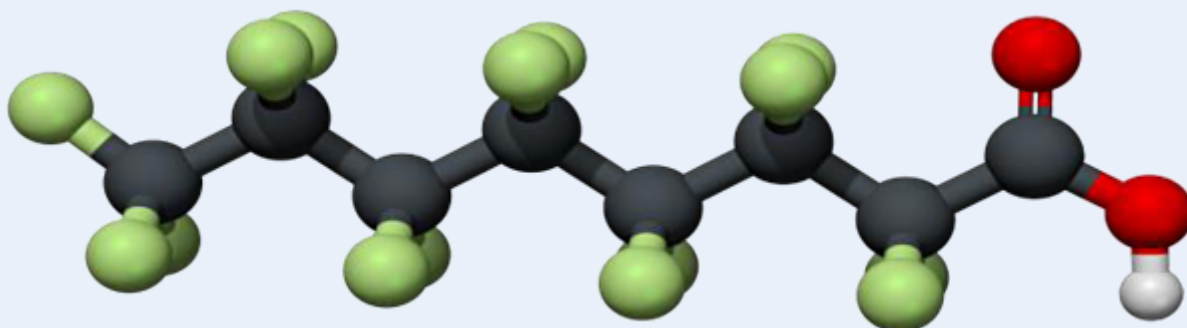


2.2 Chemistry, Terminology, and Acronyms

This section focuses on chemistry, terminology, names, and acronyms for those PFAS most commonly reported in the environment, identified in scientific literature, and those PFAS most commonly tested for by current analytical methods. Other important classes of PFAS are introduced. This section also introduces the chemical manufacturing processes that influence the types of PFAS that are found in the environment.

General Concepts of Organofluorine Chemistry for PFAS

Organofluorine Chemistry: A branch of organic chemistry involving organic molecules with a carbon-fluorine bond. Organofluorine molecules have many commercial uses. They include PFAS, such as PFOA, shown below:



EXAMPLE: 3D model of a PFOA (perfluorooctanoic acid) molecule, in its acid form.

Source: Manuel Almagro Rivas (Own work using: Avogadro, Discovery Studio, GIMP) [CC BY-SA 4.0] (<https://creativecommons.org/licenses/by-sa/4.0/>), via Wikimedia Commons.

<https://commons.wikimedia.org/wiki/File:PFOA-3D.png>

Gray spheres represent carbon atoms linked together in a chain; there are eight of them, so “octane” is used in the name. Green spheres represent fluorine atoms bonded to carbon atoms. Red spheres represent oxygen atoms. White sphere represents a hydrogen atom that dissolves away in water, which makes this an acid. Fluorine atoms are attached to all possible bonding sites, making this **per**fluorinated. If some of the fluorine atoms were replaced by other atoms (such as oxygen or hydrogen), it would be **poly**fluorinated. Without the hydrogen, the “head end” takes on a negative charge and can bond to things through electrostatic attraction. The fluorine “tail end” is strong and stable, giving it lipid- and water-repelling properties, but also making it persistent in the environment.

Isomer: A molecule with the same molecular formula as another molecule, but with a different chemical structure. Isomers contain the same number of atoms of each element, but have different arrangements of their atoms. See [Figure 2-13](#) for an example; linear and branched PFOS contain the same number of carbon, fluorine, oxygen, and sulfur atoms, but these atoms are arranged differently depending on whether it is a linear or branched isomer of PFOS.

Homologue Groups and Homologous Series: A group of organic compounds, usually listed in order of increasing size, that has a similar structure (and therefore also similar properties) and whose structures differ only by the number of carbon atoms in the chain. For example, all of the linear and branched isomers of PFOS would be in the C₈ homologue group, while all of the linear and branched isomers of perfluorohexane sulfonic acid (PFHxS) would be in the C₆ homologue group. The C₄-C₁₂ PFASs are a homologous series of perfluorosulfonates.

2.2.1 Naming Convention Considerations

There is confusion among the environmental community and the public due to overgeneralization when describing PFAS and the lack of consistent naming of specific PFAS. The use of consistent naming conventions would reduce confusion and support clearer communication ([Buck et al. 2011](#)) ([Wang, DeWitt, et al. 2017](#)).

“PFAS,” not “PFASs”: The acronym “PFAS” stands for “per- and polyfluoroalkyl substances.” No single chemical within the PFAS class can be both perfluorinated and polyfluorinated, so by definition “PFAS” is plural and a small “s” is not needed. Some authors elect to add a small “s” to this acronym (PFASs) to emphasize the fact that it is plural, but it is not needed. When referring to a single chemical within the PFAS class, it is more accurate to simply name that specific chemical.

Consistent naming also helps to distinguish PFAS from other organic compounds that contain fluorine. As defined in the literature, PFAS include only fluorinated aliphatic (carbon chain) substances. PFAS do not include fluorinated compounds that contain aromatic (carbon ring) features in their structures (for example, active pharmaceutical ingredients, crop protection agents, or chlorofluorocarbons (refrigerants)). This definition distinguishes PFAS from the more generic term “PFC,” which can include aromatic compounds.

The use of nonspecific acronyms, such as perfluorinated compound (PFC), has hampered clarity of investigative results. The acronym “PFC” is poorly defined in the scientific literature, but typically refers to “perfluorinated compounds.” It does not include “polyfluorinated substances,” which are increasingly recognized as important contaminants at many PFAS sites.

In the future, it may be necessary to expand the current naming conventions and acronym approaches to ensure that standardized naming is available for additional members of the PFAS family of compounds. Buck et al. (2011) is an open-access paper that provides a more detailed explanation of PFAS terminology, classification, and origins, and recommends specific and descriptive terminology, names, and acronyms for PFAS.

CAS numbers are another helpful tool for clearly identifying the chemical that is being referenced; however, care must be taken in selecting the correct CAS number to avoid confusion regarding the chemistry and behavior of the chemical being described. Some PFAS may occur in various ionic states, such as acids, anions (negatively charged), cations (positively charged), and zwitterions (both positively and negatively charged dipolar molecules), and each has its own CAS number (and some have no CAS number). The ionic state determines electrical charge and physical and chemical properties, which in turn control fate and transport in the environment and potential human health and ecological effects. The ionic state of individual PFAS can result in significantly different physical and chemical properties, such as solubility, volatility, and bioaccumulative potential.

Chemicals in the PFAS family can exist in various ionic states (for example, acids, anions, cations), which have important implications for their chemical and physical properties. In most cases for PFAAs, this section uses the anionic form of a given PFAS name, as this is the state in which most PFAAs exist in the environment.

2.2.2 Introduction to the PFAS Family

PFAS encompass a wide universe of substances with very different physical and chemical properties ([Section 4](#)), including gases (for example, perfluorobutane), liquids (for example, fluorotelomer alcohols), and solid material high-molecular weight polymers (for example, PTFE). For this reason, it is helpful to group PFAS that share similar chemical and physical properties.

As shown in [Figure 2-2](#), the PFAS family may be divided into two primary classes: polymers and nonpolymers. Each class may contain many subclasses, groups, and subgroups, some of which are shown in the figure. This document focuses primarily on those nonpolymer PFAS most commonly detected in the environment and those PFAS that may be significant as “precursors” that can transform to more persistent forms.

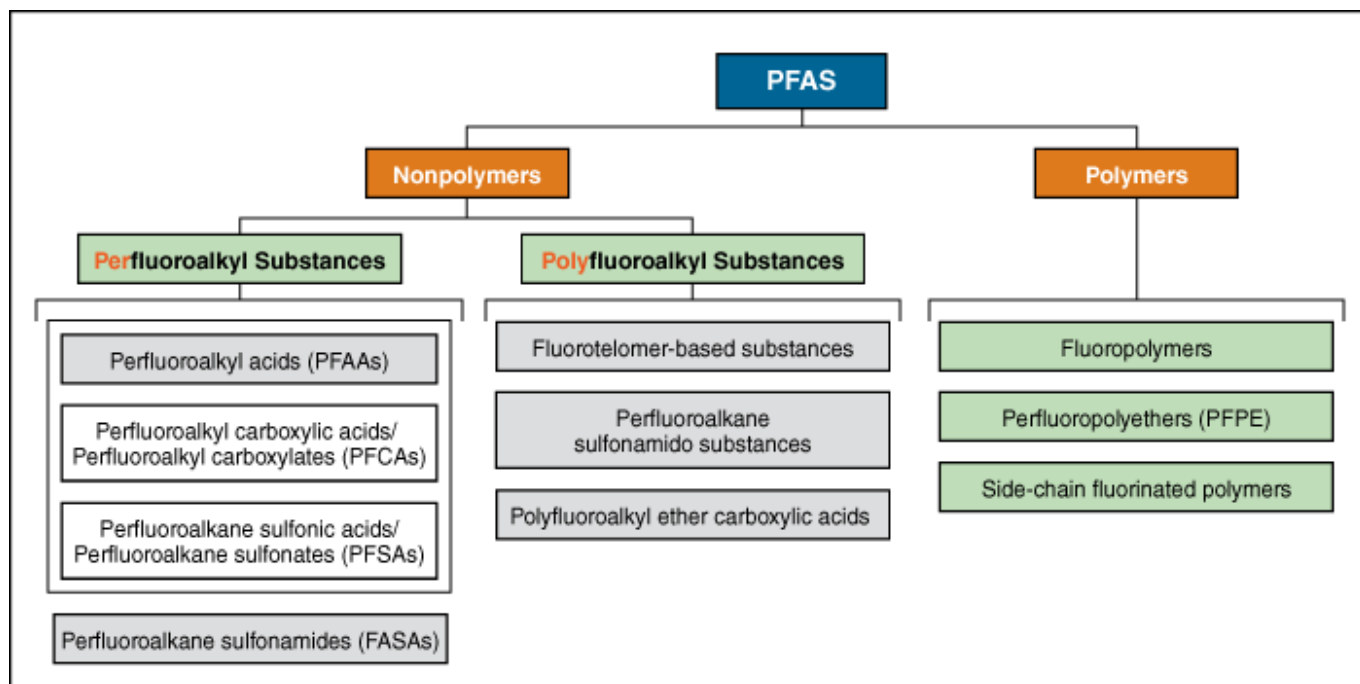


Figure 2-2. The PFAS family.

The family tree is further expanded in [Figure 2-3](#), based on nomenclature provided in [Buck et al. \(2011\)](#), Organisation for Economic Co-operation and Development [OECD \(2015b\)](#), and [Wang, DeWitt, et al. \(2017\)](#), with further introduction to some of these chemicals provided later in this section.

Future updates to the family tree and nomenclature are expected to be necessary given the evolving public knowledge of these compounds. For example, other PFAS without analytical standards are being identified using nontarget analyses by research laboratories ([Section 11](#)). These PFAS do not necessarily have an associated CAS number but are being identified by molecular structure.

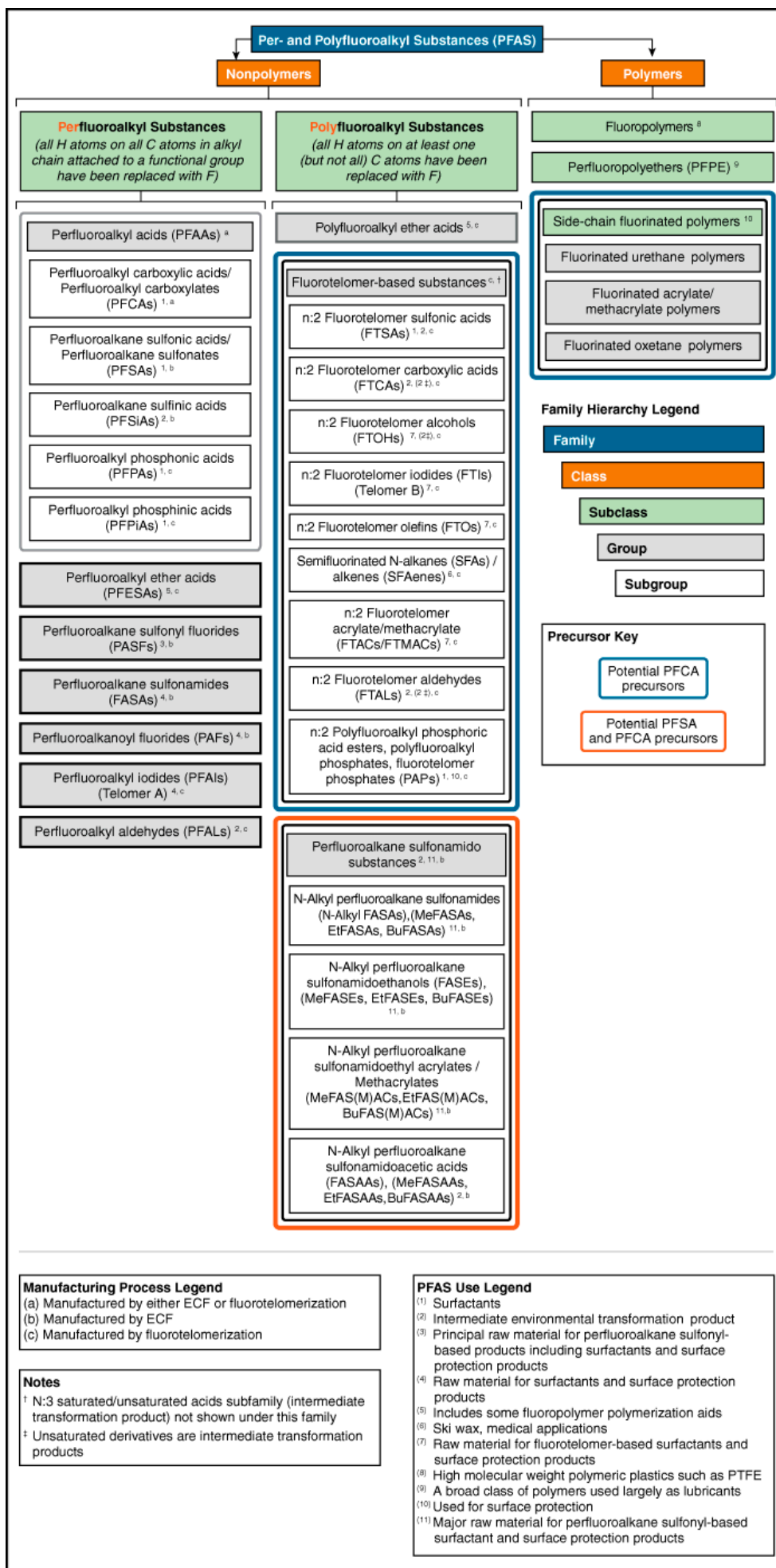


Figure 2-3. PFAS family tree.

Adapted from a graphic provided courtesy of Paul Caprio, EA Engineering.

A stand-alone [PDF version of Figure 2-3](#) is available.

2.2.2.1 Polymer PFAS

Polymers are large molecules formed by combining many identical smaller molecules (or monomers (which are shorter chain molecules with no repeating units)) in a repeating pattern. Oligomers are smaller polymers, with relatively fewer repeating units.

The PFAS polymer class includes fluoropolymers, perfluoropolyethers, and side-chain fluorinated polymers ([Henry et al. 2018](#); [Buck et al. 2011](#); [Wang, Cousins, et al. 2013](#)):

- Fluoropolymers contain a carbon-only polymer backbone with fluorines directly attached to the carbon. Fluoropolymers include polymers like PTFE, ETFE, copolymer FEP, and PFA, which were historically made using ammonium perfluorooctanoate (APFO) or sodium perfluorooctanoate (NaPFO), which are salts of perfluorooctanoate (PFOA). Fluoropolymers also include polyvinylidene fluoride (PVDF), which was historically made using ammonium perfluoronanoate (APFN), the ammonium salt of perfluoronanoate (PFNA) ([OECD 2015b](#)), ([Buck et al. 2011](#)).
- The specific fluoropolymers PTFE, FEP, ETFE, and PFA have been referred to as “polymers of low concern” because they have high molecular weight and are extremely stable. PTFE has been demonstrated to not be bioavailable (Henry et al. 2018). Based on this, Henry et al. (2018) suggest polymers of low concern should be considered separately from other PFAS when evaluating risk. Polymers of low concern are reported to pose little environmental or health risk once in a consumer product.
- Perfluoropolyethers (PFPE) contain a carbon and oxygen polymer backbone with fluorines directly attached to carbon. Relatively little is known about these chemicals in the environment.
- Side-chain fluorinated polymers contain a nonfluorinated polymer backbone, off of which fluorinated side chains branch. These PFAS include fluorinated urethane polymers, fluorinated acrylate/methacrylate polymers, and fluorinated oxetane polymers. Some side-chain fluorinated polymers may become precursors for PFAAs, [Section 2.2.3.1](#), when the point of connection of a fluorinated side chain on a polymer is broken to release a PFAA.

During the manufacture and manufacturing uses of some fluoropolymers, controls are necessary to mitigate potential releases of nonpolymer PFAS. Nonpolymer PFAS may be used as processing aids in the manufacture of some fluoropolymer PFAS, and may be found as impurities in some fluoropolymer products, and due to potential degradation of some fluoropolymers ([3M Company 1999b](#); [CalEPA 2018](#); [Washington et al. 2018](#)), see also [Section 5.4.5](#).

2.2.2.2 Nonpolymer PFAS

Nonpolymer PFAS encompass two major subclasses: **perfluoroalkyl substances** and **polyfluoroalkyl substances**, which include many groups and subgroups of chemicals. [Figure 2-4](#) provides general classification and chemical structures, examples of each group, and examples of the primary uses of the nonpolymer PFAS highlighted in [Figure 2-2](#) and [Figure 2-3](#).

Nonpolymer PFAS were selected as the focus of this document because:

- they are the PFAS most commonly detected (to date) in humans, biota, and other environmental media and appear to be relatively more abundant at PFAS investigation sites ([Section 6](#))
- data may be available regarding potential human health and ecological effects from environmental exposure for some of these chemicals ([Section 7](#))
- state or federal standards or guidance values may exist for some of these chemicals ([Section 8](#))
- they are included in most laboratory PFAS analyte lists ([Section 11](#)).

Nonpolymers

Perfluoroalkyl Substances

Perfluoroalkyl acids (PFAAs)

Perfluoroalkyl carboxylic acids/ Perfluoroalkyl carboxylates (PFCAs)

Example	Chemical Structure	Uses
Perfluorooctanoic acid (PFOA)	$C_7F_{15}COOH$	Surfactant
Perfluorooctanoate (PFOA)	$C_7F_{15}CO_2^-$	Surfactant

Perfluoroalkane sulfonic acids (PFSAs)/ Perfluoroalkane sulfonates (PFSAs)

Example	Chemical Structure	Uses
Perfluorooctane sulfonic acid (PFOS)	$C_8F_{17}SO_3H$	Surfactant
Perfluorooctane sulfonate (PFOS)	$C_8F_{17}SO_3^-$	Surfactant

Perfluoroalkyl ether carboxylic acids (PFECAs)

Example	Chemical Structure	Uses
Hexafluoropropylene oxide dimer acid (HFPO-DA)	$CF_3CF_2CF_2OCF_2COOH$	Surfactant

Perfluoroalkane sulfonamides (FASAs)

Example	Chemical Structure	Uses
Perfluorooctane sulfonamide (FOSA)	$C_8F_{17}SO_2NH_2$	Major raw material for surfactant and surface protection products

Polyfluoroalkyl Substances

Polyfluoroalkyl ether carboxylic acids

Example	Chemical Structure	Uses
4,8-dioxa-3H-perfluorononanoic acid (ADONA)	$CF_3OCF_2CF_2CF_2-OCHFCF_2COOH$	Surfactant

Fluorotelomer-based substances

n:2 Fluorotelomer alcohols (FTOHs)

Example	Chemical Structure	Uses
10:2 Fluorotelomer alcohol	$C_{10}F_{21}CH_2CH_2OH$	Major raw material for surfactant and surface protection products

n 2: Fluorotelomer carboxylic acids (FTCAs)

Example	Chemical Structure	Uses
8:2 Fluorotelomer carboxylic acid (8:2 FTSA)	$C_8F_{17}CH_2COOH$	Surfactant and environmental transformation products

n:2 Fluorotelomer sulfonic acids (FTSAs)

Example	Chemical Structure	Uses
8:2 Fluorotelomer sulfonic acid (8:2 FTSA)	$C_8F_{17}CH_2CH_2SO_3H$	Surfactant and environmental transformation products

Perfluoroalkane sulfonamido substances

N-Alkyl perfluoroalkane sulfonamides (FASAs), (MeFASAs, EtFASAs, BuFASAs)

Example	Chemical Structure	Uses
N-Ethyl perfluorooctane sulfonamide (nEtFOSA)	$C_8F_{17}SO_2N(C_2H_5)H$	Major raw material for surfactant and surface protection products

N-Alkyl perfluoroalkane sulfonamidoethanols (FASEs), (MeFASEs, EtFASEs, BuFASEs)

Example	Chemical Structure	Uses
N-Ethyl perfluorooctane sulfonamidoethanol (nEtFOSE)	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	Major raw material for surfactant and surface protection products

N-Alkyl perfluoroalkane sulfonamido acetic acids (FASAAAs), (MeFASAAAs, EtFASAAAs, BuFASAAAs)

Example	Chemical Structure	Uses
N-Ethyl perfluorooctane sulfonamido acetic acid (nEtFOSAA)	$C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$	Intermediate environmental transformation product

Figure 2-4. Nonpolymer PFAS subclasses discussed in this document.

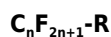
Source: Adapted with permission from Buck, R.C., J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voigt, A. A. Jensen, K. Kannan, S. A. Mabury, and S. P. van Leeuwenet. 2011. "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins." *Integrated Environmental Assessment and Management*, 7:513-541. Open access. Copyright 2011 SETAC. <http://dx.doi.org/10.1002/ieam.258>

2.2.3 Perfluoroalkyl Substances

Perfluoroalkyl substances are fully fluorinated alkane molecules that include (but are not limited to):

- perfluoroalkyl acids (PFAAs) and
- perfluoroalkane sulfonamides (FASAs).

The basic chemical structure is a chain (or *tail*) of two or more carbon atoms with a charged functional group (or *head*) attached at one end. The functional groups commonly are carboxylates or sulfonates, but other forms are also detected in the environment. Fluorine atoms are attached to all possible bonding sites along the carbon chain of the tail, except for one bonding site on the last carbon where the functional group head is attached. This structure, which is illustrated in [Figure 2-5](#) for PFOS and PFOA, can be written as:



where " C_nF_{2n+1} " defines the length of the perfluoroalkyl chain tail, " n " is ≥ 2 , and " R " represents the attached functional group head. Note that the functional group may contain one or more carbon atoms, which are included in the total number of carbons when naming the compound.

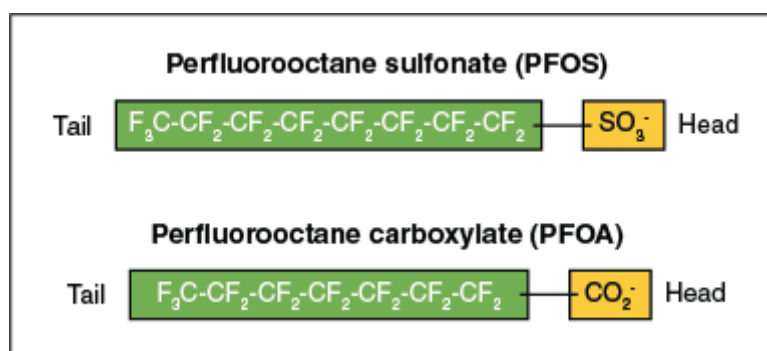


Figure 2-5. The tail and head structure of PFOS and PFOA molecules.

2.2.3.1 Perfluoroalkyl Acids (PFAAs)

PFAAs are some of the least complex PFAS molecules. They are essentially non-degradable under normal environmental conditions. Biotic and abiotic degradation of many polyfluoroalkyl substances may result in the formation of PFAAs. As a result, PFAAs are sometimes referred to as "terminal PFAS" or "terminal degradation products," meaning no further degradation products will form from them under environmental conditions. Polyfluoroalkyl substances that degrade to create terminal PFAAs are referred to as "**precursors**." Longer chain PFAAs do not degrade to shorter chain PFAAs.

The PFAA group is divided into two major subgroups (as shown in [Table 2-1](#) and [Figure 2-3](#)).

- **Perfluoroalkyl carboxylic acids** (PFCAs), or perfluoroalkyl carboxylates, are used commercially and can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as FTOHs. An example PFCA is PFOA.
- **Perfluoroalkane sulfonic acids** (PFSAs), or perfluoroalkyl sulfonates, also are used commercially and can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as perfluoroalkyl sulfonamide ethanols (PFOSEs). An example PFSA is PFOS.

Other subgroups of PFAAs are introduced in [Section 2.2.3.3](#). Some of those are compounds that are receiving increasing

attention, are being added to commercial laboratory target analyte lists, and are being detected in the environment.

PFAAs are the group of PFAS that make up the majority of PFAS typically included in commercial laboratory target analyte lists and are the primary PFAS for which federal or state health-based guidance values have been established. As a result, PFAAs tend to drive site investigation and remediation decisions, so it is helpful to understand the naming conventions for this class. Many of the commonly detected PFAAs are denoted using the structural shorthand:

PFXY where:

PF = perfluoro

X = the carbon chain length (using the same naming conventions as hydrocarbons based on the number of carbons (for example, *B* for butane or 4 carbons, *Pe* for pentane or 5 carbons)

Y = the functional group (for example, *A* = carboxylate or carboxylic acid and *S* = sulfonate or sulfonic acid)

Table 2-1 illustrates how this naming structure works for the PFCAs and PFSAs, which collectively are referred to as PFAAs.

Table 2-1. Basic naming structure and shorthand for PFAAs

X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = carboxylate or carboxylic acid	PFBA	Perfluorobutanoate ¹	$C_3F_7CO_2^-$	45048-62-2
			Perfluorobutanoic acid ¹	C_3F_7COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$	45187-15-3
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$	45167-47-3
			Perfluoropentanoic acid	C_4F_9COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$	175905-36-9
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$	92612-52-7
			Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$	108427-53-8
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$	120885-29-2
			Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$	146689-46-5
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
			Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1

X	Y	Acronym	Name	Formula	CAS No.
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$	72007-68-2
			Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$	474511-07-4
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	68259-12-1
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	$C_9F_{19}CO_2^-$	73829-36-4
			Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3^-$	126105-34-8
			Perfluorodecane sulfonic acid	$C_{10}F_{21}SO_3H$	335-77-3
Un = undeca (11 carbon)	A = Carboxylate or carboxylic acid	PFUnA or PFUnDA	Perfluoroundecanoate	$C_{10}F_{21}CO_2^-$	196859-54-8
			Perfluoroundecanoic acid	$C_{10}F_{21}COOH$	2058-94-8
	S = Sulfonate or sulfonic acid	PFUnS PFUnDS	Perfluoroundecane sulfonate	$C_{11}F_{23}SO_3^-$	441296-91-9
			Perfluoroundecane sulfonic acid	$C_{11}F_{23}SO_3H$	749786-16-1
DoD = dodeca (12 carbon)	A = Carboxylate or carboxylic acid	PFDoDA	Perfluorododecanoate	$C_{11}F_{23}CO_2^-$	171978-95-3
			Perfluorododecanoic acid	$C_{11}F_{23}COOH$	307-55-1
	S = Sulfonate or sulfonic acid	PFDoDS	Perfluorododecane sulfonate	$C_{12}F_{25}SO_3^-$	343629-43-6
			Perfluorododecane sulfonic acid	$C_{12}F_{25}SO_3H$	79780-39-5
TrD = trideca (13 carbon)	A = Carboxylate or carboxylic acid	PFTrDA	Perfluorotridecanoate	$C_{12}F_{25}CO_2^-$	862374-87-6
			Perfluorotridecanoic acid	$C_{12}F_{25}COOH$	72629-94-8
	S = Sulfonate or sulfonic acid	PFTrDS	Perfluorotridecane sulfonate	$C_{13}F_{27}SO_3^-$	NA
			Perfluorotridecane sulfonic acid	$C_{13}F_{27}SO_3H$	NA
TeD = tetradeca (14 carbon)	A = Carboxylate or carboxylic acid	PFTeDA	Perfluorotetradecanoate	$C_{13}F_{27}CO_2^-$	365971-87-5
			Perfluorotetradecanoic acid	$C_{13}F_{27}COOH$	376-06-7
	S = Sulfonate or sulfonic acid	PFTeDS	Perfluorotetradecane sulfonate	$C_{14}F_{29}SO_3^-$	NA
			Perfluorotetradecane sulfonic acid	$C_{14}F_{29}SO_3H$	NA
NA = not available					
¹ Older nomenclature may use butyrate or butyric acid.					

Note that for PFCAs, the total number of carbons used for naming the compound includes the carbon in the carboxylic acid functional group (COOH). For example, although PFOA has seven carbons in its fluoroalkyl tail, all eight of the carbons in the molecule are used to name it, hence *perfluorooctanoate*. But in terms of chemical behavior, PFOA would be more analogous to seven-carbon perfluoroheptane sulfonate (PFHpS) than to eight-carbon perfluorooctane sulfonate (PFOS).

[Table 2-1](#) shows the PFAA names and formulas in both the anionic (also referred to as “deprotonated” or negatively charged) and acid (also referred to as protonated or neutral) forms. The anionic form is the state in which PFAAs are found in the environment, except in very rare situations (for example, extremely low pH). The anionic and acid forms of PFAA names are often incorrectly used interchangeably (for example, perfluorooctane sulfonate and perfluorooctane sulfonic acid), and the same acronym (in this case, PFOS) applies to both forms. However, as discussed below and in [Section 4](#), their physical and

chemical properties are different, and it is important to know which form is being described.

Until recently, PFCAs and PFSAs have been the subgroups most commonly tested for in the environment; however, a wide range of PFAS with other functional groups exists for which the same “PFXY” shorthand shown above may or may not apply. For naming conventions for these compounds, please refer to [Buck et al. \(2011\)](#).

2.2.3.2 Long-Chain Versus Short-Chain Distinction

PFAS, predominantly PFAAs, are sometimes described as *long-chain* and *short-chain* as a shorthand way to categorize PFCAs and PFSAs that may behave similarly in the environment; however, it is important not to generalize about PFAA behavior based only on chain length. As recent research suggests, other factors besides chain length may affect bioaccumulation potential of PFAS ([Ng and Hungerbühler 2014](#)).

According to the [OECD \(2013\)](#):

- *Long-chain* refers to:
 - PFCAs with eight or more carbons (seven or more carbons are perfluorinated)
 - PFSAs with six or more carbons (six or more carbons are perfluorinated)
- *Short-chain* refers to:
 - PFCAs with seven or fewer carbons (six or fewer carbons are perfluorinated)
 - PFSAs with five or fewer carbons (five or fewer carbons are perfluorinated)

[Table 2-2](#) illustrates the differences in the short-chain and long-chain PFCAs and PFSAs.

Table 2-2. Short-chain and long-chain PFCAs and PFSAs

Number of Carbons	4	5	6	7	8	9	10	11	12
PFCAs	Short-chain PFCAs				Long-chain PFCAs				
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFSAs	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
	Short-chain PFSAs			Long-chain PFSAs					

Anions Versus Acids

As noted above, the names for the anionic and acid forms of PFAAs are often used interchangeably, but it is critical to know which form is being discussed because of differences in their physical and chemical properties and behavior in the environment ([Section 6](#)). Some important things to keep in mind regarding the anionic versus acid forms are:

- Most PFAAs are present in environmental and human matrices in their anionic form. For example, PFOS is present in the environment in the anionic form, perfluorooctane sulfonate.
- Although laboratories may be reporting PFOA or PFOS using the acid form of their name, they are actually measuring the anionic form (for example, perfluorooctanoate or perfluorooctane sulfonate), as this is the form that exists in the environment.
- The acid form and their associated cationic salts have CAS numbers, while the anionic forms may not ([Table 2-1](#)). For example, PFOS can exist as different salts (cationic), including sodium, lithium, potassium, or ammonium. Each of these salts will have a different CAS number:
 - PFOS, acid form CAS No.: 1763-23-1
 - PFOS, potassium salt CAS No.: 2795-39-3
 - PFOS, ammonium salt CAS No.: 29081-56-9
- When the salt or acid exists in water or other liquids, it will dissociate (lose its hydrogen atom), and the salt or acid will break off and form the anion (for example, COO⁻ or SO₃⁻). [Figure 2-6](#) illustrates the dissociation of PFBA.

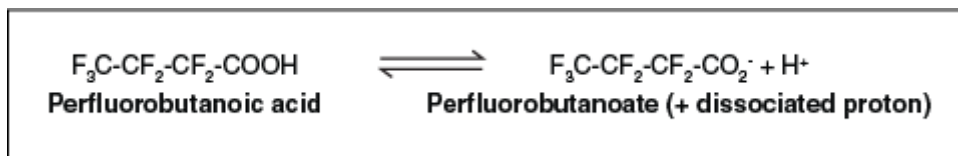


Figure 2-6. Dissociation of PFBA.

- It is most important to distinguish between the acid form and anionic form when reporting the physical and chemical properties. The discussion of PFAS properties in this guidance document generally refers to the anionic form; it will be specifically called out if the acid form is being discussed.

A Note About PFAS Naming in Laboratory Reports (see [Section 11](#))

*Even though PFAAs occur as anions in the environment, some laboratories report all of their results in the acidic form, while others may report PFCAs as acids (for example, **perfluorooctanoic acid**) and PFSAs as anions (for example, **perfluorooctane sulfonate**). Different naming conventions in laboratory reports have led to confusion regarding exactly which form of the PFAA the labs are measuring. Although the lab is measuring the concentration of PFAA anions present in the sample, where the results are reported as an acid, the lab has adjusted for the H+ cation (which has so little mass, this does not affect the resulting concentration). It should be noted that the standards used by laboratories to perform analyses may be prepared from PFAA salts, as is often the case for sulfonate standards. If so, the lab must adjust the reported concentration to account for the mass of the counterion (typically Na+ or K+). The calculation to do this is described in Section 7.2.3 of EPA Method 537 ([Shoemaker, Grimmitt, and Boutin 2009](#)).*

2.2.3.3 Other PFAAs

Other PFAAs include:

- perfluoroalkyl sulfinic acids (PFSiAs), associated with the electrochemical fluorination (ECF) process and also occur as intermediate environmental transformation products
- perfluoroalkyl phosphonic acids (PFPAs) and phosphinic acids (PFPIAs), associated with the fluorotelomerization process and used as surfactants

2.2.3.4 Perfluoroalkane Sulfonamides (FASAs)

FASAs, such as perfluorooctane sulfonamide (FOSA), are used as raw material in the ECF process to make perfluoroalkyl sulfonamide substances that are used for surfactants and surface treatments. FASAs can degrade to form PFAAs such as PFOS.

2.2.3.5 Other Perfluoroalkyl Substances

Other perfluoroalkyl substances shown on [Figure 2-3](#) include:

- perfluoroalkane sulfonyl fluorides [PASFs, such as perfluorooctane sulfonyl fluoride (POSF) and perfluorobutane sulfonyl fluoride (PBSF)], and perfluoroalkanoyl fluorides (PAFs), associated with the ECF process
- perfluoroalkyl iodides (PFAIs) and perfluoroalkane aldehydes (PFALs), associated with the fluorotelomerization process
- perfluoroalkyl ether carboxylic acids (PFECAs) and perfluoroalkyl ether sulfonic acids (PFESAs)

As discussed in [Section 2.4](#), some PFECAs have been developed or used as replacements for other PFAS that are phased out of production and use. This includes GenX chemicals (see text box). Other emerging fluorinated replacement PFECAs more recently detected in the environment, such as perfluoro-2-methoxyacetic acid (PFMOAA), are described in [Sun et al. \(2016\)](#).

GenX Chemicals

A PFCEA, commonly referred to by the trade name “GenX,” has been used by one manufacturer as a replacement for APFO (PFOA) as a surfactant and polymerization aid in the production of their PTFE product. GenX actually refers to the GenX processing aid technology, while the major chemicals used include:

- hexafluoropropylene oxide (HFPO) dimer acid (HFPO-DA, CAS No. 13252-13-6, also known as 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid [PFPrOPrA] or FRD-903) and
- its ammonium salt (ammonium, 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate [$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COO}^-\text{NH}_4^+$, CAS No. 62037-80-3, also known as FRD -902]) ([Wang, Cousins, et al. 2013](#)) ([Buck 2015](#)) ([USEPA 2018d](#)).

Prior to their use in PTFE production, GenX chemicals were produced as a byproduct of other manufacturing processes ([NC DEQ 2018](#)). HFPO also is used to manufacture other HFPO-DA derivatives, fluoropolymers (including polyethers), and other specialty agrochemical, semiconductor, and pharmaceutical applications ([ATSDR 2018e](#)). HFPO-trimer acid and longer polymer fluorides can be formed from reaction of HFPO-DA.

Further discussion of the GenX chemicals is provided in [Section 2.4.6](#). The chemical structure of the ammonium salt is shown in [Figure 2-7](#).

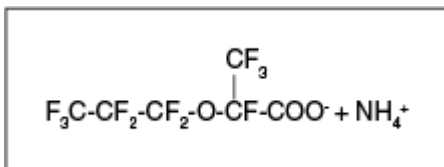


Figure 2-7. Example replacement chemistry structure for GenX Ammonium Salt.

2.2.4 Polyfluoroalkyl Substances

Polyfluoroalkyl substances and some side-chain fluorinated polymers are increasingly being identified as important to understanding the occurrence, fate, and transport of PFAS at release sites and in the environment ([OECD 2013](#)) ([Butt, Muir, and Mabury 2014](#)) ([Liu and Mejia Avendaño 2013](#)) ([Wang et al. 2011](#)) ([Mejia-Avendaño et al. 2016](#)). [Figure 2-2](#) and [Figure 2-3](#) highlight the groups of polyfluoroalkyl substances that, to date, have most commonly been detected at PFAS sites (see [Barzen-Hanson et al. 2017](#)). ([OECD 2018](#)) indicates that of the approximately 4,700 PFAS identified in that study, about 90% were potential precursors to PFAAs.

Polyfluoroalkyl substances are distinguished from perfluoroalkyl substances by not being fully fluorinated. Instead, they have a nonfluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain tail are fully fluorinated ([Figure 2-4](#)).

The carbon-hydrogen (or other nonfluorinated) bond in polyfluoroalkyl molecules creates a “weak” point in the carbon chain that may be susceptible to biotic or abiotic degradation. As a result, many polyfluoroalkyl substances that contain a perfluoroalkyl $\text{C}_n\text{F}_{2n+1}$ group are potential precursor compounds that have the potential to be transformed into PFAAs.

[Figure 2-8](#) provides examples of degradation pathways for environmentally relevant polyfluoroalkyl precursors derived from two PFAS production methods, fluorotelomerization and ECF, respectively ([Buck et al. 2011](#); [Liu and Mejia Avendaño 2013](#); [Butt, Muir, and Mabury 2014](#)). Note that these figures include some PFAS not discussed in this guidance document, but described in [Buck et al. \(2011\)](#). Refer to [Section 5.4](#), for further information on transformation processes, noting that not all degradation products will be formed through every environmental transformation process.

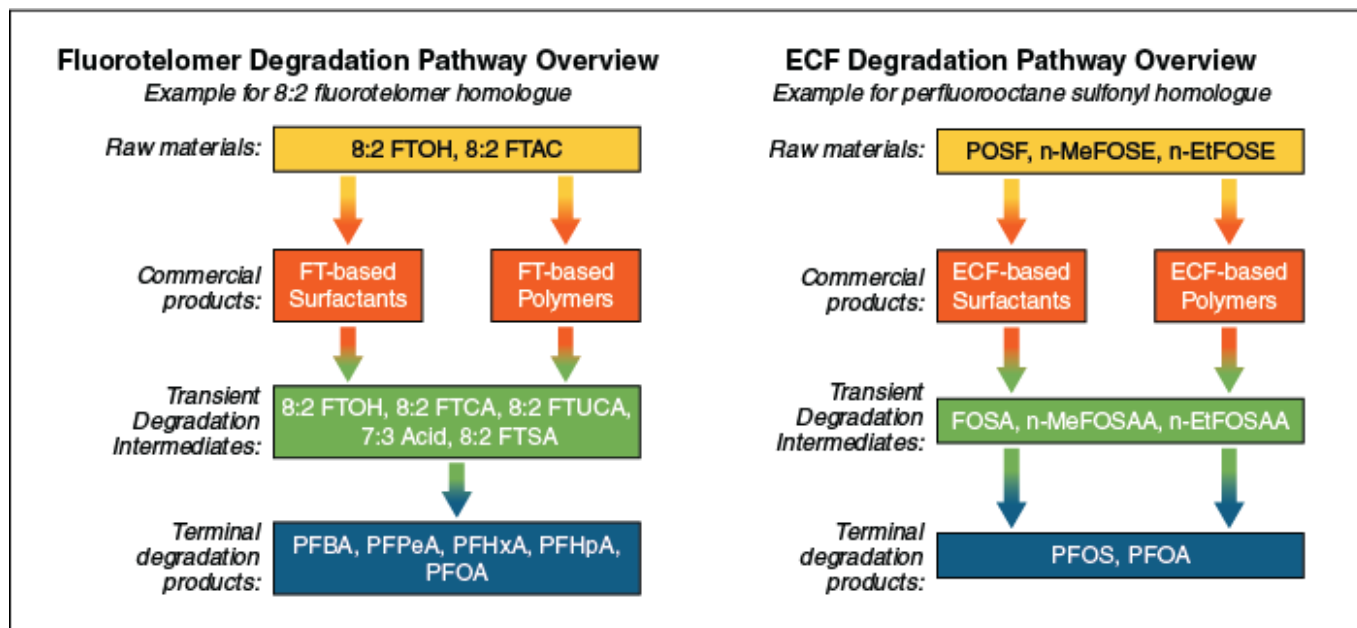


Figure 2-8. Example polyfluoroalkyl substance degradation pathways.

(Note that degradation of POSF-based products is for the terrestrial environment, but transformation into lower homologues of PFCAs and PFSAs in the atmosphere is also possible.)

2.2.4.1 Fluorotelomer Substances

Fluorotelomer substances are polyfluoroalkyl substances produced by the fluorotelomerization process. As shown in Figure 2-8, the degradation of fluorotelomer-based substances is a potential source of PFCAs in the environment, but not PFSAs (Buck et al. 2011).

Fluorotelomer-based polyfluoroalkyl substances are named using an “n:x” prefix where “n” indicates the number of fully fluorinated carbon atoms ($n \geq 2$) and “x” indicates the number of carbon atoms that are not fully fluorinated ($x \geq 1$). An example of a polyfluoroalkyl substance is shown in Figure 2-9, which also illustrates the “n:x” naming convention.

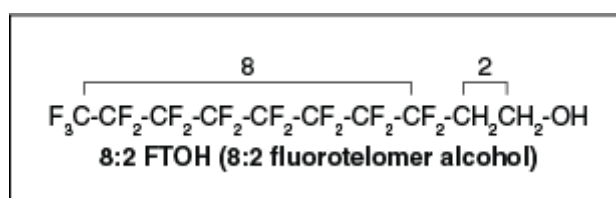


Figure 2-9. Example of a polyfluoroalkyl substance.

The following fluorotelomer substances are those most commonly detected in the environment to date (Section 6):

- *Fluorotelomer alcohols* (FTOH): The n:2 fluorotelomer alcohols (n:2 FTOHs) are key raw materials in the production of n:2 fluorotelomer acrylates and n:2 fluorotelomer methacrylates (Buck et al. 2011).
- *Fluorotelomer sulfonic acids* (FTSA): The n:2 fluorotelomer sulfonic acids (n:2 FTSA) have been detected in environmental matrices at sites where aqueous film-forming foam (AFFF) has been used, and also in wastewater treatment plant effluents and landfill leachate. FTSA are precursor compounds and can undergo aerobic biotransformation to form PFCAs (Buck et al. 2011).
- *Fluorotelomer carboxylic acids* (FTCA): These compounds form through the biodegradation of FTOHs (Figure 2-8; (Buck et al. 2011; Liu and Mejia Avendaño 2013) and have been detected in landfill leachate. Note that the -COOH functional group on these fluorotelomer compounds means they may have either an even or odd number of carbons, so they may have n:2 or n:3 prefixes.

2.2.4.2 Perfluoroalkane Sulfonamido Substances

The subgroups of perfluoroalkane sulfonamido substances shown in [Figure 2-3](#) and discussed below have been detected in the environment and humans (Buck et al. 2011). Perfluoroalkane refers to the fully fluorinated carbon chain tail, but these compounds also contain one or more CH₂ groups in the head of the molecule attached to the sulfonamido spacer ([Figure 2-10](#)). They are either used as raw materials for surfactant and surface treatment products, or they are present as intermediate transformation products of these raw materials. As shown in the degradation pathways in [Figure 2-8](#), some perfluoroalkane sulfonamido substances have been found to degrade to PFOS ([Mejia Avendaño and Liu 2015](#)). Environmentally relevant perfluoroalkane sulfonamido substances include:

- *N-Alkyl perfluoroalkane sulfonamides* (N-alkyl FASAs) are intermediate environmental transformation products that include N-methyl perfluorooctane sulfonamide (MeFOSA) and N-ethyl perfluorooctane sulfonamide (nEtFOSA).
- *Perfluoroalkane sulfonamido ethanols* (FASEs) and *N-alkyl perfluoroalkane sulfonamido ethanols* (MeFASEs, EtFASEs, BuFASEs) are raw materials for surfactant and surface treatment products ([Buck et al. 2011](#)). [Figure 2-10](#) illustrates the structure of nEtFOSE
- *Perfluoroalkane sulfonamido acetic acids* (FASAAs) and *N-alkyl perfluoroalkane sulfonamido acetic acids* (MeFASAAs, EtFASAAs, BuFASAAs) are intermediate transformation products of FASEs, MeFASEs, EtFASEs, and BuFASEs ([Figure 2-8](#)) ([Buck et al. 2011](#)).

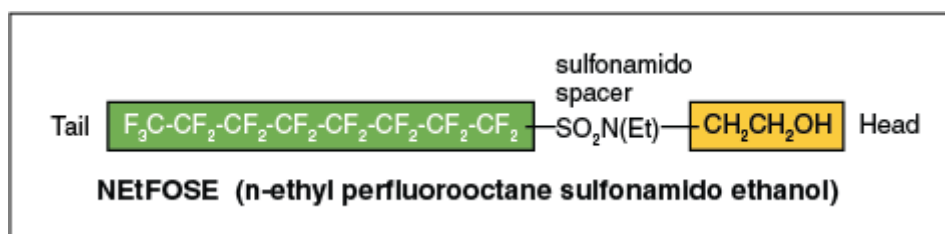


Figure 2-10. Example of a perfluoroalkane sulfonamido ethanol (FASE).

2.2.4.3 Other Polyfluoroalkyl Substances

Other polyfluoroalkyl substances shown in [Figure 2-3](#) include:

- polyfluoroalkyl ether sulfonic acids (PFESAs)
- polyfluoroalkyl ether carboxylic acids
- other fluorotelomer (FT)-based substances.

As discussed in [Section 2.4.6](#), some PFAS have been developed or used as replacements for other PFAS that are phased out of use and production.

One replacement compound for the use of PFOA as a polymerization aid in the production of PTFE is a polyfluoroether carboxylate surfactant: ammonium 4,8-dioxa-3H-perfluorononanoate ($CF_3OCF_2CF_2CF_2-OCHF_2COO^-NH_4^+$ (CAS No. 958445-44-8), commonly referred to by the trade name ADONA ([Gordon 2011](#)). The chemical structure is shown in [Figure 2-11](#).

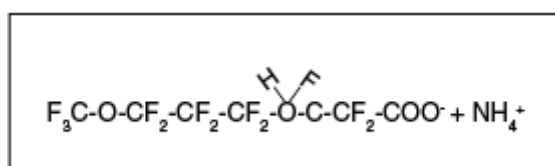


Figure 2-11. Chemical structure for ADONA.

Other replacement polymerization compounds for the manufacture of PTFE and polyvinylidene fluoride (PVDF) include cyclic or polymeric functionalized perfluoropolyethers (PFPEs) ([Wang, Cousins, et al. 2013](#)). A sample chemical structure is shown

in [Figure 2-12](#).

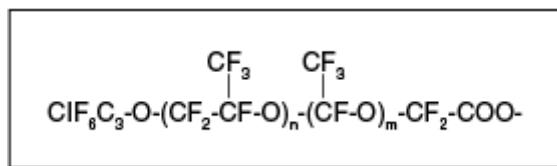


Figure 2-12. Sample chemical structure for a PFPE.

2.2.5 Chemical Manufacturing

To differentiate among PFAS in understanding a conceptual site model for environmental risk assessment, it is important to know about the chemical manufacturing processes. The various manufacturing processes produce different types of PFAS, such as linear and branched isomers (as discussed in this section), which may affect the environmental fate, treatment, toxicology, and site forensics for these chemicals. The type of PFAS that might be formed by the transformation of precursor PFAS at or related to an environmental release site also may depend on the manufacturing process (refer to the family tree in [Figure 2-3](#)).

2.2.5.1 Processes

Two major processes, *electrochemical fluorination (ECF)* and *fluorotelomerization*, have been (and are) used to manufacture PFAS substances that contain perfluoroalkyl chains: side-chain fluorinated polymers, perfluoroalkyl acids and polyfluoroalkyl surfactants ([USEPA 2003b](#)) ([Benskin, DeSilva, and Martin 2010](#)) ([KEMI 2015b](#)) ([OECD 2018](#)). The fluorotelomerization process may also be characterized as “oligomerization,” as it involves using tetrafluoroethylene (TFE) monomer and adding one to nine TFE monomers to form a perfluoroalkyl chain ([Kissa 2001](#); [Rao and Baker 1994](#)). ECF and telomerization can be used to create some of the same PFAS, as shown on [Figure 2-3](#). PFSAs are produced only using the ECF process, whereas PFCAs can be produced by both ECF and telomerization ([USEPA 2003b](#)) ([CONCAWE 2016](#)).

More than 600 intermediate processes have been used to further produce certain PFAS and the associated final products. Further discussion of the intermediate processes may be found in the general scientific literature and numerous textbooks specifically written about fluorinated organics and fluoropolymers ([Banks, Smart, and Tatlow 1994](#)).

Electrochemical Fluorination (ECF)

The Simons ECF process was licensed by 3M in 1945; 3M subsequently built an ECF pilot in 1949 and started commercial production in 1951 ([3M Company 1999a](#)). In the ECF process, an electric current is passed through a solution of an organic feedstock and liquid anhydrous hydrogen fluoride, which causes the hydrogen atoms to be replaced by fluorine atoms, thereby creating carbon-fluorine bonds ([3M Company 1999a](#); [USEPA 2003b](#); [Buck et al. 2011](#)). ECF is used to create perfluoroalkane sulfonyl fluorides (PASFs), which are the building blocks for other sulfonyl-based PFAS, as well as perfluoroalkyl carboxylate derivatives. These ECF-synthesized PFAS can contain a variable mixture of linear and branched perfluorinated isomers, as well as other homologues, byproducts, and impurities (USEPA 2003 #858, Buck et al. 2011). The variable composition is caused by the process conditions, raw materials, and equipment used by the ECF process (3M Company 1999#82, Concawe 2016). Subsequent processes (for example, hydrolysis, base neutralization) are then used to refine the compounds (USEPA 2003#82).

Historically, the ECF process was primarily used to produce POSF-based compounds. This includes PFOS, which is often a terminal degradation product of POSF-based compounds. ECF was also used to produce perfluorooctanyl derivatives (for example, using perfluorooctane carbonyl fluoride to produce PFOA and its salts, such as APFO). As part of the phaseout of production of select long-chain PFAS in the United States, 3M has ceased using ECF to make certain long-chain PFAS, such as POSF-based compounds (PFOS and PFHxS) and PFOA (Buck et al. 2011) ([Section 2.4.1](#)). 3M’s phaseout did not include other, shorter chain PASF-based products, such as those based on PBSF ([3M Company 2018](#)).

Fluorotelomerization

Fluorotelomerization involves the reaction of perfluoroethyl iodide (PFEI, $\text{CF}_3\text{CF}_2\text{-I}$) with tetrafluoroethylene (TFE, $\text{CF}_2=\text{CF}_2$) to yield a mixture of even-numbered carbon linear perfluoroalkyl iodides ($\text{C}_n\text{F}_{2n+1}\text{-I}$, $n = 4, 6, 8, 10$, etc.), commonly known as “Telomer A.” Telomer A is then reacted with ethylene to make “Telomer B” (perfluoroalkylethyl iodides (PFEIs),

$C_nF_{2n+1}CH_2CH_2-I$, $n = 4, 6, 8, 10$, etc.). Telomer B is reacted to make fluorotelomer alcohols (FTOHs, $C_nF_{2n+1}CH_2CH_2-OH$, $n = 4, 6, 8, 10$, etc.) Telomer A, Telomer B, and FTOHs are the basic raw materials used to manufacture fluorotelomer-based surfactant (nonpolymer) and polymer products (Kissa 2001; Rao and Baker 1994).

As part of the USEPA 2010/2015 Stewardship Program (USEPA 2018a) (Section 2.4.3), eight major global fluorotelomer manufacturers phased out production of long-chain (Table 2-2) fluorotelomer-based products that were potential precursors to PFOA and other long-chain perfluorocarboxylic acids (PFCAs). Today, the major global fluorotelomer manufacturers are reported to have refined their processes and predominantly manufacture short-chain (C6) fluorotelomer-based products (www.fluorocouncil.org). Some manufacturers outside of the United States (for example, China, India) have not phased out long-chain PFAS production (Song et al. 2018).

Fluorotelomerization has been primarily used to produce linear (straight-chain) PFAS isomers with an even number of carbon atoms (Buck et al. 2011), although some sources indicate that the process can also produce compounds with an odd number of carbons and branched chains (Lindstrom, Strynar, and Libelo 2011) (Danish EPA 2015).

2.2.5.2 Linear and Branched Isomers of PFAS

Many PFAS may be present as mixtures of linear and branched isomers (Figure 2-13) depending on the manufacturing process that was used. These structural differences are important because they may affect how the compounds behave in the environment and may provide an indicator of their source. Structural differences are described below:

- A *linear isomer* is composed of carbon atoms bonded to only one or two carbons, which form a straight carbon backbone. There can be only one linear isomer in a C_n homologue (compounds with the same number of carbons in their tail) series.
- In a *branched isomer*, at least one carbon atom is bonded to more than two carbon atoms, which forms a branching of the carbon backbone. There can be many isomers per C_n homologue series.

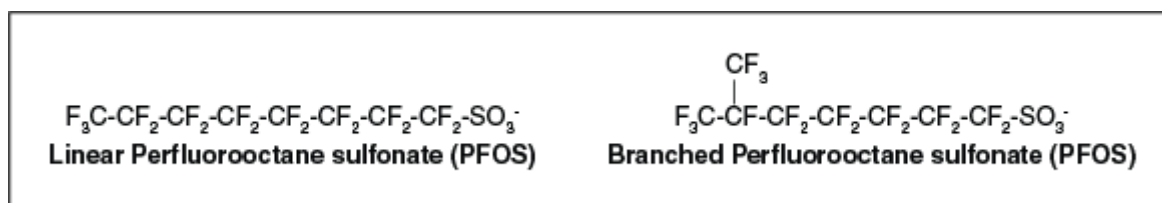


Figure 2-13. Linear and one branched isomer of PFOS.

For simplicity, both linear and branched isomers are abbreviated using the same acronym in this document. Note that other nomenclature conventions further identify PFAS by labeling linear isomers (for example, n-PFOS) and branched isomers based on the location of the branch in the carbon chain (for example, 5m-PFOS) (Benskin, DeSilva, and Martin 2010).

The formula " C_nF_{2n+1} " (where n is greater than or equal to 3) includes linear and branched structures. For example, PFOS and PFHxS are routinely present in environmental samples as a mixture of linear and branched isomers (Beesoon et al. 2011) (Beesoon et al. 2012) (Benskin, DeSilva, and Martin 2010).

Accurate quantification of PFAS that are mixtures of linear isomers and branched isomers in environmental matrices can be difficult (Riddell et al. 2009). However, the relative contributions of isomers may be useful in understanding sources of PFAS and the age of the source, because the production of isomers varies by manufacturing processes. For example, as discussed above, the fluorotelomerization process has been primarily used to produce mostly linear PFAAs, whereas the ECF process produces a mixture of linear and branched PFAA isomers (Table 2-3). Refer to Section 10.3 for more information on PFAS source identification. The presence of linear and branched isomers may also have implications for partitioning, transport, and bioaccumulation (Section 10.5).

Table 2-3. Manufacturing processes and potential PFAAs produced

Manufacturing Process	Commonly Found Polyfluorinated Substance (Precursors)	Potential PFAAs Produced
Fluorotelomerization	FTSA ¹	Linear PFCAs ³
	FTCA ²	Linear PFCAs ³
	FTOH	Linear PFCAs ³
Electrochemical fluorination	FASE	Branched and linear PFCAs Branched and linear PFSAAs
	FASAA	Branched and linear PFCAs Branched and linear PFSAAs
<p>¹Fluorotelomer sulfonate: for example, may be found at AFFF sites</p> <p>²Fluorotelomer carboxylic acids: for example, 5:3 acid may be found in landfill leachate</p> <p>³Under certain instances, can produce mixture of linear and branched PFCAs</p>		

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