

Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins

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ABSTRACT

The primary aim of this article is to provide an overview of perfluoroalkyl and polyfluoroalkyl substances (PFASs) detected in the environment, wildlife, and humans, and recommend clear, specific, and descriptive terminology, names, and acronyms for PFASs. The overarching objective is to unify and harmonize communication on PFASs by offering terminology for use by the global scientific, regulatory, and industrial communities. A particular emphasis is placed on long-chain perfluoroalkyl acids, substances related to the long-chain perfluoroalkyl acids, and substances intended as alternatives to the use of the long-chain perfluoroalkyl acids or their precursors. First, we define PFASs, classify them into various families, and recommend a pragmatic set of common names and acronyms for both the families and their individual members. Terminology related to fluorinated polymers is an important aspect of our classification. Second, we provide a brief description of the 2 main production processes, electrochemical fluorination and telomerization, used for introducing perfluoroalkyl moieties into organic compounds, and we specify the types of byproducts (isomers and homologues) likely to arise in these processes. Third, we show how the principal families of PFASs are interrelated as industrial, environmental, or metabolic precursors or transformation products of one another. We pay particular attention to those PFASs that have the potential to be converted, by abiotic or biotic environmental processes or by human metabolism, into long-chain perfluoroalkyl carboxylic or sulfonic acids, which are currently the focus of regulatory action. The Supplemental Data lists 42 families and subfamilies of PFASs and 268 selected individual compounds, providing recommended names and acronyms, and structural formulas, as well as Chemical Abstracts Service registry numbers. *Integr Environ Assess Manag* 2011;7:513–541. © 2011 SETAC

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INTRODUCTION

“Fluorinated substances” is a general, nonspecific name that describes a universe of organic and inorganic substances that contain at least 1 F atom, with vastly different physical, chemical, and biological properties (Banks et al. 1994). Synonyms include “fluorochemicals” and “fluorinated chemicals.” A subset of fluorinated substances is the highly fluorinated aliphatic substances that contain 1 or more C atoms on which all the H substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety $C_nF_{2n+1}-$. These compounds are hereafter referred to as “perfluoroalkyl and polyfluoroalkyl substances” and denoted by the acronym PFASs, justification for the choice of which is provided below.

Since 1950, PFASs and surfactants and polymers made with the aid of PFASs have been widely used in numerous industrial and commercial applications (Kissa 2001). The C–F bond is extremely strong and stable (Smart 1994). The chemical and thermal stability of a perfluoroalkyl moiety, in addition to its hydrophobic and lipophobic nature, lead to highly useful and enduring properties in surfactants and polymers into which the perfluoroalkyl moiety is incorporated (Kissa 1994, 2001). Polymer applications include textile stain and soil repellents and grease-proof, food-contact paper (Rao and Baker 1994). Surfactant applications that take advantage of the unparalleled aqueous surface tension-lowering properties include processing aids for fluoropolymer manufacture, coatings, and aqueous film-forming foams (AFFFs) used to extinguish fires involving highly flammable liquids (Kissa 1994; Taylor 1999; Kissa 2001). Numerous additional applications have been described (3M Company 1999; Kissa 2001).

As a consequence of the widespread use of PFASs and their resulting emissions, a broad range of these substances have been detected in the environment, wildlife, and humans. The global extent of such contamination was first demonstrated

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for perfluorooctane sulfonic acid, $C_8F_{17}SO_3H$ (PFOS) in wildlife by Giesy and Kannan (2001). (It should be noted that, throughout this article, we refer to all PFASs containing an acid functionality as “acids,” regardless of whether or not they are likely to be highly or completely ionized in environmental or human matrices). At about the same time as the study by Giesy and Kannan, Hansen et al. (2001) discovered that PFOS, perfluorooctanoic acid (PFOA, $C_8F_{17}COOH$), and other PFASs were present in numerous samples of human blood purchased from biological supply companies. This latter study suggested that PFASs were responsible for a substantial fraction of the organic F detected in human serum in earlier pioneering studies on individuals not occupationally exposed to PFASs (e.g., Taves 1968; Belisle 1981). The blood of a group of fluorochemical industry workers had already been confirmed to contain PFOA (Ubel et al. 1980). The relative significance of various human exposure pathways for PFOS, PFOA, and related substances, i.e., via food, food-contact materials, drinking water, breast milk, airborne dust, air, and so forth, is a crucially important question that has been the focus of much research, reviewed recently by D'Hollander et al. (2010). Another important research topic, directly related to exposure of humans and wildlife, is the question of how and how fast PFOS and PFOA, as well as their homologues and precursors, are transported away from their emission sources over long distances in air and/or water (Armitage et al. 2006; Prevedouros et al. 2006; Wallington et al. 2006; Yarwood et al. 2007; Wania 2007; Schenker et al. 2008; Armitage et al. 2009a, 2009b; Stemmler and Lammel 2010).

The global regulatory community is specifically interested in “long-chain” perfluoroalkyl sulfonic acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$, PFASs) and perfluoroalkyl carboxylic acids ($C_nF_{2n+1}COOH$, $n \geq 7$, PFCAs) and their corresponding anions (USEPA 2009; OECD 2011), which have been shown to be more bioaccumulative than their short-chain analogues (Martin et al. 2003a, 2003b; Conder et al. 2008; Olsen et al. 2009). PFOS and PFOA are the 2 “long-chain” perfluoroalkyl acids most often reported and discussed in the scientific literature.

As explained, for example, by Paul et al. (2009) and Prevedouros et al. (2006), the presence of PFOS, PFOA, and similar substances in the environment originates from the industrial use and environmental release of these substances, from use and disposal of consumer products that may contain them as an impurity, and from the abiotic or biotic degradation of larger functional derivatives and polymers that contain a perfluoroalkyl moiety and degrade in the environment to form PFOS, PFOA, and similar substances. These precursor substances are more commonly used commercially and may be released to the environment from industrial raw materials and products and from consumer products and articles.

Concerns about the potential environmental and toxicological impact of long-chain PFASs and PFCAs have led to: 1) the phase-out of production of PFOS and related compounds and PFOA by their major global manufacturer in 2000 to 2002 (3M Company 2000a; USEPA 2000); 2) the conclusion of a stewardship agreement between the US Environmental Protection Agency (USEPA) and 8 leading global companies to reduce emissions and product content of PFOA and related chemicals by 95% by 2010 and to work toward their elimination by 2015 (USEPA 2006b); 3) a similar agreement

between the Canadian environmental and health authorities and 5 companies to restrict PFCAs in products (Environment Canada 2010); 4) a European Union Marketing and Use Directive restricting the use of “perfluorooctane sulfonates” in the European Union (European Parliament 2006b); 5) the inclusion of PFOS in the Stockholm Convention on Persistent Organic Pollutants as an Annex B substance, i.e., restricted in its use (UNEP 2009); and 6) other regulatory and voluntary initiatives intended to reduce environmental emissions of this family of compounds.

The concern over potential environmental and human health impacts of PFASs has led to the launching of several large research programs to elucidate their environmental origin, fate, and impact, funded by various authorities in, for example, the European Union (de Voogt et al. 2006; de Voogt 2009), the United States (USEPA 2010), and Canada (INAC 2009). Moreover, alternative PFASs intended to be replacements for the long-chain PFASs and PFCAs have been developed and implemented in certain cases (Visca et al. 2003; Higuchi et al. 2005; Hintzer et al. 2005; Brothers et al. 2008; Ishikawa et al. 2008; Peschka et al. 2008; Gordon 2011).

Since the first reports revealing the widespread global occurrence of PFOS in wildlife (Giesy and Kannan 2001) and the frequent detection of PFASs in human blood (Hansen et al. 2001) were published a decade ago, the scientific literature on the environmental and toxicological aspects of PFASs has burgeoned rapidly, and the rate of publication currently exceeds 400 articles per year. In the existing body of literature, including governmental reports, authors have created terminology, names, and acronyms to describe these substances. Unfortunately, inconsistencies have inevitably arisen between various groups of authors. In the absence of any concerted effort between scientists to agree on a common terminology to designate the substances, a given compound has often been denoted by a variety of different names and acronyms, or a given acronym has been used to represent different substances. In addition, names to describe broad groups of substances have proliferated that in some instances mistakenly portray substances that are very different from one another as being the same. As a result, the scientific literature for these substances has at times become confusing. There is a need for harmonized terminology, names, and acronyms that clearly and specifically describe PFASs.

OBJECTIVES

The primary aim of this article is to recommend clear, specific, and descriptive terminology, names, and acronyms for PFASs, so as to promote a sound, unified understanding among all players in the PFAS industry, the environmental science related to it, and the bodies responsible for the regulation of chemicals, hence facilitating meaningful communication among all concerned.

A particular emphasis is placed on the long-chain perfluoroalkyl acids, substances related to the long-chain perfluoroalkyl acids, and substances intended as alternatives to the use of the long-chain perfluoroalkyl acids or their precursors. We trust that the terminology, names, and acronyms suggested will be broadly adopted by the “perfluoroalkyl and polyfluoroalkyl substances community” at large, leading to harmonized usage and the avoidance of

misnomers. We have nevertheless refrained from creating an all new nomenclature but have retained—as far as possible—the most popular terms and acronyms used by authors to date. In other words, our proposals result from a pragmatic compromise among textbook and/or International Union for Pure and Applied Chemistry (IUPAC) chemical nomenclature, universal consistency, and frequently adopted “legacy” usage.

It is important to note that the substance terminology, names and acronyms proposed in this article are in no way intended to compete with or supplant IUPAC or Chemical Abstracts Service (CAS) nomenclature. The latter names are the designations of choice when a specific substance needs to be unequivocally identified, e.g., in official regulatory documents. Our intention is to provide terminology, names, and acronyms for pragmatic everyday use within the scientific community. Thus, for example, the IUPAC name for the substance $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{OH}$ is “N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)octane-1-sulfonamide,” but it is more convenient to use the less rigorous but shorter designation “N-ethyl perfluorooctane sulfonamidoethanol” (or the corresponding acronym EtFOSE) for use in publications aimed at specialist readers. Rigor can always be ensured by appending the appropriate CAS Registry Number when each compound is first mentioned in a publication. We encourage this practice and provide CAS numbers for many commonly discussed compounds in the Supplemental Data.

In addition to recommending terminology, names, and acronyms, this article provides a brief review of certain topics useful for understanding the occurrence of and relationships between various families of PFASs in the environment. First, we describe the major commercial processes for synthesizing perfluoroalkyl moieties and the resulting compositions, including formation of isomers and/or homologues of the targeted main products. Second, we present the interrelationships between families of PFASs that may be precursors to or products of one another as a result of abiotic or biotic transformations that may occur under industrial, environmental, or metabolic conditions.

A large number of PFASs have been commercially produced (OECD 2007), and not all are covered here. We have included the main families, individual compounds, and their degradation products that have been detected in environmental and human samples related to long-chain perfluoroalkyl acids, precursors to these substances, and their short-chain fluorinated alternatives. We provide literature references for studies that demonstrate how one family of PFASs may be transformed into another under abiotic or biotic conditions, and/or report the presence of the various families in the environment or humans. Nevertheless, given the vast number of publications on the most common PFASs, such as the perfluoroalkyl sulfonic and carboxylic acids and their anions and salts, the reader is referred to published reviews and extensive surveys for comprehensive literature compilations for these compounds (e.g., Kannan et al. 2004; Houde et al. 2006; Lau et al. 2007; van Leeuwen and de Boer 2007; Jahnke and Berger 2009; Loos et al. 2009; Pistocchi and Loos 2009; Rayne and Forest 2009b; Butt, Berger, et al. 2010; de Voogt 2010; Kwok et al. 2010; Loos et al. 2010; Sturm and Ahrens 2010; Ahrens 2011; Houde et al. 2011). Furthermore, because an emphasis here is on how the various categories of PFASs are interrelated, our citations on transformation

processes and environmental presence often refer to families of substances, so the reader should consult the original publications for details on individual substances.

It should be noted that in this article, the terms “substance,” “compound,” “chemical,” and “species” are used interchangeably for designating a given molecular structure, although it is recognized that in other contexts their meanings may not be identical. For example, in the European REACH legislation (European Parliament 2006a), a “substance” may include impurities and stabilizers in addition to the main constituent.

KEY TERMINOLOGY AND USAGE ASSOCIATED WITH PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES

Perfluoroalkyl and polyfluoroalkyl substances and perfluorocarbons defined

As defined above, PFASs are aliphatic substances containing one or more C atoms on which all the H substituents present in the nonfluorinated analogues from which they are notionally derived have been replaced by F atoms, in such a manner that PFASs contain the perfluoroalkyl moiety $\text{C}_n\text{F}_{2n+1}-$. More explicitly, we recommend that the family of compounds denoted by the acronym PFAS should encompass:

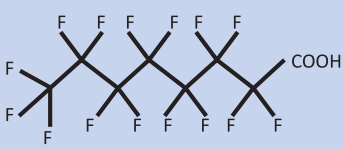
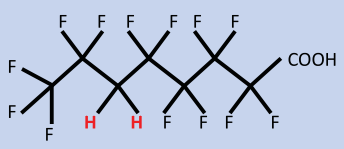
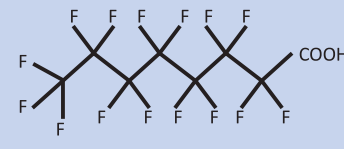
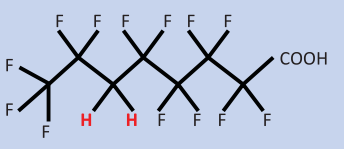
- Perfluoroalkyl substances, which are defined as aliphatic substances for which *all* of the H atoms attached to C atoms in the nonfluorinated substance from which they are notionally derived have been replaced by F atoms, except those H atoms whose substitution would modify the nature of any functional groups present. This usage is consistent with the definition of “perfluoro” and “perfluorinated” provided by Banks et al. (1994, p. 2).
- Polyfluoroalkyl substances, defined here as aliphatic substances for which all H atoms attached to at least one (but not all) C atoms have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety $\text{C}_n\text{F}_{2n+1}-$ (e.g., $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$). Thus, whereas the general chemical concept of “polyfluorination” embraces compounds containing “scattered” multiple F atoms (such as in $\text{CH}_2\text{FCH}_2\text{FCH}_2\text{FCH}_2\text{OH}$), as well as “grouped” ones (such as in $\text{CF}_3\text{CF}_2\text{CH}_2\text{COOH}$), we consider that only those polyfluorinated substances having at least one perfluoroalkyl moiety $\text{C}_n\text{F}_{2n+1}-$ belong to the PFAS family.

The differences between perfluoroalkyl and polyfluoroalkyl substances are illustrated by 2 concrete examples in Table 1.

Polyfluoroalkyl substances have the potential (i.e., the demonstrated or theoretical capability under appropriate conditions) to be transformed abiotically or biotically into perfluoroalkyl substances. For example, $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{NHCH}_2\text{CH}_2\text{OH}$ (a polyfluoroalkyl substance) may degrade in the environment to $\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$ (a perfluoroalkyl substance).

The general term “perfluoroalkyl(ated) substance,” with the acronym PFAS, was the first to be defined and widely used to describe the broad class of highly fluorinated substances observed in the environment (Hekster et al. 2002; Hekster et al. 2003). It has been employed by the groups of scientists who collaborated in the finalized European Union PERFORCE project (de Voogt et al. 2006) and others who have

Table 1. Examples of the correct and incorrect (or undesirable) uses of the proposed nomenclature for perfluoroalkyl and polyfluoroalkyl substances (PFASs)

Example	Example statements	
	Correct	Incorrect or <i>undesirable</i>
	Both are PFASs, within the family of perfluoroalkyl and polyfluoroalkyl substances	- Both are: - Perfluoroalkyl substances, chemicals, compounds - Perfluorinated substances, chemicals, compounds - Polyfluoroalkyl substances - Polyfluorinated substances - Fluorocarbons - Perfluorocarbons - Fluorinated substances, chemicals, compounds - Perfluorochemicals - Perfluorinated chemicals - Both contain fluorocarbons
	Both are carboxylic acids	
	- All H atoms on all C atoms in the alkyl chain attached to the carboxylic acid functional group are replaced by F - This is a: PFAS, perfluoroalkyl acid (PFAA), perfluoroalkyl carboxylic acid (PFCa) - Specifically, this is perfluorooctanoic acid, CAS number 335-67-1	- This is a: - Perfluorinated substance, chemical, compound - Fluorinated substance, chemical, compound - Fluorocarbon - Perfluorocarbon
	- The alkyl chain attached to the carboxylic acid functional group is polyfluorinated - This is a: PFAS, polyfluoroalkyl acid, polyfluoroalkyl carboxylic acid - Specifically, this is 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid	- This is a: - Polyfluorinated substance, chemical, compound - Fluorinated substance, chemical, compound - Perfluorinated substance, chemical, compound - A portion of this compound is perfluorinated

followed their example. Soon thereafter, many authors began using the acronym PFC and have defined it in many different ways. As a result, the meaning of the acronym PFC is unclear and not well defined. Moreover, we consider this choice to have been an unfortunate and inappropriate one, given that the acronym PFC has been used in official Kyoto Protocol documents since its adoption in 1997 to specifically designate perfluorocarbons (United Nations 1998), one of the families of greenhouse gases regulated by this important multilateral international agreement. Clearly, a given acronym may legitimately be used in different spheres of activity to denote different concepts, provided these activities are sufficiently disconnected from each other. However, both PFCs and PFASs belong to the overall family of fluorinated chemicals and, hence, are too closely related to share a common acronym. We, therefore, strongly urge the community to adopt henceforth the use of the term PFASs (singular PFAS) as an acronym for “perfluoroalkyl and polyfluoroalkyl substances” and the term PFCs (singular PFC) exclusively for “perfluorocarbons.” PFCs are notionally derived from hydrocarbons by replacing all H atoms by F atoms, so that they contain only the elements C and F, and functional groups are absent. Examples of PFCs are tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6), octafluorocyclobutane (C_4F_8),

and perfluorodecalin ($\text{C}_{10}\text{F}_{18}$). Those PFCs that contain a $\text{C}_n\text{F}_{2n+1}$ moiety are, by definition, members of the PFAS family, but PFCs are chemically very stable substances, and it is uncertain whether any of them can actually degrade in the environment (e.g., in the upper atmosphere) to give functionalized PFASs such as PFCAs that might ultimately be deposited to the Earth’s surface.

“Fluorinated polymers” and “fluoropolymers” defined

We recommend using the broad generic term “fluorinated polymers” to encompass all polymers for which one or more of the monomer units contains the element F, in the backbone and/or in side chains. Fluorinated polymers may or may not be PFASs, depending on whether they contain perfluoroalkyl moieties.

In compliance with time-honored usage within the industry, we recommend further that the term “fluoropolymers” be applied only to a distinct subset of fluorinated polymers, namely, those made by (co)polymerization of olefinic monomers, at least one of which contains F bound to one or both of the olefinic C atoms, to form a carbon-only polymer backbone with F atoms directly attached to it, e.g., polytetrafluoroethylene.

Chain length terminology

PFASs, especially the perfluoroalkyl acids and their anions, are frequently referred to as “long-chain” or “short-chain.” To avoid any subjectivity associated with these adjectives, we urge scientists to adopt the definition provided by the Organisation for Economic Co-operation and Development (OECD 2011), which stipulates that “long-chain” refers to:

- perfluoroalkyl carboxylic acids with eight carbons and greater (i.e., with 7 or more perfluorinated carbons) and,
- perfluoroalkane sulfonates with six carbons and greater (i.e., with 6 or more perfluorinated carbons).

The “long-chain” definitions for PFCAs and PFSA are different in number of C atoms because a PFSA (e.g., PFHxS, $C_6F_{13}SO_3H$) with a given number of carbons (6 in the example given) has a greater tendency to bioconcentrate and/or bioaccumulate than a PFCA with the same number of C atoms (e.g., PFHxA, $C_5F_{11}COOH$) (Martin et al. 2003a, 2003b). Although the OECD definition does not include perfluoroalkyl substances other than carboxylates and sulfonates, one may consider that a perfluoroalkyl chain with 7 or more C atoms, e.g., $C_7F_{15}^-$, is, in any case, “long.”

Linear and branched terminology

Many PFASs exist as families of isomers due to branching of the main C backbone (Alsmeyer et al. 1994). Linear isomers, for which there can only be 1 congener per C_n homologue group, are composed of carbons that are bonded to only 1 or 2 other C atoms. Branched isomers, for which there can be several or many congeners per C_n homologue group, are composed of C atoms that may be bound to more than 2 C atoms, resulting in a branching of the C backbone. For example, PFOS is routinely present in many environmental samples as a mixture of the linear isomer and 10 branched isomers (Riddell et al. 2009), whereas 89 congeners are theoretically possible (Rayne et al. 2008). To address the characterization of the numerous isomers and homologues arising during the electrochemical fluorination process (see below), a systematic numbering system for unequivocally identifying the linear and branched congeners of several families of PFASs has been proposed (Rayne et al. 2008). In the following text and in the Supplemental Data, we will designate perfluoroalkyl moieties, in general, by the formula $C_nF_{2n+1}^-$, thereby including both linear and branched structures, even for substances that, given their manufacturing process (see discussion below), may be presumed to be predominantly linear, so that $C_nF_{2n+1}^-$ is equivalent to $F(CF_2)_n^-$.

The mixture of linear and branched isomers presents challenges in providing an accurate quantification of many PFASs in environmental matrices (Riddell et al. 2009). Nevertheless, the study of linear and branched isomers is useful for understanding sources of PFASs (De Silva and Mabury 2004, 2006; De Silva et al. 2009; Benskin, De Silva, et al. 2010; Benskin, Yeung, et al. 2010), because the production of isomers varies by manufacturing process. The telomerization process produces primarily or exclusively linear PFASs, whereas the electrochemical fluorination process produces a mixture of branched and linear isomers, as discussed below.

Use of acronyms for acids and their anions

Many PFASs are acids and may be present as protonated or anionic forms, or a mixture of both, depending on the pH of the environmental matrix and the compound's acid dissociation constant (pK_a). The pK_a values for many of the PFASs (e.g., PFOA) are under review or are unknown, and for simplicity, we will refer to all PFASs with an acid functionality as “acids,” rather than as carboxylates, sulfonates, and so forth, although recognizing that the dissociated forms may well predominate in environmental and human matrices. Furthermore, given that these acids are generally analyzed as their anions (Larsen and Kaiser 2007), we recommend using the same substance acronym to cover both the protonated and ionized forms. However, an exception is made to this general rule when it is essential to make a distinction between the protonated acid form and the anionic form, such as when reporting physicochemical properties or modeling environmental fate and transport (Armitage et al. 2009b; Webster et al. 2010). In these cases, it is recommended to designate PFCA anions by removing the “A” from the individual substance acronym (e.g., PFO for perfluorooctanoate), maintain the original abbreviation for the acid (e.g., PFOA for perfluorooctanoic acid), and refer to both chemical forms using a collective abbreviation involving parentheses surrounding the “A,” e.g., PFO(A) for combined perfluorooctanoate and perfluorooctanoic acid. In the case of PFSA, it is suggested to add the prefix “H-” to the generic substance acronym to form the abbreviation for the neutral species. This leads, for example, to the abbreviations H-PFOS, PFOS, and (H)-PFOS for the protonated, anionic, and combined forms of the 8-C PFSA, respectively.

Surfactant terminology

Many PFASs are used as surfactants. Traditional surfactants comprise a water-soluble hydrophilic portion and a water-insoluble hydrophobic portion. Surfactants lower the surface tension of a liquid, or the interfacial tension between 2 liquids, or between a liquid and a solid. In fluorinated surfactants, the hydrophobic portion contains F bound to C, often as a perfluoroalkyl moiety. The extent of fluorination and location of the F atoms affect the surfactant properties. PFAS surfactants, often referred to as “fluorinated surfactants,” “fluorosurfactants,” “fluorinated tensides,” or “fluorotensides,” are superior in their aqueous surface tension reduction at very low concentrations and are useful as wetting and leveling agents, emulsifiers, foaming agents, or dispersants (Kissa 1994; Taylor 1999; Kissa 2001). The term “tenside” is encountered most frequently in publications of German origin, and the synonym “surfactant” is preferred in English. Examples of fluorinated surfactants are $NH_4^+ C_7F_{15}CO_2^-$ and $Na^+ C_6F_{13}CH_2CH_2SO_3^-$.

Terminology describing direct and indirect sources of PFASs to the environment

The sources of PFAS (e.g., PFOS or PFOA) emissions to the environment are from their purposeful manufacture, use, and disposal, from their being present as impurities in substances that are emitted to the environment or from precursor substances that degrade abiotically or biotically in the environment. Harmonizing the terminology for describing “sources” is needed. We recommend that the term “direct”

emission sources should refer to emissions of a specific PFAS as such, throughout its product life cycle from manufacture to use and disposal, including emissions from a product in which the PFAS is present as an impurity. On the other hand, the term “indirect” emissions should apply to formation of a specific PFAS by transformation of precursor substances in the environment, wildlife, or humans, such as PFOA formed from the biotransformation of 8:2 fluorotelomer alcohol (FTOH), or C_4F_9COOH from the atmospheric degradation of perfluorobutane sulfonamidoethanol. These definitions depart somewhat from those of Prevedouros et al. (2006) who considered emissions of impurities present in a product to be “indirect.” These alternative definitions do not create large differences in the emissions allocated to direct and indirect sources in the case of PFOA, because the majority of direct emissions are derived from manufacturing sources.

MANUFACTURING PROCESSES

For a better understanding of the environmental occurrence and behavior of PFASs, as well as the relationships between families of PFASs, it is useful to describe briefly the 2 principal manufacturing processes used to produce compounds containing perfluoroalkyl chains.

Electrochemical fluorination

Electrochemical fluorination (ECF) is a technology in which an organic raw material (e.g., octane sulfonyl fluoride [OSF], $C_8H_{17}SO_2F$) undergoes electrolysis in anhydrous HF, leading to the replacement of all the H atoms by F atoms (Alsmeyer et al. 1994). The free-radical nature of the process leads to C chain rearrangement and breakage, resulting in a mixture of linear and branched perfluorinated isomers and homologues of the raw material, as well as PFCs and other species (Alsmeyer et al. 1994). The ratio of linear to branched

perfluorinated C chains formed in the ECF process varies depending on how the process is controlled but is roughly 70% to 80% linear and 20% to 30% branched in the case of the synthesis of PFOS and PFOA (3M Company 1999; Reagen et al. 2007; Lehmler 2009; Benskin, De Silva, et al. 2010). The ECF of $C_8H_{17}SO_2F$ yields 1) perfluorooctane sulfonyl fluoride (POSF, $C_8F_{17}SO_2F$), which is the major raw material used to manufacture PFOS (Figure 1a); 2) a series of functional raw materials such as sulfonamides, sulfonamido alcohols, and sulfonamido acrylate monomers; and 3) a family of surfactants and polymers derived therefrom (3M Company 1999; Lehmler 2005). Likewise, the ECF of octanoyl fluoride, $C_7H_{15}COF$, is the major historic process used to manufacture perfluorooctanoyl fluoride, $C_7F_{15}COF$, which is further reacted to make PFOA and its salts (Figure 1b) (Kissa 1994). The major global historic manufacturer using the ECF process produced 6-, 8-, and (to a lesser extent) 10-carbon perfluoroalkane sulfonyl derivatives and products therefrom (3M Company 2000c). In 2001, the company announced it would no longer manufacture these substances or PFOA. Others continued to use the ECF process to make these substances and there are now new manufacturers of both PFOS and PFOA. The major historic manufacturer is now making alternative products using the ECF process based on perfluorobutane, rather than perfluorooctane, sulfonyl chemistry (Renner 2006; Olsen et al. 2009; Ritter 2010).

Telomerization

Telomerization (Figure 2), which is a second important process for manufacturing perfluoroalkyl substances, is a technology in which a perfluoroalkyl iodide, $C_mF_{2m+1}I$ (PFAI), most commonly pentafluoroethyl (or perfluoroethyl) iodide, C_2F_5I (PFEI), is reacted with tetrafluoroethylene, $CF_2=CF_2$ (TFE) to yield a mixture of perfluoroalkyl iodides

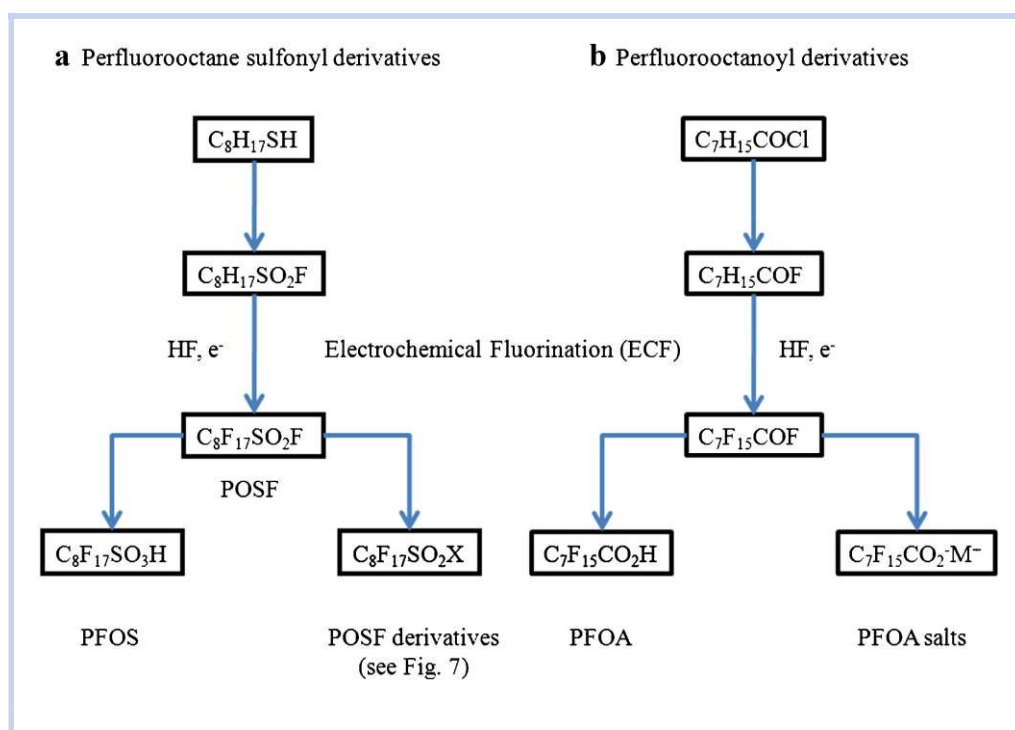


Figure 1. Synthesis, by electrochemical fluorination, of building blocks leading to PFOS, PFOA, and derivatives.

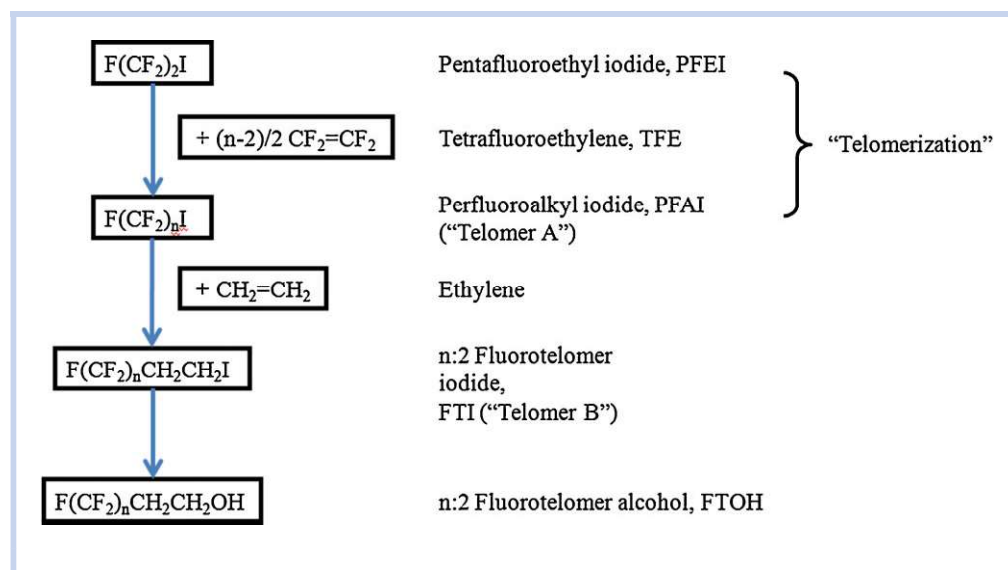


Figure 2. Synthesis, by telomerization, of building blocks leading to fluorotelomer alcohols.

with longer perfluorinated chains $\text{C}_m\text{F}_{2m+1}(\text{CF}_2\text{CF}_2)_n\text{I}$. The starting iodide is referred to as the “telogen” and the TFE as the “taxogen.” The product perfluoroalkyl iodide mixture is often then reacted further, in a 2nd process step, where ethylene is inserted, to give $\text{C}_m\text{F}_{2m+1}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{I}$. The perfluoroalkyl iodides, $\text{C}_m\text{F}_{2m+1}(\text{CF}_2\text{CF}_2)_n\text{I}$, commonly known as Telomer A, resulting from telomerization, the 1st step, and the “fluorotelomer iodides,” $\text{C}_m\text{F}_{2m+1}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{I}$, commonly known as Telomer B, formed in the 2nd step, are raw material intermediates used to produce additional building blocks that are further reacted to create a family of “fluorotelomer-based” surfactant and polymer products. This process is illustrated in Figure 2 for the synthesis of a fluorotelomer alcohol (FTOH), whereas Figure 3 shows how a range of products can be synthesized from the perfluoroalkyl iodide intermediate (exemplified for a starting PFAI with 8 C atoms).

It should be noted that, in the “X:Y” designation, e.g., 8:2 fluorotelomer alcohol ($\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$, 8:2 FTOH), used for naming fluorotelomer-based substances, X is the number of perfluorinated C atoms and Y is the number of non-fluorinated C atoms that originate from the commercial synthesis. As with products derived from ECF, the major global fluorotelomer manufacturers are making available alternative shorter-chain products, in this case based on 6 (rather than 8) perfluoroalkyl C atoms (Renner 2006; Ritter 2010).

The most widely used commercial telomerization process uses PFEI and TFE. When a linear telogen and taxogen are employed in the telomerization process, the resulting perfluoroalkyl iodides have exclusively linear perfluoroalkyl chains. If a branched and/or odd C number telogen, e.g., $(\text{CF}_3)_2\text{CFI}$, is employed and reacted with TFE, the resulting product mixture will be branched and/or will contain an odd number of C atoms, despite the incorporation of an even number of taxogen $-\text{CF}_2-$ units from the TFE. The extent to which branched and/or odd C number telogens may have been actually used in commercial practice is unclear. Such telogens have been described in patents (e.g., Katsushima et al. 1964; Millauer 1971; Grottenmüller et al. 2000), but

this does not necessarily mean that they have been employed commercially. Nevertheless, in certain environmental samples, “isopropyl branched PFCA isomers,” i.e., ones with a terminal $(\text{CF}_3)_2\text{CF}-$ group, have been observed, albeit at low levels compared to their linear counterparts, whereas other branched isomers were either absent or present at much lower levels. This is the case, inter alia, for PFCAs with 9, 11, or 13 C atoms, i.e., perfluorononanoic, perfluoroundecanoic, and perfluorotridecanoic acids (PFNA, PFUnDA, and PFTrDA, respectively), which are believed to be manufactured by the ozonation of a mixture of fluorotelomer olefins (FTOs, $\text{C}_n\text{F}_{2n+1}\text{CH}=\text{CH}_2$) (Ukihashi et al. 1977; Aoyama and Chiba 1997) and which may be formed by the environmental transformation of telomer-derived precursor PFASs. The isopropyl branched isomers of these PFCAs observed in the environment (Furdui et al. 2008; De Silva et al. 2009; Benskin, De Silva, et al. 2010; Zushi et al. 2010) may therefore originate from the use of branched telogens for manufacturing specific isomers of PFNA, PFUnDA, and PFTrDA or their precursors. Nevertheless, the interpretation of branched-to-linear isomer concentration ratios is not straightforward, because certain environmental samples were found to contain up to 3 other PFNA isomers (for example) in addition to the linear and isopropyl branched forms (De Silva and Mabury 2006; Benskin et al. 2007; De Silva et al. 2009). Furthermore, the fact that individual isomers have different physicochemical properties means the patterns in the environment and biota will be transformed relative to the pattern in the emission source.

FAMILIES OF PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES

There are numerous families of PFASs (Figure 4), each with many individual homologous members and isomers thereof (Tables 2, 3, and 4). This section provides a hierarchical overview of the common substance names, acronyms, and chemical formulas of those families of compounds and selected individual substances that have been detected in environmental and human matrices. The discussion includes references to manufacturing processes and