

# Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance



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No. 61

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# **Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance**

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# Executive Summary

This report summarizes recent efforts by the OECD/UNEP Global PFC Group between June 2018 and March 2021 in reviewing the universe and terminology of per- and polyfluoroalkyl substances (PFASs) to provide recommendations and practical guidance to all stakeholders with regard to the terminology of PFASs. In particular, this report highlights (1) a revised PFAS definition to comprehensively reflect the universe of PFASs and a comprehensive overview of the PFAS universe (Chapter 2), (2) practical guidance on how to use the PFAS terminology (Chapter 3), (3) a systematic approach to characterization of PFASs based on molecular structural traits to assist stakeholders, including non-experts, in making their own categorization based on their needs (Chapter 4), and (4) areas in relation to the PFAS terminology that warrant further development (Chapter 5). It should be noted that this report does not address the nomenclature and understanding of individual PFASs, including the sources of exposure and the actual composition of commercial products.

PFASs comprise a class of synthetic compounds that have attracted much public attention since the late 1990s and early 2000s, when the hazards and ubiquitous occurrence of two PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wider range of PFASs. Early communications used many different terminologies (e.g. per- and polyfluorinated chemicals, perfluorinated organics, perfluorochemical surfactants, highly fluorinated compounds). In 2011, to unify and harmonize communication on PFASs, Buck et al. published a milestone paper, providing a first clear structural definition of PFASs and recommendations on names and acronyms for over 200 individual PFASs.

Currently, there is a growing interest by regulators and scientists across the globe to assess legacy and novel PFASs. In 2018, the OECD/UNEP Global PFC Group prepared a new list of PFASs that may have been on the global market. In total, a set of substances with over 4730 CAS numbers have been identified, including substances that contain such fully fluorinated carbon moieties, but do not meet the PFAS definition in Buck et al. (2011) due to a lack of a  $-CF_3$  group in the molecular structures. In addition, recent advancement of non-target screening analytical techniques using high-resolution mass spectrometry has enabled identification of many unknown substances in different environmental and product samples. The identification of these substances motivates the present work to reconcile the terminology of the universe of PFASs, including a renewed look at the PFAS definition in Buck et al. (2011).

It is key to have a coherent and consistent logic behind the PFAS definition to adequately reflect all compounds with the same structural traits, i.e. the PFAS universe. Building on the OECD 2018 PFAS List and recent non-target screening studies, Chapter 2 first identifies four major gaps in the previous PFAS definition by Buck et al. (2011) in representing the PFAS universe. Then, Chapter 2 recommends a revised PFAS definition, with detailed elaboration on individual changes provided:

PFASs are defined as fluorinated substances that contain at least one **fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)**, i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group ( $-\text{CF}_3$ ) or a perfluorinated methylene group ( $-\text{CF}_2-$ ) is a PFAS.

The rationale behind the revision is to have a general PFAS definition that is coherent and consistent across compounds from the chemical structure point of view and is easily implementable for distinguishing between PFASs and non-PFASs, also by non-experts. The decision to broaden the definition compared to Buck et al. is not connected to decisions on how PFASs should be grouped in regulatory and voluntary actions. Based on the revised definition of PFASs, Chapter 2 further illustrates (1) how PFASs fit into organofluorine compounds, (2) a comprehensive overview of PFAS groups, their structural traits, examples and notes on whether common nomenclatures (including acronyms) exist for them, and (3) some common synthesis routes of different individual or groups of PFASs.

As PFASs are a chemical class with diverse molecular structures and physical, chemical and biological properties, it is highly recommended that such diversity be properly recognized and communicated in a clear, specific and descriptive manner. The term “PFASs” is a broad, general, non-specific term, which does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety. In particular, Chapter 3 provides practical guidance to governments and other stakeholders on how to use the PFAS terminology, starting from the distinction between the general definition and user-specific working scopes of PFASs. In particular, the general definition of PFASs is based on molecular structure alone and serves as a starting and reference point to guide individual users to have a comprehensive understanding of the PFAS universe and to keep the big picture of the PFAS universe in mind. At the same time, individual users may define their own working scope of PFASs for specific activities according to their specific needs by combining the general definition of PFASs with additional considerations (e.g. specific properties, use areas). This report does not make any recommendation on how working scopes should be set up, in terms of which factors to be considered (which depends highly on specific local context), nor on PFAS grouping. However, when a working scope of PFASs is used, this report highly recommends that users clearly provide the context and rationale for selecting their PFAS working scope in order to provide transparency and avoid confusion by others. Further, the report recommends to use and build upon existing common terminologies such as in this report, in Buck et al. (2011) and common practices in organic chemistry as set by IUPAC and CAS, unless it is essential to deviate from existing naming conventions, in order to keep the consistence and coherence of the PFAS terminology.

As users often define their own working scope of PFASs according to their specific needs, they need to characterize PFASs based on pre-defined traits and categorize them (e.g. whether a compound with certain traits falls or does not fall into their working scope). However, given the high complexity and diversity of PFASs, it can be a challenging task to characterize and categorize PFASs based on chemical structures in a coherent and consistent manner, particularly for non-experts. In addition, different users may have very different needs, and there is no single categorization/grouping system that can meet all needs. Therefore, Chapter 4 provides a standardized approach for systematic characterization of different PFASs based on molecular structural traits that will allow stakeholders to make their own categorization in a coherent and consistent manner. In addition to the manual application of the system to characterize and categorize PFASs, the elements presented here may also be used as inputs for developing cheminformatic tools that would allow automated characterization and categorization of PFASs.

While this report makes advancement on several important points regarding PFAS terminology and practical guidance of how to use the PFAS terminology, Chapter 5 also recognizes four areas that warrant further work, in order to facilitate clear and unambiguous communication of PFASs and beyond: (1) a centralized PFAS nomenclature database/platform; (2) further development of cheminformatics-based tools for automated systematic characterizing and categorizing PFASs; (3) further work on the characterization and reporting of polymers; and (4) work on organofluorine compounds other than PFASs including many fluorinated aromatics.





# List of Acronyms

ADONA	Ammonium 4,8-dioxa-3H-perfluorononanoate
Br	Bromine atom
CAS	Chemical Abstracts Service
CAS Nos.	Chemical Abstracts Service registry numbers
Cl	Chlorine atom
CTFE	Chlorotrifluoroethylene
ECHA	European Chemicals Agency
ETFE	Ethylene-tetrafluoroethylene copolymer
EU	European Union
FASAs	Perfluoroalkane sulfonamides
FASEs	Perfluoroalkane sulfonamidoethanols
FEP	Fluorinated ethylene propylene co-polymer
FPs	Fluoropolymers
FTABs	Fluorotelomer sulfonamide alkylbetaines
FTEOs	Fluorotelomer ethoxylates
FTIs	Fluorotelomer iodides
FT(MA)ACs	Fluorotelomer (meth)acrylates
FTOs	Fluorotelomer olefins
FTOHs	Fluorotelomer alcohols
FTSAs	Fluorotelomer sulfonic acids
HFCs	Hydrofluorocarbons
HFEs	Hydrofluoroethers
HFOs	Hydrofluoroolefins
HFP	Hexafluoropropylene
HFPO	Hexafluoropropylene oxide
HFPO-DA	Hexafluoropropylene oxide dimer acid
H	Hydrogen atom
I	Iodine atom
ICCM	International Conference on Chemicals Management
InChI	International chemical identifier

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InChIKey	A hashed version of the full InChI
ITRC	Interstate Technology & Regulatory Council in the United States
IUPAC	International Union of Pure and Applied Chemistry
OBS	Sodium <i>p</i> -perfluorous noenoxybenzenesulfonate
OECD	Organisation for Economic Co-operation and Development
PACFs	Perfluoroalkanoyl fluorides
PASFs	Perfluoroalkane sulfonyl fluorides
PCTFE	Polychlorotrifluoroethylene
PFA	Perfluoroalkoxyl polymer
PFAAs	Perfluoroalkyl acids
PFAIs	Perfluoroalkyl iodides
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkyl carboxylic acids
PFdiCAs	Perfluoroalkyl dicarboxylic acids
PFdiSAs	Perfluoroalkane disulfonic acids
PFECAs	Perfluoroalkylether carboxylic acids
PFEI	Perfluoroethyl iodide
PFESAs	Perfluoroalkylether sulfonic acids
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPAAs	Perfluoroalkyl phosphonic acids
PFPEs	Perfluoropolyethers
PFPIAs	Perfluoroalkyl phosphinic acids
PFSAAs	Perfluoroalkane sulfonic acids
PFSlAs	Perfluoroalkane sulfinic acids
PolyFCAs	Polyfluoroalkyl carboxylic acids
PolyECAs	Polyfluoroalkylether carboxylic acids
PolyESAs	Polyfluoroalkylether sulfonic acids
POPs	Persistent Organic Pollutants
POSF	Perfluorooctane sulfonyl fluoride
PPVE	Perfluoropropylvinyl ether
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
PVF	Polyvinyl fluoride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (EC 1907/2006)
SaMPAPs	Perfluorooctane sulfonamidoethanol phosphate esters
SFAs	Semifluorinated alkanes

SMILES	Simplified molecular input line entry specification
TFE	Tetrafluoroethylene
THV	Terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride
UNEP	United Nations Environment Programme
VDF	Vinylidene fluoride



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# Chapter 1. Background, motivation and scope

The OECD/UNEP Global PFC<sup>1</sup> Group was established to respond to the Resolution II/5 adopted at the second session of the UN International Conference on Chemicals Management (ICCM 2) in 2009, which calls upon intergovernmental organizations, governments and other stakeholders to “consider the development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals of concern in products and to work toward global elimination, where appropriate and technically feasible”. Further work on this resolution was reaffirmed in Resolution III/3 adopted at ICCM 3 in 2012 noting that a significant need remains for additional work to support implementation of Resolution II/5. This report is prepared within the framework of the Group. For more details on the Group and its work, see the OECD PFAS web portal (<https://oe.cd/2M9>).

This report summarizes recent efforts by the OECD/UNEP Global PFC Group between June 2018 and March 2021 in reviewing the universe and terminology of per- and polyfluoroalkyl substances (PFASs<sup>2</sup>) to provide recommendations and practical guidance to all stakeholders (governments, industry, academia, civil society organizations, etc.) regarding the terminology of PFASs. In particular, this report highlights (1) a revised PFAS definition to comprehensively reflect the universe of PFASs and a comprehensive overview of the PFAS universe (Chapter 2), (2) a practical guidance on how to use the PFAS terminology, from a general PFAS definition to user-specific working scopes to naming conventions of individual PFASs (Chapter 3), (3) a systematic approach to characterization of PFASs based on molecular structural traits to assist stakeholders, including non-experts, in making their own categorization based on their needs (Chapter 4), and (4) areas in relation to the PFAS terminology that warrant future work (Chapter 5). It should be noted that this report does not address the nomenclature and understanding of individual PFASs, including the sources of exposure and the actual composition of commercial products. It also does not address organofluorine compounds other than PFASs.

PFASs comprise a class of synthetic compounds that have attracted much public attention since the late 1990s and early 2000s, when the hazards and ubiquitous occurrence of two PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wider range of PFASs [e.g. 3M's voluntary global phase-out of C<sub>6-10</sub> perfluoroalkane sulfonic acids (PFASs), PFOA and related chemistries in 2000–2002]. It is noted that early communications used many different terminologies (e.g. per- and polyfluorinated chemicals, perfluorinated organics, perfluorochemical surfactants, highly fluorinated compounds).

In 2011, to unify and harmonize communication on PFASs, Buck et al. published a milestone paper on a first comprehensive overview of PFASs detected in the environment, wildlife, and humans. It provided a first clear structural definition of PFASs. A particular emphasis of Buck et al. (2011) was placed on long-chain perfluoroalkyl acids [PFAAs, i.e., perfluoroalkyl carboxylic acids (PFCAs) with seven or more perfluorinated carbons and PFASs with six or more perfluorinated carbons]<sup>3</sup>, substances related to the long-chain PFAAs, and substances intended as alternatives to the long-chain PFAAs or their precursors<sup>4</sup>.

In addition, Buck et al. (2011) provided a list of 42 families and subfamilies<sup>5</sup> of PFASs and 268 selected individual compounds, including recommended names and acronyms, structural formulas, and Chemical Abstracts Service registry numbers (CAS Nos.).

Today, several long-chain PFAAs have been recognized as global contaminants of high concern. For example, PFOS, its salts, and perfluorooctane sulfonyl fluoride (POSF<sup>6</sup>), as well as PFOA, its salts, and PFOA-related compounds have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) for global actions. In addition, the POPs Review Committee to the Stockholm Convention decided in 2019 to recommend that the Conference of the Parties to the Stockholm Convention consider listing perfluorohexane sulfonic acid (PFHxS, C<sub>6</sub> PFSA), its salts and PFHxS-related compounds at its tenth meeting. In response to these actions, an industrial transition has taken place to replace long-chain PFAAs and their precursors with alternative chemicals, many of which are still PFASs, including short-chain PFAAs and their precursors as well as perfluoroalkylether-based substances (for examples, see Buck et al., 2011, Wang et al., 2013, 2016 and references therein). It is noted that there is a growing interest by regulators<sup>7</sup> and scientists across the globe to assess legacy and novel PFASs other than long-chain PFAAs and their well-known precursors.

In particular, various efforts have been made to identify overlooked PFASs. In 2018, the OECD/UNEP Global PFC Group prepared a new list of PFASs<sup>8</sup> that may have been on the global market using a systematic search of substances that have a  $-C_nF_{2n-}$  ( $n \geq 3$ ) or  $-C_nF_{2n}OC_mF_{2m-}$  ( $n$  and  $m \geq 1$ ) moiety in different publicly accessible sources. In total, a set of substances with over 4730 CAS Nos. have been identified, including substances that contain fully fluorinated carbon moieties and are structurally similar to or related to commonly known PFASs [e.g. perfluoroalkyl dicarboxylic acids (PFdiCAs) to PFCAs], but do not meet the PFAS definition in Buck et al. (2011) due to a lack of a  $-CF_3$  group in the molecular structures (for more details, see Section 2.2). Meanwhile, recent advancement of non-target screening analytical techniques using high-resolution mass spectrometry has enabled identification of many unknown substances in different environmental and product samples [e.g.  $H-(CF_2CH_2)_n-CF_2COOH$  by Newton et al. (2017)].

The identification of overlooked PFASs motivates the present work to reconcile the terminology of the universe of PFASs, including a renewed look at the PFAS definition in Buck et al. (2011) (see Chapter 2). In light of these newly identified substances and building on existing common terminology provided in Buck et al. (2011), this report and others, this report also looks into practical guidance on how to use the PFAS terminology, including uses of user-specific working scopes (see Chapter 3). In addition, the OECD 2018 PFAS List and recent non-target screening studies show the complexity and diversity of the PFAS universe, resulting in challenges for non-experts in conducting their own categorization of PFASs based on molecular structures. Therefore, this report also looks into systematic approaches to characterization and categorization of PFASs to assist stakeholders in making their own categorization based on their needs (see Chapter 4). Further, this report highlights open questions in relation to PFAS terminology for future consideration (see Chapter 5).

## Notes

<sup>1</sup> “PFCs” here refer to “per- and polyfluorinated chemicals”, and not to “perfluorocarbons”. As stated below, “per- and polyfluorinated chemicals” was a term commonly used before the term “per- and polyfluoroalkyl substances” was recommended by Buck et al.. As it is part of the Group official name, it remains unchanged.

<sup>2</sup> This report uses the acronym “PFASs” for “per- and polyfluoroalkyl substances” as stated in Buck et al. (2011), and its corresponding singular form “PFAS” refers to either a perfluoroalkyl or polyfluoroalkyl substance. It is noted that there is a notion of using “PFAS” as the acronym for both the singular and plural forms. This report does not make any recommendation to address this notion, as it is a trivial point that is difficult for everyone to comprehend, particularly for non-PFAS experts and non-English native speakers. While recognizing that readers may make their own decision which acronym they would use, this report encourages readers to always use the acronym consistently in their documents (for more details on practice guidance on how to identify and use the PFAS terminology, see Section 3.2 below).

<sup>3</sup> Note that the definition of “long-chain PFAAs” here is based on the OECD definition (<https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/>), and the definitions of “long-chain PFAAs” may differ by jurisdiction.

<sup>4</sup> PFAA precursors refer to chemicals that can transform and form PFAAs in the environment and biota.

<sup>5</sup> Note that in the literature, some authors have used other taxonomy terminologies, e.g. “groups and subgroups” instead of “families and subfamilies”. This report does not propose a new taxonomy terminology for PFASs, but makes some practical guidance on how to use taxonomy terminologies (see Chapter 3 below).

<sup>6</sup> Note that the acronym “POSF” here is used in accordance with the recommendations by Buck et al. (2011), whereas under the Stockholm Convention, another acronym “PFOSF” is used.

<sup>7</sup> For example, five European Union (EU) member states have agreed to prepare a joint REACH restriction proposal to limit the risks to the environment and human health from the manufacture and use of a wide range of PFASs, and thus launched a public call for evidence in May 2020 with regard to substances that contain at least one aliphatic  $-CF_2-$  or  $-CF_3$  element. For more details, see <https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas>. In addition, multiple PFASs other than long-chain PFAAs and their precursors are listed in ECHA’s Public Activities Coordination Tool (PACT) to be assessed by ECHA or EU member states (<https://echa.europa.eu/pact>).

<sup>8</sup> The Excel Spreadsheet version of the OECD 2018 PFAS list can be found at <https://www.oecd.org/chemicalsafety/risk-management/global-database-of-per-and-polyfluoroalkyl-substances.xlsx>. In addition, several other entities have curated the OECD 2018 PFAS list into their databases, with features such as an easier overview of chemical structures and links to other information, including the US EPA CompTox Chemicals Dashboard ([https://comptox.epa.gov/dashboard/chemical\\_lists/PFASOECD](https://comptox.epa.gov/dashboard/chemical_lists/PFASOECD)), NORMAN Network (<https://www.norman-network.com/?q=suspect-list-exchange>) and PubChem (<https://pubchem.ncbi.nlm.nih.gov/classification/#hid=101>).

In addition, the US EPA CompTox Chemicals Dashboard also provides a number of other PFAS lists intended to address different research and regulatory interests, including PFASSTRUCT that is compiled from all the records with a structure assigned in the Dashboard using a pre-defined set of substructural filters and contains over 8000 compounds, as of 23 November, 2020 (for more details including the list of substructural filters, see [https://comptox.epa.gov/dashboard/chemical\\_lists/PFASSTRUCT](https://comptox.epa.gov/dashboard/chemical_lists/PFASSTRUCT)). Note that these lists may also include substances that are not regarded as PFASs in accordance with the revised PFAS definition below.



# Chapter 2. Reconciling Terminology of the Universe of PFASs

## 2.1. The previous PFAS definition in Buck et al. (2011)

In Buck et al. (2011), **PFASs** were defined as “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<sub>n</sub>F<sub>2n+1</sub>-**” (i.e. must contain at least -CF<sub>3</sub>). The definition highlights the presence of at least one fully fluorinated saturated carbon atom in the PFAS molecules.

## 2.2. Gaps in the previous PFAS definition by Buck et al. (2011)

It is key to have a coherent and consistent logic behind the PFAS definition to reflect all compounds with shared structural traits, i.e. the PFAS universe. Building on the OECD 2018 PFAS List and recent non-target screening studies, this section identifies gaps in the previous PFAS definition by Buck et al. (2011) in representing the PFAS universe. Note that the gaps identified in this report are not exhaustive and additional gaps in the PFAS definition may be identified in the future; therefore, an iterative approach is guaranteed to ensure the consistency between the PFAS universe and terminology when new knowledge of gaps in the PFAS definition is generated.

**Case 1:** The fully fluorinated saturated carbon moiety<sup>9</sup> is connected with functional groups on both ends, including having a single H/Br/Cl atom on one end. As such, it does not meet the structural requirement of “-C<sub>n</sub>F<sub>2n+1</sub>” in the previous definition. In the example of a1 in Figure 1, it is a PFdiCA with a similar structure to PFCAs (e.g. PFOA in the example of A in Figure 1), but having carboxylic groups on both ends of the perfluoroalkanediyli moiety. In addition, for the example of a2 in Figure 1, it would meet the previous definition if the H atom was moved to a secondary carbon atom (i.e. CF<sub>3</sub>CFHCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>COOH, a positional isomer).

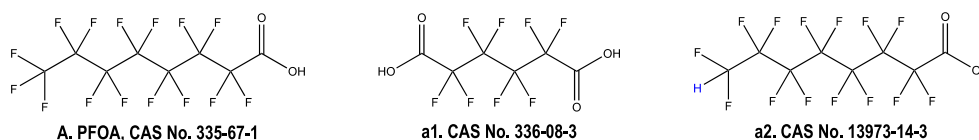


Figure 1. PFOA and examples of substances with similar molecular structures, but having functional groups (including single atoms such as hydrogen) on both ends of the perfluoroalkanediyli moiety.

Furthermore, functionalized fluoropolymers and perfluoropolyethers<sup>10</sup> (i.e. those that have functional groups on both ends of the polymer backbone, e.g. Fomblin HC/P2 1000<sup>11</sup>) do not meet the structural



requirement of “ $-C_nF_{2n+1}$ ” in the previous definition, whereas their closely related analogues with only fluorine atoms on each end of the polymer backbone would meet the previous definition.

**Case 2:** The substance is a fully fluorinated aliphatic cyclic compound which may or may not have a fully fluorinated alkyl side chain. As such, it may not meet the structural requirement of “ $-C_nF_{2n+1}$ ” in the previous definition. For example, b1 in Figure 2 meets the previous definition, whereas its shorter-chain homologue, b2 in Figure 2, does not meet the previous definition.

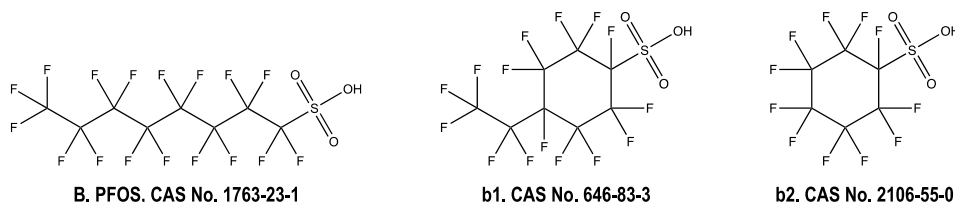


Figure 2. PFOS, an example of a cyclic PFSA, and a shorter-chain homologue of the cyclic PFSA

**Case 3:** The functional group contains an aromatic ring. Thus, it may not meet the term “**aliphatic substances**” in the previous definition, although the example of c1 in Figure 3 is a derivative of 6:2 fluorotelomer iodide, i.e. a 6:2 fluorotelomer-based compound.

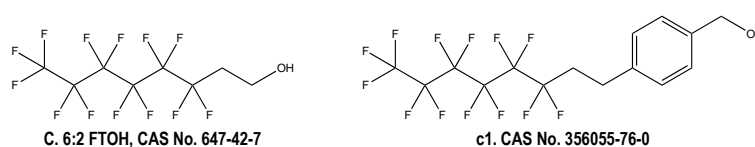


Figure 3. 6:2 FTOH, and a 6:2 fluorotelomer iodide derivative with one aromatic ring in the functional group

**Case 4:** The description “highly fluorinated” in the previous definition is an ambiguous, problematic term. It cannot and should not be literally translated to, e.g., the weight percentage of fluorine atoms in the molecules, using three 6:2 fluorotelomer-based compounds as an example (see Figure 4):

- $C_6F_{13}C_2H_4OH$  (6:2 FTOH; CAS No. 647-42-7) has a fluorine content of 67.8 wt%,
- $C_6F_{13}C_2H_4SO_2NHC_3H_6N(O)(CH_3)_2$  used in Forafac® 1183 (CAS No. 80475-32-7) has a fluorine content of 46.7 wt%, and
- 6:2 fluorotelomer ethoxylates  $[C_6F_{13}-(CH_2CH_2O)_n-H]$ ,  $n = 0-13$  in a commercial product (Frömel and Knepper, 2010) would have even lower fluorine content when  $n > 4$ .

But they are all 6:2 fluorotelomer-based compounds and may act as precursors to perfluorohexanoic acid (PFHxA) in the environment and biota.

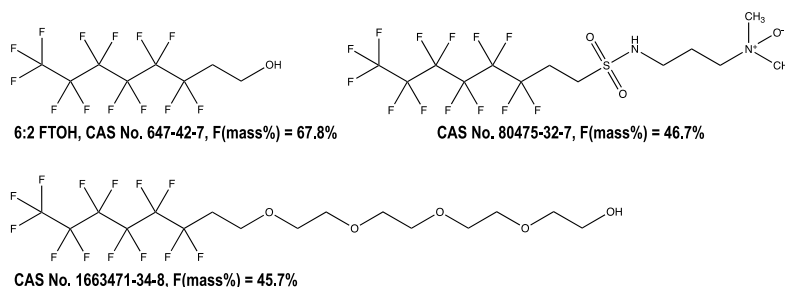


Figure 4. 6:2 FTOH and two 6:2 fluorotelomer derivatives, and their corresponding fluorine contents

### 2.3. A revised PFAS definition

Therefore, there is a need to revisit the previous definition in Buck et al. (2011) to address these gaps (i.e. the previous definition was not comprehensive enough and contained ambiguous descriptions). A clear distinction of the logical relationship needs to be made here: the intention of the revision of the PFAS definition is not to expand the PFAS universe, but to comprehensively reflect it. More concretely, the rationale behind the revision is to have a general PFAS definition that is coherent and consistent across compounds from the chemical structure point of view and is easily implementable for distinguishing between PFASs and non-PFASs, also by non-experts.

**This revised PFAS definition** reads,

PFASs are defined as fluorinated substances that contain at least one **fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)**, i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group ( $-\text{CF}_3$ ) or a perfluorinated methylene group ( $-\text{CF}_2-$ ) is a PFAS.

Both a perfluorinated methyl group and a perfluorinated methylene group are saturated and aliphatic. Note that the carbon in a  $\text{R}-\text{CF}_2-\text{O}-$  or  $\text{R}-\text{CF}_2-\text{Si}-$  group ( $\text{R} \neq \text{H/Cl/Br/I}$ ) is a perfluorinated methylene carbon. A perfluorinated methylene group may also be represented as " $>\text{CF}_2$ ", where " $>$ " denotes two single bonds. A fully fluorinated carbon that is bound to the rest of the molecule by a double bond is a perfluorinated *methylidene* carbon atom ( $=\text{CF}_2$ ). This distinction is important. Further, a perfluorinated methine carbon moiety ( $>\text{CF}-$ ) alone does not meet this revised PFAS definition.

It should be noted that this general PFAS definition is based only on chemical structure, and the decision to broaden this definition compared to Buck et al. (2011) is not connected to decisions on how PFASs should be grouped and managed in regulatory and voluntary actions. For further practical guidance on how to use this general PFAS definition, see Section 3.1.

Figure 5 illustrates substances that are PFASs, and Figure 6 shows those that are not PFASs. Note that tetrafluoroethylene (TFE, CAS No. 116-14-3,  $\text{CF}_2=\text{CF}_2$ ) is not a PFAS as both fully fluorinated carbon atoms are unsaturated; its longer-chain homologue hexafluoropropylene (HFP, CAS No. 116-15-4,  $\text{CF}_2=\text{CF}-\text{CF}_3$ ) is a PFAS due to the presence of a fully fluorinated methyl carbon atom ( $-\text{CF}_3$ ).

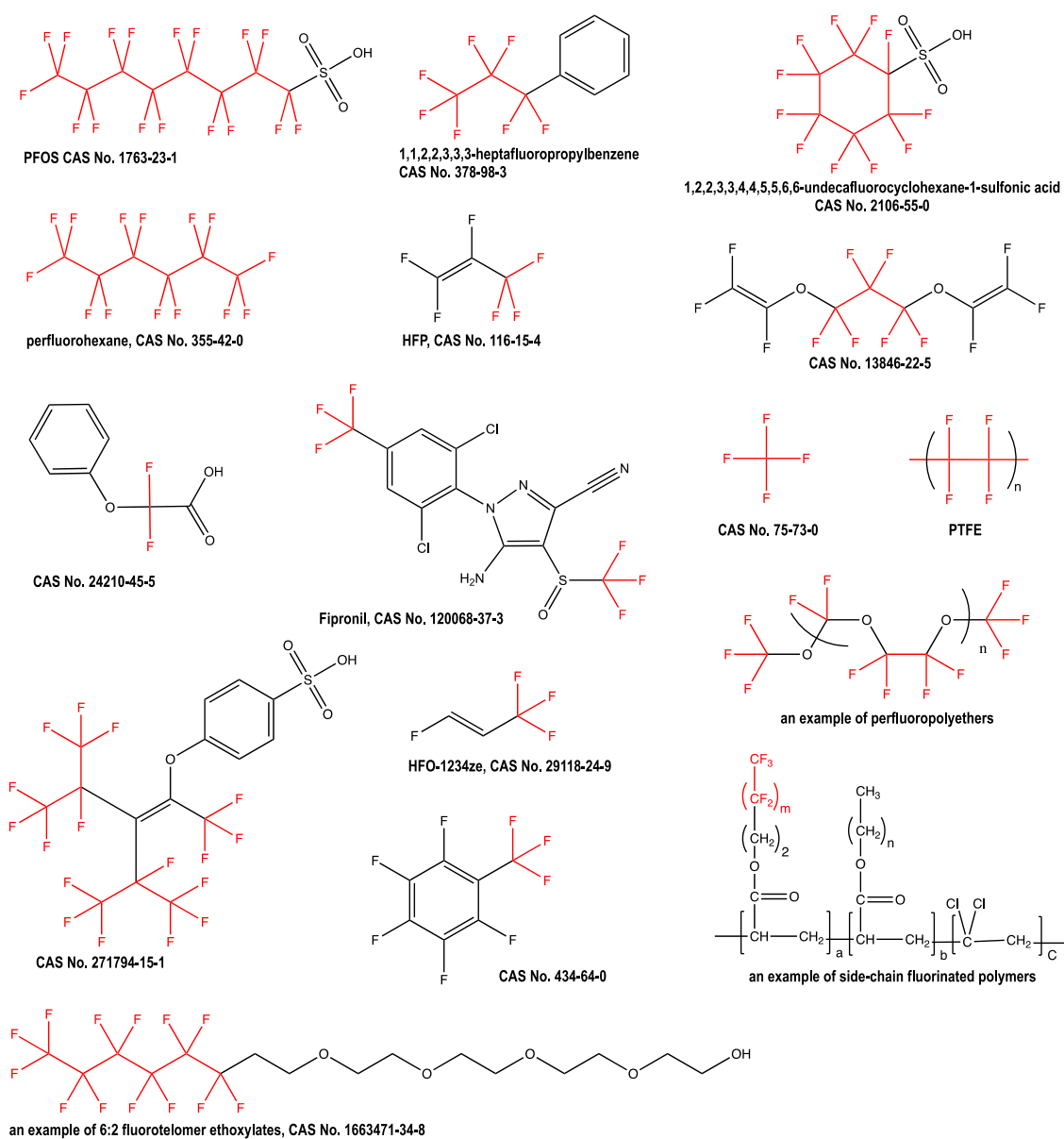


Figure 5. Examples of PFASs. The fully fluorinated methyl or methylene carbon atoms are highlighted in red.

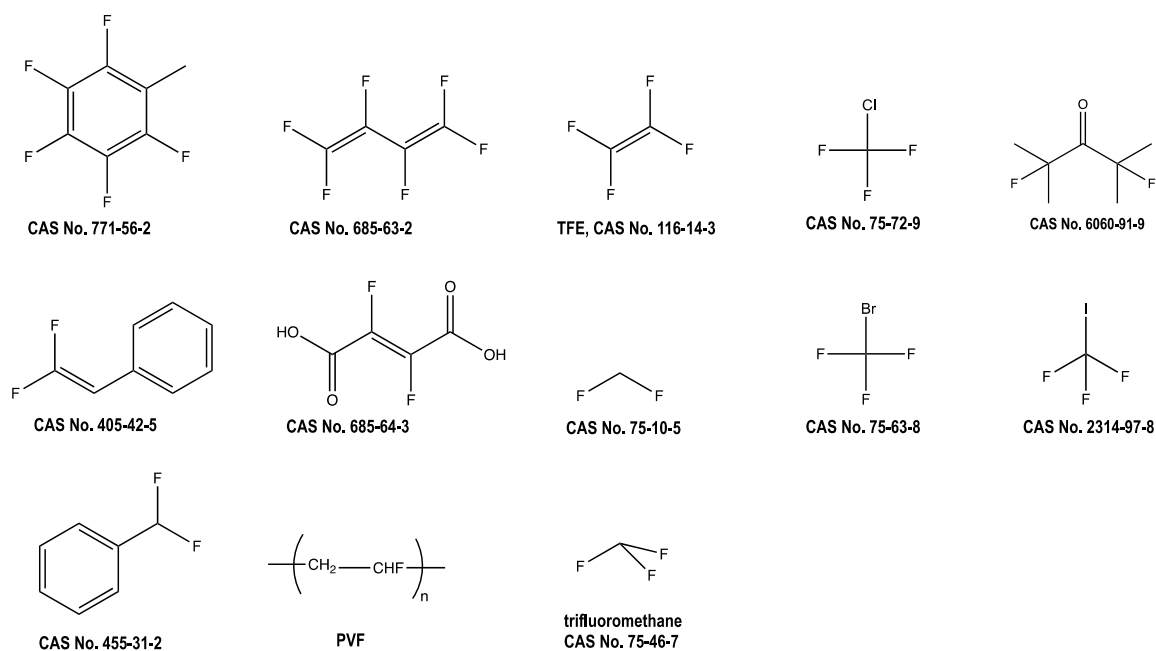


Figure 6. Examples of compounds that are not PFASs due to a lack of fully fluorinated methyl or methylene carbon atoms.

The rationale for making such changes is detailed as follows.

- **Change from “highly fluorinated aliphatic substances” to “fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)”:**

First, the qualifier “highly” is removed from the definition, as it is not meaningful when the fluorinated carbon chain can cleave from the substance to produce a new molecule that is more highly fluorinated [see Section II in FOEN (2017) and references therein].

Second, the term “aliphatic” is removed from the definition. As shown in Case 3 in Figure 3, aromatic ring(s) may be present as a part of the functional group connecting to a fully fluorinated methyl or methylene carbon moiety. Using the previous definition by Buck et al. (2011), such compounds would not be recognized as PFASs, whereas compounds with similar structures but without aromatic ring(s) are recognized as PFASs. This may easily create confusion as to when a substance is or is not a PFAS, particularly for non-experts. The change of wording here is also to make the definition more straightforward. At the same time, the new wording “substances that contain at least one fully fluorinated methyl or methylene carbon atom” means that this revised definition is still constrained to the key trait of having an aliphatic fully fluorinated saturated carbon moiety and excluding those fluorinated aromatics that only have fluorine directly attached to the aromatic rings. Overall, this revised definition includes side-chain fluorinated aromatics [i.e. aromatics that have one or more aliphatic fully fluorinated saturated carbon moiety on the side chain(s) attached to the aromatic ring(s), an analogy to “side-chain fluorinated polymers”<sup>12</sup> as in Buck et al. 2011] as PFASs; for examples, see c1 in Figure 3 and Figure 7 below.

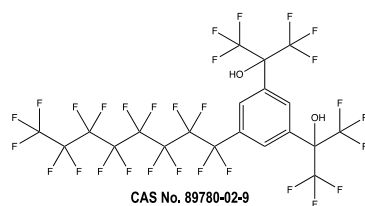


Figure 7. An example of side-chain fluorinated aromatics.

- **Change from “the perfluoroalkyl moiety  $C_nF_{2n+1}$ ” to “at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)”:**

This change is to accommodate those that have functional groups on both ends of the fully fluorinated saturated carbon moieties (Case 1) and those that have cyclic structure(s) at the end of the fully fluorinated saturated carbon moieties (Case 2).

In addition, two more specific descriptions are made here to make the definition clearer. First, the term “methyl or methylene carbon atom” is added to describe the fully fluorinated saturated carbon moiety, which was not clear from the description “that contain only 1 or more C atoms on which all the H substituents ... have been replaced by F atoms”, but only implicitly mentioned in the description “in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}$ ”. Second, adding “without any H/Cl/Br/I atom attached to it” highlights that the carbon atom is considered non-fully fluorinated, when a H/Cl/Br/I atom is attached to it.

## 2.4. A comprehensive overview of the PFAS universe

Based on this revised definition of PFASSs, a first scheme can be drawn to illustrate how PFASSs fit into organofluorine compounds (see Figure 8). It can be seen that besides PFASSs, there are many other organofluorine compounds, including (1) fluorinated aliphatic substances that do not have a fully fluorinated methyl or methylene carbon atom [e.g. trifluoromethane (HFC-23) and difluoromethane (HFC-32)], (2) fluorinated aromatic substances with no side chain(s) (e.g. hexafluorobenzene, CAS No. 392-56-3), and (3) fluorinated aromatic substances with non-fluorinated side chain(s) (e.g. pentafluorobenzoic acid, CAS No. 602-94-8). These other organofluorine compounds are beyond the scope of this report, and future work on them is encouraged.

Looking at the PFAS universe, it is a highly complex chemical class with compounds having diverse functional groups attached to the fully fluorinated saturated carbon moiety/-ies. Figure 9 provides a comprehensive overview of PFAS groups, their structural traits, examples and notes on whether common nomenclatures (including acronyms) exist for them, building on Buck et al. (2011) and the OECD 2018 List. Figure 10 illustrates some common synthesis routes of different individual or groups of PFASSs based on publicly accessible sources. It should be noted that, while Figures 9 and 10 aim to be comprehensive, they are by no means exhaustive. For more information on individual PFAS groups (e.g. major compounds in the group, synthesis routes, major uses, regulatory status, environmental occurrence, etc.), readers may consult the PFAS Fact Cards published on the OECD PFAS Web portal: <https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/>.

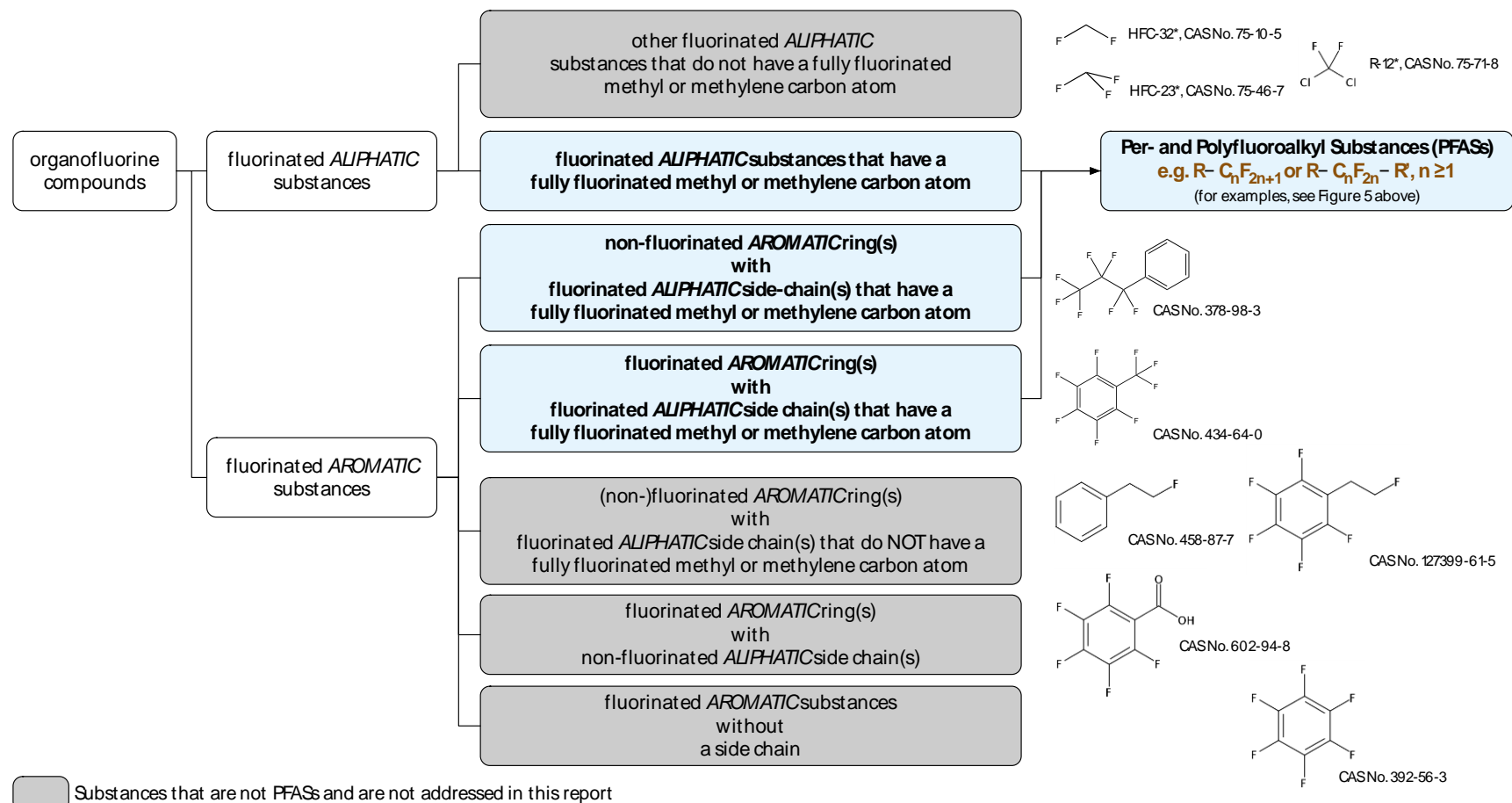
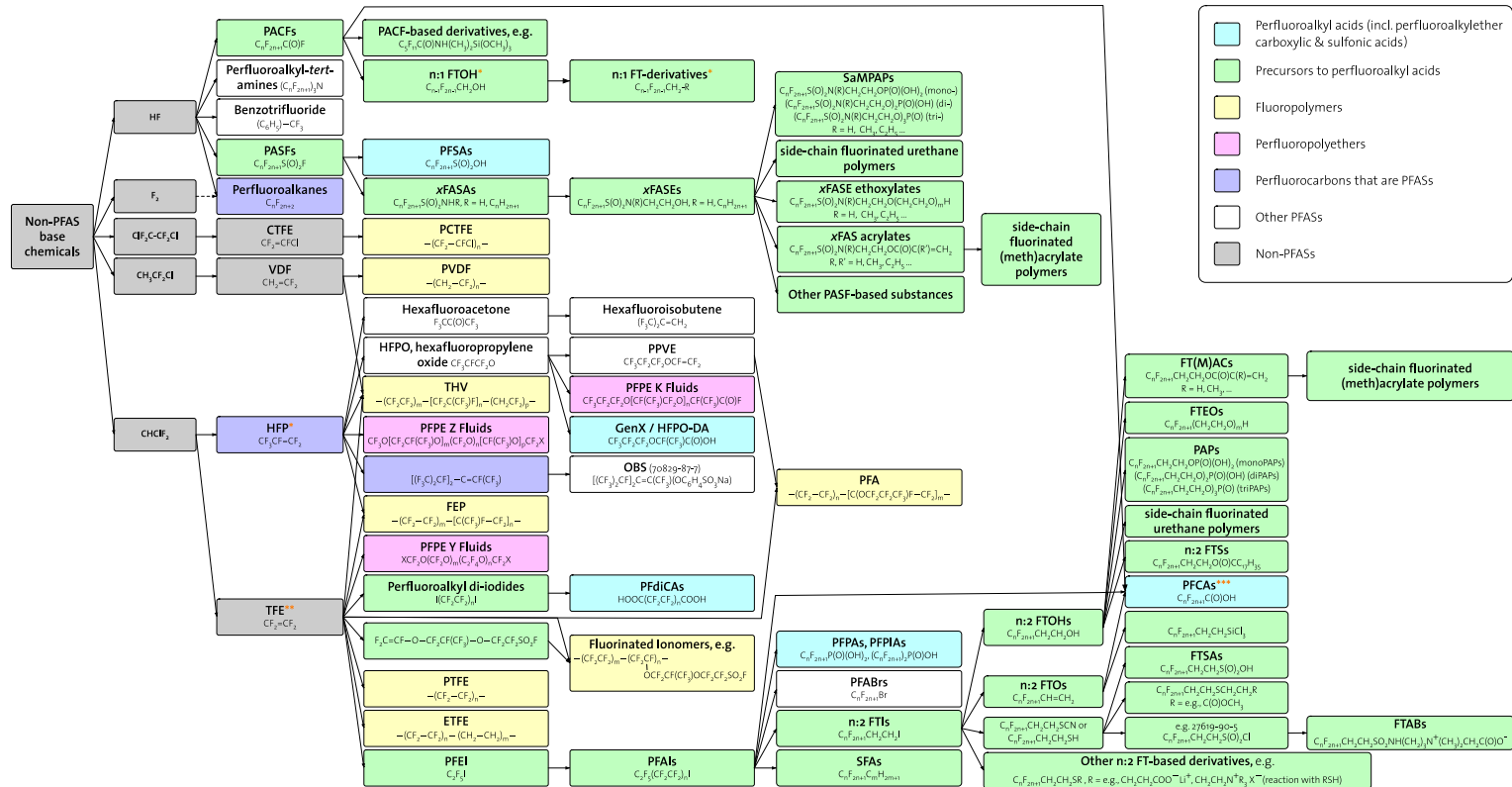


Figure 8. An illustrative scheme of how PFASs fit into the universe of organofluorine compounds





Figure 9. A comprehensive overview of PFAS groups, their structural traits, examples and notes on whether corresponding common nomenclatures (including acronyms) exist.



\* Strictly speaking, these substances are not fluorotelomers, as they are not derived from the telomerization process. Despite this, they are termed here "n:1 fluorotelomer-based" substances for readability. Future work may consider to identify more proper terminology for this group of PFASS.  
 \*\* Note that for many compounds such as HFP and TFE, there are different synthesis routes with different starting materials, and here shows only one of them.  
 \*\*\* Note that there are three synthesis routes shown here for manufacturing of PFCAs, from PACFs, PFAIs and n:2 FTIs. Note that different synthesis routes may generate PFCAs with different perfluorocarbon chain lengths.  
 Sources: (1) Siegemund G, Schwetfeger W, Feiring A, Smart B, Behr F, Vogel H, McKusick B. *Fluorine Compounds, Organic*, 3rd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; Vol. 33. (2) Banks RE, Smart BE, Tatlow JC. Organofluorine Chemistry: Principles and Commercial Applications. New York: Plenum, 1994. (3) Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, De Voogt P, Jensen AA, Kannan K, Mabury SA, van Leeuwen SPI. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr Environ Assess Manag* 2011, 7 (4), 513–541. (4) Wang Z, Cousins IT, Scheringer M, Buck RC, Hungerbühler K. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030. Part I: production and emissions from quantifiable sources. *Environ Int* 2014, 70, 62–75. (5) Moffett RH, Howell JL, Hoerter JM, Sitarov AB, Jannerfeldt G, Johnston SB, Keenan J, Warriner C, Closser DM. *Perfluoroalkylpolyethers in Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology* (third edition), Edited by Rudnick LR. 2020. CRC Press. ISBN: 978-1-138-06821-6. (6) Grot W. *Fluorinated Ionomers*. William Andrew 2011. ISBN: 978-1-437-74457-6.

Figure 10. An overview of some common synthesis routes of different individual or groups of PFASSs based on publicly accessible source

## Notes

<sup>9</sup> Note that a “saturated carbon moiety” means no unsaturated bonds occurring in the moiety, including double bond (=), triple bond ( $\equiv$ ) or aromatic rings, and thus, a saturated carbon moiety is always considered aliphatic.

<sup>10</sup> According to Buck et al., fluoropolymers are “*carbon-only* polymer backbone with F directly attached to backbone C atoms”, whereas perfluoropolyethers are “*ether* polymer backbone with F atoms directly attached” (i.e. having –C–O–C– moieties on the polymer backbone).

<sup>11</sup> (HO)<sub>2</sub>(O)PO–(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>–CH<sub>2</sub>CF<sub>2</sub>–(OCF<sub>2</sub>)<sub>p</sub>–(OCF<sub>2</sub>CF<sub>2</sub>)<sub>q</sub>–OCF<sub>2</sub>CH<sub>2</sub>–(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>–OP(O)(OH)<sub>2</sub>; Trier X, Granby K, Christensen JH. Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. *Environ Sci Pollut Res Int.* 2011;18(7):1108-1120. doi:10.1007/s11356-010-0439-3

<sup>12</sup> In Buck et al. (2011), side-chain fluorinated polymers are defined as “nonfluorinated polymer backbone with fluorinated side chains”.

# Chapter 3. Practical Guidance on How to Use the PFAS Terminology

As shown above, PFASs are a chemical class with diverse molecular structures (e.g. neutral, anionic, cationic or zwitterionic; with or without aromatic rings; non-polymers or polymers; low molecular weight or high molecular weight) and thus diverse physical, chemical and biological properties (e.g. involatile or volatile; water soluble or water insoluble; reactive vs. inert; bioaccumulative or non-bioaccumulative). Therefore, it is highly recommended that such diversity be properly recognized and communicated in a clear, specific and descriptive manner. The following sections aim to provide practical guidance to governments and other stakeholders on how to use the PFAS terminology, starting from the distinction between the general definition described here and user-specific working scopes of PFASs. An overarching rationale behind the practical guidance is to use and build upon existing common terminologies such as in this report, in Buck et al. (2011) and common practices in organic chemistry as set by IUPAC and CAS, unless it is essential to deviate from existing naming conventions in order to keep the consistence and coherence of the PFAS terminology.

## 3.1. Distinction between the General Definition and User-Specific Working Scopes of PFASs

It should be noted that the revised definition of PFASs in Section 2.3 refers to a general definition of PFASs that is coherent and consistent across compounds based on chemical structure and is easily implementable for distinguishing between PFASs and non-PFASs, also by non-experts. It does not include any minimal or maximal chain length requirements, or any other considerations beyond chemistry. It also does not conclude that all PFASs have the same properties, uses, exposure and risks.

While this general definition of PFASs may be viewed as too broad, encompassing thousands or more compounds, for anyone to address all of them at once, it serves as a starting and reference point to guide individual users to have a comprehensive understanding of the PFAS universe and to keep the big picture of the PFAS universe in mind. At the same time, individual users may define their own PFAS working scope for a specific activity according to their specific needs by combining this general definition of PFASs with additional considerations (e.g. specific properties, use areas). For example, the US Interstate Technology & Regulatory Council (ITRC)<sup>13</sup> used a working scope of “C<sub>n</sub>F<sub>2n+1</sub>” (n>2) in making its own PFAS fact sheets. Another example is the working scope used in compiling the OECD 2018 PFAS List, namely –C<sub>n</sub>F<sub>2n</sub>– (n ≥3) and –C<sub>n</sub>F<sub>2n</sub>OC<sub>m</sub>F<sub>2m</sub>– (n and m ≥1). Also, the addition of criteria such as bioavailability and persistence in Gore Fabrics’ Goal and Roadmap<sup>14</sup> for Eliminating PFCs of Environmental Concern may be regarded as a way of setting working scopes.

This report does not make any recommendation on how a working scope should be set up regarding which factors to consider (which depend on specific local context)<sup>15</sup>, nor on PFAS grouping<sup>16</sup>. However, when a working scope of PFASs is used, this report highly recommends that users clearly provide the context and rationale for selecting their PFAS working scope in order to provide transparency and avoid confusion by others.

### 3.2. Practical guidance on how to identify and use suitable PFAS terms

The term “PFASs” does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety. In addition, particularly for PFASs without an assigned CAS No., a lot of parallel and often non-intuitive acronyms are employed, potentially prohibiting effective communication and creating barriers for synthesizing knowledge. This section aims to provide practical guidance on how to identify and use suitable terms to foster communication around PFASs with the aim of being accurate, precise, understandable by others, and consistent.

First, it is strongly recommended that the PFAS terminology be used in a clear, specific and descriptive manner. It should be noted that “PFASs” is a broad, general, non-specific term, which should only be used when talking about all the substances included in the PFAS definition described here (or the user should clearly define the scope of which substances are being referred to as PFASs in the documents they prepare). Otherwise, it would introduce ambiguity and even factual error in the statements (as occurred sometimes in past literature). For example, not all PFASs are surfactants, and thus, a statement “PFASs are surfactants” is factually inaccurate. Table 1 highlights examples of ambiguous statements, which when are overgeneralized may lead to ambiguity, and factual inaccuracies and miscommunication in some cases. Therefore, it is recommended that users always ask the following two questions when drafting a statement: (1) Am I referring to all PFASs or not? (2) If not, what term(s) would mostly clearly describe the substance(s) that my statement is referring to? There could be multiple ways by users to locate the right levels of terms that are clear, specific and descriptive for specific statements, by combining and ordering traits such as polymeric vs. non-polymeric, PFAAs vs. PFAA precursors, or side-chain fluorinated polymers vs. fluoropolymers vs. perfluoropolyethers. Figure 11 shows different levels of PFAS terms and their respective characteristics in terms of clarity and specificity, along with examples; one may either start from Level 1 (most general) and move downwards (with the question of whether it is specific enough), or Level 5 (most specific) and move upwards (with the question of whether it can be further generalized), to locate the right level of terms for a specific statement. Table 1 also includes examples of good practice to refine ambiguous statements using more suitable terms. Furthermore, individual PFASs need to be named in a clear, specific and descriptive manner.

**Table 1.** Examples of ambiguous statements and associated good practices of using more specific PFAS terminology to refine these statements

<b>Examples of ambiguous statements (which may also result in factual inaccuracy in some cases)</b>	<b>Examples of good practices of using the PFAS terminology to avoid errors and reduce ambiguity</b>	
	<b>(1) Using more specific PFAS terms</b>	<b>(2) Adding qualifiers (less favorable than (1), as it remains quite ambiguous)</b>
PFASs were investigated in human milk.	<b>C<sub>4</sub>–C<sub>14</sub> PFCAs</b> were investigated in human milk.	<b>15 non-polymeric</b> PFASs were investigated in human milk.
PFASs are used to make protective coatings on common household products.	<b>Fluorotelomer-based side-chain fluorinated polymers</b> are used to make protective coatings on common household products.	<b>A number of polymeric</b> PFASs are used to make protective coatings on common household products.
PFASs are relatively ubiquitous in the environment at low concentrations. (factually inaccurate)	<b>PFCAs</b> are relatively ubiquitous in the environment at low concentrations.	<b>A number of</b> PFASs are relatively ubiquitous in the environment at low concentrations.
PFASs are water repellent, oil, grease and dirt repellent surfactants. (factually inaccurate)	<b>Many perfluorooctane sulfonyl fluoride-based derivatives</b> are water-, as well as oil-, grease- and dirt-repellent surfactants.	<b>A number of</b> PFASs are water-, as well as oil-, grease- and dirt-repellent surfactants.

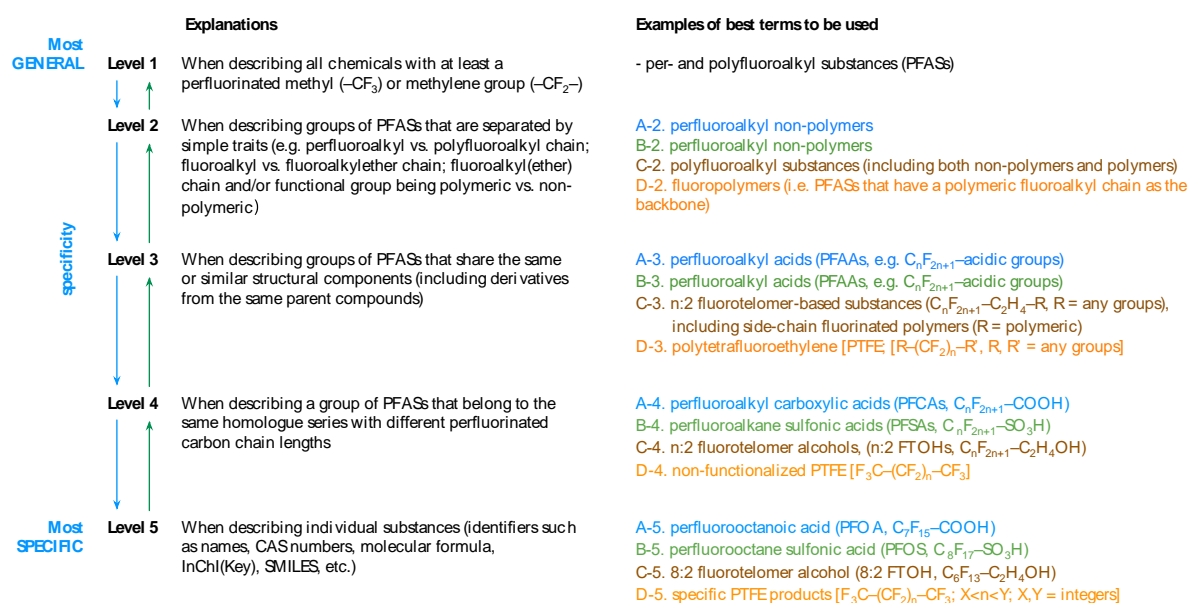


Figure 11. A visual guide to identify the best terms to use for a specific statement with four examples (increasing level of specificity illustrated with same colour within examples).

Second, if users are not sure about how to name a specific compound, it is recommended to first check whether a common nomenclature (including a common acronym) already exists, e.g., in Buck et al. (2011), Barzen-Hanson et al. (2017)<sup>17</sup>, this report and other studies, before creating their own naming conventions. For example, for CAS No. 678-39-7, a common name “8:2 fluorotelomer alcohol” and a common acronym “8:2 FTOH” already exist, and should be used instead of other synonyms.

Third, acronyms are often necessary in communicating PFASs to avoid writing very long names all the time; however, the same acronym may refer to different full names or different forms of the same substance (e.g. the parent acid, the anion form, and various salt forms), depending on context and personal understanding. To avoid confusion, it is recommended that acronyms be spelled out when being mentioned for the first time in the text and used consistently throughout the text.

Fourth, while chemical names and associated acronyms are the most common chemical identifiers being used, it is also recommended that other more specific identifiers such as CAS No., SMILES (simplified molecular input line entry specification), InChI (international chemical identifier), InChIkey (a hashed version of the full InChI) and/or structural formula<sup>18</sup> are provided for possibilities of cross-checking. This may also be useful in reporting the chemical identities of PFASs that have been registered as substances of unknown or variable composition, complex reaction products, or biological materials (UVCBs, e.g., CAS No. 69991-67-9 = 1-propene, 1,1,2,3,3,3-hexafluoro-oxidized, polymd.)<sup>8</sup>.

## Notes

<sup>13</sup> The latest version of the fact sheet on naming conventions of PFASs is from April 2020: [https://pfas-1.itrcweb.org/fact\\_sheets\\_page/PFAS\\_Fact\\_Sheet\\_Naming\\_Conventions\\_April2020.pdf](https://pfas-1.itrcweb.org/fact_sheets_page/PFAS_Fact_Sheet_Naming_Conventions_April2020.pdf)

<sup>14</sup> Here it refers to the version published on January 31, 2017, which can be found at: [https://drive.google.com/file/d/0BxvQ\\_I44P\\_9eeTlwYUJCekhLNIE/view](https://drive.google.com/file/d/0BxvQ_I44P_9eeTlwYUJCekhLNIE/view)

<sup>15</sup> Future work compiling various existing practices of defining working scope under different context may be beneficial to provide further guidance to governments and other stakeholders on this matter.

<sup>16</sup> In a recent scientific article, various grouping strategies for PFASs were reviewed and the motivations, advantages and disadvantages for each approach were discussed; for more details, see Cousins et al. 2020. *Environmental Science: Processes & Impacts*, 22, 1444–1460, <https://doi.org/10.1039/D0EM00147C>

<sup>17</sup> In the Supporting Information, Barzen-Hanson et al. developed a simplified, manual IUPAC-based naming system for the PFASs that they identified in their non-target screening. For more details, see Barzen-Hanson et al. 2017. *Environmental Science & Technology*. 51(4), 2047–2057. <https://doi.org/10.1021/acs.est.6b05843>

<sup>18</sup> These identifiers may be found and verified using online databases, such as the CAS Common Chemistry (<https://commonchemistry.cas.org>), ChemSpider (<http://www.chemspider.com>), NORMAN Suspect List Exchange (<https://www.norman-network.com/?q=suspect-list-exchange>), OECD eChemPortal (<https://www.echemportal.org/echemportal/>), PubChem (<https://pubchem.ncbi.nlm.nih.gov/classification/#hid=101>), SciFinder (<http://scifinder.cas.org>) and US EPA CompTox Chemicals Dashboard ([https://comptox.epa.gov/dashboard/chemical\\_lists/PFASOECD](https://comptox.epa.gov/dashboard/chemical_lists/PFASOECD)).



## Chapter 4. Systematic characterization and categorization of PFASs

As users often define their own working scope of PFASs according to their specific needs (see Section 3.1), they need to characterize PFASs based on molecular structures (and other considerations) and then categorize them by comparing characterization traits against specific needs (e.g. whether a compound falls or does not fall into their working scope). For example, the recent listing of PFOA and PFOA-related compounds under the Stockholm Convention requires regulators across the world to be able to identify PFOA-related compounds from a pool of PFASs.

However, given the high complexity and diversity of PFASs, it can be a challenging task to characterize and categorize PFASs based on their chemical structures in a coherent and consistent manner, particularly for non-experts. Detailed challenges may include needs of specialized chemistry knowledge (e.g. on transformation), different interpretations of structural traits by users for different groups of PFASs, and potential for human errors including oversights and typing errors (Sha et al. 2019). In addition, different users may have very different needs, and there is no single categorization/grouping system that can meet all needs.

Therefore, this section provides a standardized system for systematic characterization of different PFASs based on molecular structural traits that will allow stakeholders to make their own categorization in a coherent and consistent manner. Molecular structure-based elements of such a characterization system are provided in Table 2, with some examples of applications given in Table 3. For example, if someone would like to have the grouping of linear PFCAs, they would just need to search for molecules with the right characterization traits as defined in Table 3: under “fluorinated carbon chain (A)”, having “alkyl”, “perfluoro”, “linear”, “saturated”, “non-polymeric”; under “functional group B”, having “COOH” and “non-polymeric”; and under “stoichiometry between A and B”, having “1:1”. The system is flexible for future refinement including possible addition of new elements as needed and also applications to new groups of PFASs as identified.

In addition to manual application of the system to characterize and categorize PFASs, the elements presented here may also be used as inputs for developing cheminformatic tools that would allow automatized characterization and categorization of PFASs, as demonstrated in Sha et al. (2019).

In that study, an algorithm was developed to systematically parse a PFAS molecule into three fragments namely  $C_nF_{2n+1}-X-R$ , where  $C_nF_{2n+1}-$  refers to the fluorinated carbon moiety and  $-X-R$  refers to functional group moiety. X was used to identify whether a PFAS molecule falls into the target group of perfluoroalkane sulfonyl fluoride-derivatives (where  $X = SO_2$ ), perfluoroalkanoyl fluoride derivatives (where  $X = CO$ ), n:1 fluorotelomer-based compounds (where  $X = CH_2$  and R does not have a  $CH_2$  or  $CH$  moiety connecting with X), or n:2 fluorotelomer-based compounds (where  $X = CH_2CH_2$ ). The algorithm was applied to a set of 770 PFASs from the OECD 2018 PFAS List and identified PFASs from the target four groups as intended. The algorithm was also able to identify PFASs that were mis-categorized in the OECD 2018 PFAS List, as the original categorization was done manually.

The algorithm developed in Sha et al. (2019) serves as a proof-of-concept, and thus has its limitations in terms of its purpose (i.e. to identify whether a PFAS falls into one of the four target groups) and function



(e.g. it cannot handle PFASs with more than one functional group moieties). However, it shows the potential of such cheminformatics approaches, which can be expanded using the elements provided here for systematic characterization and categorization of PFASs in a coherent and consistent manner, particularly for non-PFAS experts. It needs to be noted that tools proposed here that integrate the concept presented in Sha et al. (2019) and the proposed elements of a characterization system is one way of developing cheminformatics-based tools for systematic characterization and categorization of PFASs. Depending on the needs, there may also be other ways of doing so, including adding other elements into consideration (e.g. a ToxPrints approach that also considers structures related to adverse outcomes<sup>19</sup>) or implementing in other ways (e.g. using Markush structures to annotate existing lists<sup>20</sup>). An outlook of future developments is provided in the next section.

**Table 2.** Molecular structure-based elements of a characterization system for PFASs.

PFASs may be parsed into the following two structural parts	Molecular structure-based elements to be considered	Note
<b>Fluorinated carbon chain (A)</b>	alkyl vs. alkylether	Whether the fluorinated carbon chain is carbon only or has oxygen-linkage(s) between fluorinated carbons e.g., $-C_nF_{2n}-$ vs. $-C_nF_{2n}-O-C_mF_{2m}-$
	perfluoro vs. polyfluoro	Whether all hydrogen on the fluorinated carbon chain are replaced by fluorine (i.e. perfluoro) or not (i.e. polyfluoro) e.g., $H-C_2F_4-$ , $Cl-C_2F_4-$ , $CF_3CF_2-C_2H_4-C_2F_4-C_2H_4-$ , $CF_3CF_2-CH_2-CF_2-CH_2-CF_2-$ , etc. = polyfluoro
	linear vs. branched vs. cyclic	Whether the fluorinated carbon chain is linear, branched or cyclic e.g., $-C_6F_{13}$ vs. $-C_3F_6CF(CF_3)_2$ vs. $-cyclo(C_6F_{12})$
	saturated vs. non-saturated	Whether there is any unsaturated bond (a double or triple bond) in the fluorinated carbon chain e.g., $-CF_2CF_2-$ vs. $-CF=CF-$
	polymeric vs. non-polymeric	Whether the fluorinated carbon chain is polymeric or non-polymeric e.g. using the OECD definition ( <a href="http://www.oecd.org/env/ehs/oecddefinitionofpolymer.htm">http://www.oecd.org/env/ehs/oecddefinitionofpolymer.htm</a> ) [Note: this may require additional consideration, e.g. whether a minimum perfluorocarbon moiety chain length of 20 would be required] <sup>21</sup>
	chain length of the fluorinated carbon chain	e.g., for perfluoroalkylether-based substances, the total length of perfluoroalkylether moieties including both carbon and oxygen atoms will be counted, and additional information on the number of oxygen atoms will be provided as supplementary information, similarly to what is in the OECD 2018 list.

<b>Functional group (B)</b>	types and structures of functional groups	<p>As there is no common classification system of functional groups, here a simplified scheme is proposed that is intended to distinguish those reactive and non-reactive (or those not so reactive) groups under natural conditions, which can be used to differentiate e.g. PFAAs and PFAA precursors.</p> <ol style="list-style-type: none"> <li>1. Non-reactive groups (or those not so reactive) <ol style="list-style-type: none"> <li>1.1. H, Cl, Br</li> <li>1.2. N, P</li> <li>1.3. COOH</li> <li>1.4. SO<sub>3</sub>H</li> <li>1.5. PO<sub>3</sub>H<sub>2</sub></li> </ol> </li> <li>2. Reactive groups <ol style="list-style-type: none"> <li>2.1. I</li> <li>2.2. SO<sub>2</sub>H – sulfinic acids</li> <li>2.3. PO<sub>2</sub>H</li> <li>2.4. CH<sub>2</sub>-R – possibly n:1 fluorotelomers</li> <li>2.5. CH<sub>2</sub>CH<sub>2</sub>-R – possibly n:2 fluorotelomers</li> <li>2.6. CO-R (other than COOH) – alkanoyl fluoride-derivatives</li> <li>2.7. SO<sub>2</sub>-R (other than SO<sub>2</sub>OH) – sulfonyl fluoride-derivatives</li> <li>2.8. C<sub>m</sub>H<sub>2m+1</sub>, OC<sub>m</sub>H<sub>2m+1</sub>, C<sub>m</sub>H<sub>2m-1</sub></li> </ol> </li> <li>3. Others (which may be refined in future work)</li> </ol>
	polymeric vs. non-polymeric	<p>Whether the non-fluorinated functional group is polymeric or non-polymeric, e.g. using the OECD definition (<a href="http://www.oecd.org/env/ehs/oecddefinitionofpolymer.htm">http://www.oecd.org/env/ehs/oecddefinitionofpolymer.htm</a>)</p> <p>[Note: this may require additional consideration of additional qualifier, e.g. whether a minimum chain length of 20 would be required]</p>
<b>stoichiometry between A and B</b>	How are fluorinated carbon chain(s) connected with non-fluorinated carbon chain(s)/functional groups?	1:0 = no functional group
		1:1/1:2/1:3 = one fluorinated carbon chain connected with 1/2/3 functional group(s)
		2:1 = two fluorinated carbon chains connected with one functional group, e.g. PFPIAs

**Table 3.** Examples using the proposed characterization system.

	Possible elements to be considered	Example 1: Linear PFCAs	Example 2: PFOA precursors	Example 3: ADONA	Example 4: 6:2 FT-acrylate polymer	Example 5: PTFE with -COOH on each end
<b>Fluorinated carbon chain (A)</b>	alkyl vs. alkylether	Alkyl	Alkyl	Alkylether	Alkyl	Alkyl
	perfluoro vs. polyfluoro	Perfluoro	Perfluoro	Polyfluoro	Perfluoro	Perfluoro
	linear vs. branched vs. cyclic	Linear	Linear + Branched	Linear	Linear	Linear
	saturated vs. non-saturated	Saturated	Saturated	Saturated	Saturated	Saturated
	polymeric vs. non-polymeric	Non-polymeric	Non-polymeric	Non-polymeric	Non-polymeric	Polymeric
	chain length	1–20	>=7 (in the case of when A and B connects via a carbon atom); >=8 (in the case of when A and B connects via other atoms other than a carbon atom)	6 + 20	6	XX
<b>Non-fluorinated functional group (B)</b>	types and structures of functional groups	1.3 COOH	2 Reactive groups	1.3 COOH	2.5 CH <sub>2</sub> CH <sub>2</sub> -R – possibly n:2 fluorotelomers	1.3 COOH
	polymeric vs. non-polymeric	Non-polymeric	Non-polymeric; polymeric	Non-polymeric	Polymeric	Non-polymeric
<b>Connection between A and B</b>	How are fluorinated carbon chain(s) connected with non-fluorinated carbon chain(s)?	1:1	1:1	1:1	n:1	1:2

## Notes

<sup>19</sup> For an example, see

[https://figshare.com/articles/presentation/PFAS\\_Toxprints\\_A\\_Hierarchical\\_Structure-Based\\_Categorization\\_Method\\_for\\_Characterization\\_of\\_Per-\\_and\\_Polyfluoroalkyl\\_Substances/12834329](https://figshare.com/articles/presentation/PFAS_Toxprints_A_Hierarchical_Structure-Based_Categorization_Method_for_Characterization_of_Per-_and_Polyfluoroalkyl_Substances/12834329). Currently, the US EPA is preparing a manuscript on this approach, including means for applying it.

<sup>20</sup> A Markush structure is a generic type of description of chemicals used to summarize a potentially very large set of closely related chemicals in a single condensed representation. It may consist of a “core” chemical structure and a list of possible substituents attached to it, with four substituent options: substituent variation (allowing different substituents at a position), position variation (allowing different attachment points for a substituent), frequency variation (allowing substituents to occur multiple times) and homology variation (using generic expressions covering many specific substituents like “alkyl”). For more details, see, e.g., Geyer P. 2013. *World Patent Information*, 35(3), 178–182, <https://doi.org/10.1016/j.wpi.2013.05.022>.

The US EPA CompTox Chemicals Dashboard uses “Markush structures” to organize its PFAS list. In brief, the Dashboard has curated 112 PFAS Markush structures with unique DTXSIDs assigned (e.g. DTXSID80893896 HOOC–(CF<sub>2</sub>)<sub>n</sub>–COOH for perfluoroalkyl (linear) dicarboxylic acids, i.e. homology variation). Each PFAS Markush structure is considered a generalized substance or “parent ID” that can be associated with one or many “child IDs” within the Dashboard (e.g. DTXSID80893896 are linked to 12 linear perfluoroalkyl dicarboxylic acids with different fluorinated carbon chain lengths in the Dashboard). For more details, see [https://comptox.epa.gov/dashboard/chemical\\_lists/EPAPFASCAT](https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASCAT).

<sup>21</sup> In many jurisdictions, a polymer is defined as a substance that has over 50 percent of the weight consisting of polymer molecules and the amount of polymer molecules presenting the same molecular weight must be less than 50 weight percent of the substance. A polymer molecule is defined as a molecule that contains a sequence of at least 3 monomer units, which are covalently bound to at least one other monomer unit or other reactant. Thus, a mixture of 8:2, 10:2 and 12:2 fluorotelomers (each 33%) can theoretically be regarded as a polymer.



## Chapter 5. Areas for Future Work

While this report makes advancement on several important points regarding the PFAS terminology and practical guidance of how to use the PFAS terminology, it also recognizes that the following four areas warrant further work within the field of PFASs (i.e. areas one and two) and beyond (i.e. areas three and four), in order to facilitate clear and unambiguous communication of PFASs.

First, a centralized PFAS nomenclature database/platform may be considered. With the further advancement and application of non-target screening methods, many more unknown PFASs are expected to be discovered in the future. Such a centralized nomenclature database/platform can help foster the use of harmonized names and acronyms for the same compounds. It can also help to link different common names and acronyms that have been used over time to specific substances.

Second, further development of cheminformatics-based tools for automated systematic characterizing and categorizing PFASs would advance the field. A solely structure-based approach proposed in the report (i.e. Chapter 4) may serve as one starting point for possible joint development of an open source tool by experts from different online databases/platforms so that such a tool may be compatible for different online databases/platforms. In addition, as cheminformatics is a fast-developing field, future work may be conducted to monitor, assess and communicate which cheminformatics tools are developed for which purposes.

Third, further work on the characterization and reporting of polymers should be considered, as well as assessment of their properties. The current definitions of polymers in many jurisdictions originate from the OECD definition of polymer that was developed in the early 1990s, and in some cases, substances containing a significant fraction of low-molecular-weight molecules may be identified as polymers, as indicated in Footnote 21. This may impact how individual substances are registered (or not registered) and subsequent regulatory requirements of safety information. Thus, chemical compositions in substances that are identified as polymers may warrant a closer look, particularly in terms of their low-molecular-weight content, based on lessons learned in the past three decades. In addition, the current reporting of many polymers are often rather ambiguous (e.g. a polymer may be named as a co-polymer of three monomers A, B and C without indicating how the monomers are connected and in which molecular ratios, reaction schemes and molecular weight range of individual compositions, which could have implications on assessing the fate, behavior and risks of specific polymer products). Thus, future international efforts are needed to look into ways to improve the understanding of polymer structures including access to necessary information, focusing on polymeric PFASs or on polymers in general.

Fourth, as shown in Figure 8, there are many groups of organofluorine substances other than PFASs. Future work could also look into these compounds, including the terminology of many fluorinated aromatics.



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This report summarizes recent efforts by the OECD/UNEP Global PFC Group in reviewing the universe and terminology of per- and polyfluoroalkyl substances (PFASs) to provide recommendations and practical guidance to all stakeholders with regard to the terminology of PFASs.

In particular, this report highlights a revised PFAS definition to comprehensively reflect the universe of PFASs, practical guidance on how to use the PFAS terminology, a systematic approach to characterization of PFASs based on molecular structural traits to assist stakeholders, including non-experts, in making their own categorization based on their needs, and areas in relation to the PFAS terminology that warrant further development.

[oe.cd/pfass](https://oe.cd/pfass)

