016).



**Figure 18** A phosphate di-ester formed from EtFOSE. These and related mono- and tri-esters are also called SAMPAPs and are among the first perfluorinated substances widely commercialized for food packaging. Prior to their removal from commerce in the U.S., SAMPAPs were reportedly the largest source of PFOS precursors in the commercial market (Benskin et al., 2012).

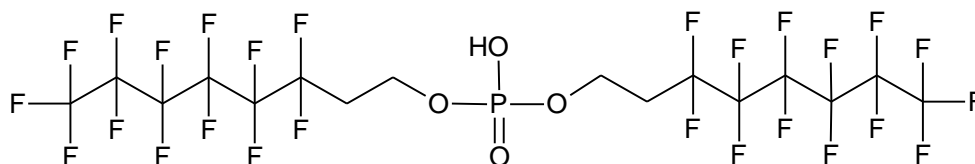
Current-use alternatives in food-contact materials may be based on:

- Short-chain replacements for the FOSE-like products, e.g., N-ethyl perfluorobutane sulfonamidoethanol (EtFBSE) (Geueke, 2016).

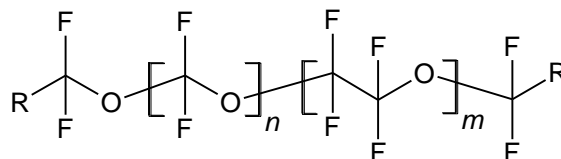


**Figure 17** Legacy carpet treatment chemistry.

- Fluorotelomer acrylate and methacrylate side-chain polymers made with short-chain fluorotelomer intermediates.
- Fluorotelomer-based mono-, di-, and triPAPs (e.g., tri-polyfluoroalkyl phosphoric acid) (Zabaleta et al., 2017).
- Perfluoropolyethers (Wang et al., 2013).



**Figure 19 A phosphate di-ester (diPAP) formed from 6:2 FTOH.**



**Figure 20 Perfluoropolyether marketed for food packaging applications (Solvay Company, n.d.). The R-groups may vary, but in some cases are likely similar to the phosphate acid groups found in the diPAP described above.**

A very recent review from the Nordic Council of Ministers includes a broad survey of PFAS food packaging chemicals worldwide (Trier et al., 2018).

## Specialty Chemicals

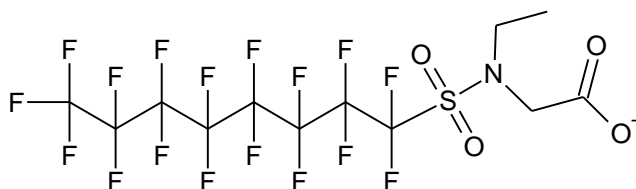
Fluorinated surfactants are used in innumerable industrial and consumer products, where they provide advantages both during application, but also in the final product performance. Paints, coatings, and sealants need to wet the solid substrate and penetrate into crevices or other imperfections. The final finish should be smooth and level. These performance characteristics are all facilitated by the very low surface tension obtained using fluorosurfactants. When appropriately formulated, the same or related surfactants can impart water, oil, and dirt resistance to painted walls, sealed grout or polished floors.

PFAS are also used in a wide-range of functional fluids. These include lubricants for use in harsh or reactive environments including space applications, vacuum pump fluids, heat transfer fluids, etc. Other specialty applications include friction reduction, anti-adhesion products, and anti-squeak products used in automotive applications. Perfluoroethers or polyethers can also be used (as illustrated below) as polymer processing aids. The patent literature and product safety data sheets (SDSs) are both good sources of PFAS structures, applications, and product families.<sup>5</sup>

---

<sup>5</sup> For example, some Chemours fluorosurfactant product SDSs are available at <https://www.3eonline.com/EeeOnlinePortal/DesktopDefault.aspx?tabid=90> using the product identifier.

Liquid-applied products vary substantially by type, and the specialty chemical market requires a broad range of surfactant designs. Knepper & Lange, 2012 provides a number of examples with supporting literature references. A study of commercial products purchased around 2010, such as, the carpet protector in Figure 14 (above), often contained a mix of PFAA chain-lengths (4-C to 12-C PFAAs were quantified) (Liu et al., 2012). The potassium salt of glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] (Chemical Abstract Services Registration Number [CASRN] 2991-51-7, also marketed as Fluorad 129, presumably discontinued) is a typical legacy POSF-based substance used in cleaning agents and polish products (Poulsen et al., 2004), Figure 21.



**Figure 21 Typical legacy POSF-based surfactant used in liquid-applied products.**

As for the applications described above, current-use surfactant products can be similar in structure to the legacy products, but with shorter perfluorinated chains. Product brochures from major manufacturers identify 4-C (PFBS) and 6-C (6:2 FTOH) chemistries for a wide-range of product types (3M, 2016; DuPont, 2008).

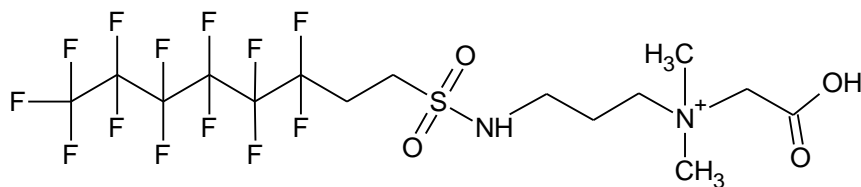
## Fire-Fighting Chemicals

PFAS-based AFFF (aqueous film forming foams) were developed in the 1960s to extinguish Class B flammable liquid fuel fires. After extinguishing the fire, the foam-surfactant film acts as a radiation barrier and vapor-sealant to prevent re-ignition or “burnback.” AFFFs are not a large use category, but they have been implicated in a great many cases of groundwater contamination (Hu et al., 2016). Many of these fires occur outdoors, often without barriers or containment. Foam may be dispersed over a wide area. Lastly, firefighting training operations have not always employed best management practices to prevent PFAS foam release to permeable surfaces.

While PFCAs were used only in the earliest AFFF formulations, POSF-based products dominated the market in the 1970s and later (Prevedouros et al., 2006). Many 1970-2000-era AFFF products were PFSA-based, with derivatives of perfluoroalkylsulfamido amines and PFOS as “major presence[s]” (Favreau et al., 2017). Formulations for the military produced in the 1980s-to-early 2000s contain perfluorinated chains up to 8-, 9-, and 10-C in some cases (Place & Field, 2012). The current generation fluorotelomer-based AFFF products are shorter perfluorinated chains, such as, the 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB, Figure 22)<sup>6</sup> (Wang et al., 2013).

---

<sup>6</sup> These can also carry a three-digit prefix indicating three types of carbons: X:Y:Z (perfluorinated-polyfluorinated-non-fluorinated) carbons (Place & Field, 2012).



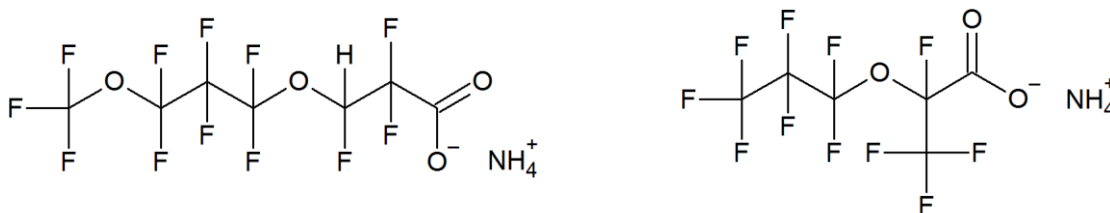
**Figure 22 6:2 FTAB surfactant typical of fire-fighting foam products. Foam concentrates may contain additional surfactants (PFAS and non-PFAS) as well as other adjuvants.**

## Polymer Processing Aids

Fluorinated surfactants are used as emulsifiers in aqueous reaction systems, for example, the emulsion polymerization of PTFE. Sodium and ammonium salts of PFOA and PFNA were widely used in the U.S. and Europe and their use continues in developing and transitional economies.

Newer processing aids identified in the literature are functionalized ethers or polyethers which contain single or multiple ether O-atoms. Among these are (Wang et al., 2013):

- Ammonium 3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid], CASRN 958445-44-8 (left, Figure 23).
- Ammonium perfluoro-2-propoxypropanoic acid (PFPrOPrA), CASRN 62037-80-3 (right, Figure 23).



**Figure 23 Two processing aids used in fluoropolymer production.**

While there is no evidence of fluoropolymer manufacture in Washington State, these PFAS ether-structures are some of the very few examples for which any literature data is available.

## References

- 3M. (2016). 3M TM Fluorosurfactants For Paints and Coatings. St. Paul. Retrieved from <http://multimedia.3m.com/mws/media/624307O/3m-fluorosurfactants-for-paints-and-coating.pdf>
- Benskin, J. P., Ikonou, M. G., Gobas, F. A. P. C., Woudneh, M. B., & Cosgrove, J. R. (2012). Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments. *Environmental Science and Technology*, 46(12), 6505–6514. <https://doi.org/10.1021/es300823m>



- Chemours Company. (n.d.). Frequently Asked Questions (FAQs) | Krytox™ Lubricants. Retrieved from [https://www.chemours.com/Lubricants/en\\_US/sales\\_support/FAQs.html](https://www.chemours.com/Lubricants/en_US/sales_support/FAQs.html)
- D'eon, J. C., Crozier, P. W., Furdui, V. I., Reiner, E. J., Libelo, E. L., & Mabury, S. A. (2009). Observation of a Commercial Fluorinated Material, the Polyfluoroalkyl Phosphoric Acid Diesters, in Human Sera, Wastewater Treatment Plant Sludge, and Paper Fibers. *Environmental Science & Technology*, 43(12), 4589–4594. <https://doi.org/10.1021/es900100d>
- De Voogt, P. (Ed.). (2010). *Reviews of Environmental Contamination and Toxicology Volume 208* (Vol. 208). New York, NY: Springer. <https://doi.org/10.1007/978-1-4419-6880-7>
- Dinglasan-Panlilio, M. J., & Mabury, S. A. (2006). Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials, 40(5), 1447–1453. <https://doi.org/10.1021/es051619+>
- DTSC. (2017). Safer Consumer Products - PFAS Public Workshop: Jan 31, 2017 - YouTube. Retrieved from <https://www.youtube.com/watch?v=MryvxUSlxbA&feature=youtu.be>
- DuPont. (2008). DuPont™ Capstone™ Products – An Overview Capstone™ -A New Generation of Short- Chain Surface Protection Products. Retrieved from [https://www.chemours.com/Capstone/en\\_US/assets/downloads/final\\_final\\_capstone\\_gen\\_summary\\_09\\_05\\_2008.pdf](https://www.chemours.com/Capstone/en_US/assets/downloads/final_final_capstone_gen_summary_09_05_2008.pdf)
- Favreau, P., Poncioni-Rothlisberger, C., Place, B. J., Bouchex-Bellomie, H., Weber, A., Tremp, J., Kohler, M. (2017). Multianalyte profiling of per- and polyfluoroalkyl substances (PFASs) in liquid commercial products. *Chemosphere*, 171, 491–501. <https://doi.org/10.1016/j.chemosphere.2016.11.127>
- Geueke, B. (2016). Dossier - Per- and polyfluoroalkyl substances (PFASs). Zurich. <https://doi.org/10.5281/zenodo.57198>
- Heydebreck, F., Tang, J., Xie, Z., & Ebinghaus, R. (2015). Alternative and Legacy Perfluoroalkyl Substances: Differences between European and Chinese River/Estuary Systems. *Environmental Science & Technology*, 49(14), 8386–8395. <https://doi.org/10.1021/acs.est.5b01648>
- Hopkins, Z. R., Sun, M., DeWitt, J. C., & Knappe, D. R. U. (2018). Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids. *Journal - American Water Works Association*, 110(7), 13–28. <https://doi.org/10.1002/awwa.1073>
- Hu, X. C., Andrews, D. Q., Lindstrom, A. B., Bruton, T. A., Schaidler, L. A., Grandjean, P., ... Sunderland, E. M. (2016). Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environmental Science and Technology Letters*, 3(10), 344–350. <https://doi.org/10.1021/acs.estlett.6b00260>
- Jiang, W., Zhang, Y., Yang, L., Chu, X., & Zhu, L. (2015). Perfluoroalkyl acids (PFAAs) with isomer analysis in the commercial PFOS and PFOA products in China. *Chemosphere*, 127, 180–187. <https://doi.org/10.1016/j.chemosphere.2015.01.049>

- KEMI. (2015). Occurrence and use of highly fluorinated substances and alternatives. Stockholm. Retrieved from <https://www.kemi.se/global/rapporter/2015/report-7-15-occurrence-and-use-of-highly-fluorinated-substances-and-alternatives.pdf>
- Knepper, T. P., & Lange, F. T. (Eds.). (2012). *Polyfluorinated Chemicals and Transformation Products* (Vol. 17). Berlin, Heidelberg: Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-642-21872-9>
- Kovalchuk, N. M., Trybala, A., Starov, V., Matar, O., & Ivanova, N. (2014). Fluoro- Vs hydrocarbon surfactants: Why do they differ in wetting performance? *Advances in Colloid and Interface Science*. <https://doi.org/10.1016/j.cis.2014.04.003>
- Krafft, M. P., & Riess, J. G. (2015). Selected physicochemical aspects of poly- and perfluoroalkylated substances relevant to performance, environment and sustainability-Part one. *Chemosphere*, 129, 4–19. <https://doi.org/10.1016/j.chemosphere.2014.08.039>
- Lassen, C., Jensen, A. A., Potrykus, A., Christensen, F., Kjølholt, J., Jeppesen, C. N., Innanen, S. (2013). Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances. LOUS-review. Danish Ministry of the Environment. Environmental Project 1475, 196. Retrieved from <http://www2.mst.dk/Udgiv/publications/2013/04/978-87-93026-03-2.pdf>
- Liu, X., Guo, Z., Krebs, K. A., Pope, R. H., & Roache, N. F. (2012). Trends of Perfluoroalkyl Acid Content in Articles of Commerce — Market Monitoring from 2007 through 2011. Research Triangle Park. Retrieved from <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100EUF3.txt>
- OECD. (2013). OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs). Paris. Retrieved from [http://www.oecd.org/env/ehs/risk-management/PFC\\_FINAL-Web.pdf](http://www.oecd.org/env/ehs/risk-management/PFC_FINAL-Web.pdf)
- OECD. (2015). OECD/UNEP Global PFC Group, Working Towards a Global Emission Inventory of PFASs: Focus on PFCAs - Status Quo and the Way Forward. Paris. Retrieved from [https://www.oecd.org/chemicalsafety/risk-management/Working Towards a Global Emission Inventory of PFASs.pdf](https://www.oecd.org/chemicalsafety/risk-management/Working_Towards_a_Global_Emission_Inventory_of_PFASs.pdf)
- Organisation for Economic Co-operation and Development. (2018). Toward a New Comprehensive Global Database of Per-and Polyfluoroalkyl Substances (PFASs): Summary Report on Updating the OECD 2007 List of Per-and Polyfluoroalkyl Substances (PFASs). Retrieved from [http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV-JM-MONO\(2018\)7&doclanguage=en](http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV-JM-MONO(2018)7&doclanguage=en)
- Pan, Y., Zhang, H., Cui, Q., Sheng, N., Yeung, L. W. Y., Sun, Y., ... Dai, J. (2018). Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water. *Environmental Science and Technology*. <https://doi.org/10.1021/acs.est.8b00829>
- Place, B. J., & Field, J. A. (2012). Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. *Environmental Science and Technology*, 46(13), 7120–7127. <https://doi.org/10.1021/es301465n>

- Poulsen, P. B., Jensen, A. A., & Wallström, E. (2004). More environmentally friendly alternatives to PFOS-compounds and PFOA. Copenhagen. Retrieved from <http://www2.mst.dk/udgiv/publications/2005/87-7614-668-5/pdf/87-7614-669-3.pdf>
- Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, Fate and Transport of Perfluorocarboxylates. *Environmental Science & Technology*, 40(1), 32–44. <https://doi.org/10.1021/es0512475>
- Renner, R. (2006, January). The long and the short of perfluorinated replacements. *Environmental Science and Technology*. American Chemical Society. <https://doi.org/10.1021/es062612a>
- Solvay Company. (n.d.). FLUOROLINK ® for Low Surface Energy Coatings. Retrieved from <https://www.acota.co.uk/wp-content/uploads/2018/11/Solvay-SpP-Fluorolink-Presentation.pdf>
- Solvay Company. (2015). Technical Data Sheet - Solvera PT 5045 PG. Retrieved from [https://www.solvay.com/sites/g/files/srpend221/files/2018-10/Solvera-PT-5045-PG\\_EN-v1.1\\_0.pdf](https://www.solvay.com/sites/g/files/srpend221/files/2018-10/Solvera-PT-5045-PG_EN-v1.1_0.pdf)
- Sun, M., Arevalo, E., Strynar, M. J., Lindstrom, A. B., Richardson, M., Kearns, B., ... Knappe, D. R. U. (2016). Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina. *Environmental Science & Technology Letters*, 3(12), 415–419. <https://doi.org/10.1021/acs.estlett.6b00398>
- Trier, D. X., Taxvig, C., Rosenmai, A. K., & Pedersen, G. A. (2018). PFAS in Paper and Board for Food Contact. Nordic Council of Ministers. <https://doi.org/10.6027/TN2017-573>
- Wang, Z., Cousins, I. T., Scheringer, M., & Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environment International*, 60(2013), 242–248. <https://doi.org/10.1016/j.envint.2013.08.021>
- Washington State Legislature. (n.d.). Chapter 173-333 WAC: PERSISTENT BIOACCUMULATIVE TOXINS. Retrieved July 9, 2017, from <http://apps.leg.wa.gov/WAC/default.aspx?cite=173-333>
- Ye, F., Zushi, Y., & Masunaga, S. (2015). Survey of perfluoroalkyl acids (PFAAs) and their precursors present in Japanese consumer products. *Chemosphere*, 127, 262–268. <https://doi.org/10.1016/j.chemosphere.2015.02.026>
- Yuan, G., Peng, H., Huang, C., & Hu, J. (2016). Ubiquitous Occurrence of Fluorotelomer Alcohols in Eco-Friendly Paper-Made Food-Contact Materials and Their Implication for Human Exposure. *Environmental Science and Technology*, 50(2), 942–950. <https://doi.org/10.1021/acs.est.5b03806>
- Zabaleta, I., Negreira, N., Bizkarguenaga, E., Prieto, A., Covaci, A., & Zuloaga, O. (2017). Screening and identification of per- and polyfluoroalkyl substances in microwave popcorn bags. *Food Chemistry*, 230, 497–506. <https://doi.org/10.1016/j.foodchem.2017.03.074>

## List of chemical acronyms

These are the chemical acronyms and names used in this chapter (excluding acronyms listed only in Table 5 or Figure 15).

<b>Acronym</b>	<b>Chemical Name</b>
6:2 FTAB	6:2 fluorotelomer sulfonamide alkylbetaine
8:2 FTI	8:2 fluorotelomer iodide
APFO	ammonium perfluorooctanoate
diPAPs	per- or polyfluoroalkyl phosphate di-esters
EtFBSE	N-ethyl perfluorobutane sulfonamidoethanol
EtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol
FTAC	fluorotelomer acrylate
FTI	fluorotelomer iodide
FTO	fluorotelomer olefin
FTOH	fluorotelomer alcohol
HFPO	hexafluoropropylene oxide
MeFOSE	N-Methyl perfluorooctane sulfonamido-ethanol
monoPAPs	per- or polyfluoroalkyl phosphate esters
PAP	per- or polyfluoroalkyl phosphate ester
PBSF	perfluorobutane sulfonyl fluoride
PFAA	perfluorinated alkyl acid
PFAS	per- and poly-fluorinated alkyl substances
PFCA	perfluoro-carboxylic acid
PFECA	perfluoroalkyl ether carboxylic acid
PFH <sub>x</sub> A	perfluorohexanoic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPE	perfluoropolyether
PFPrOPrA	perfluoro-2-propoxypropanoic acid
PFSA	perfluorooctane sulfonic acid
PFT <sub>r</sub> DA	perfluorotridecanoic acid
PFU <sub>n</sub> DA	perfluoroundecanoic acid
POSF	perfluorooctane sulfonyl fluoride
PTFE	polytetrafluoroethylene
SAmPAPs	perfluorooctane sulfonamidoethanol-based phosphate esters
triPAPs	per- or polyfluoroalkyl phosphate tri-esters