Per- and Polyfluoroalkyl Substances (PFAS)

Working Description of PFAS Based on Chemical Structure

Prepared by a Subgroup of the Michigan PFAS Action Response Team (MPART) Technical Advisory Workgroup (TAWG) supported by and in conjunction with the Michigan Department of Environment, Great Lakes, and Energy (EGLE) and the Michigan Department of Health and Human Services (MDHHS)

October 23, 2023

Executive Summary

The purpose of this document is to recommend a chemical structure-based description for per- and polyfluoroalkyl substances (PFAS). Considering information on PFAS continues to evolve, the Michigan PFAS Action Response Team (MPART) Technical Advisory Workgroup (TAWG) agreed to refer to this document as a "working PFAS description" and not a definition. This will give this description the flexibility to be revised as needed to incorporate new developments in our understanding of PFAS from the peer-reviewed literature.

The recommended PFAS working description borrows from other descriptors including from OECD 2021 and EPA Toxic Substances Control Act (TSCA). The structure would include two adjacent fluorinated carbons, with the addition of perfluoroalkyl ethers where those two fluorinated carbons are separated by an oxygen atom. This is the first step taken to identify PFAS based on chemical structure. In the future, the Subgroup will consider other physicochemical and toxicological properties.

Table of Contents

Acronyms

CAS	Chemical Abstract Service
ECHA	European Chemicals Agency
EGLE	Michigan Department of Environment, Great Lakes, and Energy
EPA	United States Environmental Protection Agency
EU	European Union
HHWG	Human Health Workgroup
HSDB	Hazardous Substances Data Bank
IRIS	Integrated Risk Information System
MPART	Michigan PFAS Action Response Team
NDAA	National Defense Authorization Act
NOL	Not Otherwise Listed
OECD	Organization for Economic Co-operation and Development
PFAS	Per- and Polyfluoroalkyl Substances
PFBS	Perfluorobutanesulfonic acid
PFC	Per- and polyfluorinated chemical
PFCA	Perfluoroalkyl carboxylic acids
PFECHS	Perfluoroethylcyclohexane sulfonate
PFNA	Perfluorinonanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PTFE	Polytetrafluoroethylene
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
SDS	Safety Data Sheet
TAWG	Technical Advisory Workgroup
TRI	Toxics Release Inventory
TSCA	Toxic Substances and Control Act
TURA	Toxics Use Reduction Act
UNEP	United Nations Environment Programme
vPvB	Very Persistent and Very Bioaccumulative

Background

During a Michigan PFAS Action Response Team (MPART) Technical Advisory Workgroup (TAWG) meeting, members of the MPART Air Quality Workgroup inquired how MPART is defining PFAS. The Executive Director asked members of the TAWG to investigate the topic and make recommendations. A Subgroup of the TAWG (hereinafter Subgroup) was formed, and a draft recommendation for PFAS description based on chemical structure was provided and presented to the TAWG on September 9, 2020. TAWG accepted the draft description with the recommendation to refer to it as a "working description of PFAS structure" rather than a PFAS definition.

Since its formation, the Subgroup has updated the working description twice based on newly available information from various peer-reviewed literature sources, government agencies, and non-government organizations. The intent is to have an inclusive description that combines available information from peer-reviewed literature, government agencies, and non-governmental organizations. See Section "MPART PFAS Descriptions," below, for all previous and current versions of the working description. Note, the knowledge of PFAS is continually evolving, and the Subgroup will continue to review new information as it becomes available.

Terminology

PFAS stands for per- and polyfluoroalkyl substances and is an entire family of thousands of chemicals. PFAS is plural since "S" in the acronym stands for "substances" and not "substance." When we say a chemical is PFAS, we intend to say it belongs to the PFAS family. No single chemical within the family can be both perfluorinated and polyfluorinated[1]. It is more accurate to simply use the acronym for that specific chemical. For example, using PFBS for perfluorobutane-sulfonic acid or PFNA for perfluorononanoic acid, etc.

For the purposes of this paper, PFAS refers to the entire family of chemicals. The word "substance" is used when referring to an individual chemical within the family. Note, organizations have used "PFASs," "PFAS compounds," and "PFAS congeners," among others, when referring to PFAS.

Current PFAS Definitions in the Literature

The Subgroup conducted a literature search in August 2022 to identify PFAS definitions in the peer-reviewed published literature. This search identified several unique definitions of PFAS since 2011. These definitions are described below in chronological order. The following resources or databases were searched using the keywords – *PFAS*, *defin**, *toxic**:

i. PubMed
ii. PubChem
iii. SciFinder
iv. ProQuest
v. Google Scholar
vi. Hazardous Substances Data Bank (HSDB)
vii. European Chemicals Agency (ECHA)
viii. National Defense Authorization Act (NDAA)
ix. Organization for Economic Co-operation and Development (OECD)
x. Toxics Use Reduction Act (TURA)
xi. United States Environmental Protection Agency (EPA)

[1] 2.2 Chemistry, Terminology, and Acronyms – PFAS — Per- and Polyfluoroalkyl Substances (itrcweb.org)

a. Integrated Risk Information System (IRIS)
b. CompTox
c. Toxic Substances and Control Act (TSCA)

xii. Peer-reviewed literature

See Appendix A for a comprehensive summary of the available working descriptions and definitions of PFAS from 2011 to 2022. The evolution in these descriptions can be seen by comparing from top to bottom, which corresponds to the time of their publication.

Note, these definitions described below are based on the chemical structure of the compounds and do not provide specific information about a compound's harm to human health and/or the environment.

1. Buck et al. (2011)

According to Buck et al., PFAS are defined as "a subset of fluorinated substances is the highly fluorinated aliphatic substances that contain 1 or more C (carbon) atoms on which all the H (hydrogen) substituents (present in the non-fluorinated analogues from which they are notionally derived) have been replaced by F (fluorine) atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1}–."

Based on this definition, a number of chemicals would classify as PFAS, but the exact number is not known. However, the article lists 42 families and subfamilies of PFAS and only 268 selected individual compounds with recommendations for names, acronyms, structural formula, and Chemical Abstract Service (CAS) registry numbers. There are more than 268 chemicals that would qualify as PFAS according to Buck et al. (2011).

The Subgroup had one concern with the Buck et al. (2011) definition. The definition does not specify the inclusion of cyclic compounds or analogues of linear PFAS, containing unsaturated hydrocarbon rings with double and single bonds. It can be interpreted that aliphatic cyclic structures that have much in common with non-cyclic or linear PFAS, described above, would fit the Buck et al. (2011) definition; however, there is confusion and inconsistencies as to how OECD and other peer-reviewers interpret the Buck et al. (2011) definition.

For example, Gluge et al. (2020) mentions:

> In contrast to the definition by Buck et al. (2011), the present study also includes (i) substances where a perfluorocarbon chain is connected with functional groups on both ends, (ii) aromatic substances that have perfluoroalkyl moieties on the side chains, and (iii) fluorinated cycloaliphatic substances.

In addition, Wang et al. (2021) detail four major limitations with the Buck et al. (2011) definition, including, "inconsistencies in dealing with homologues that are fully fluorinated aliphatic cyclic compounds with or without a fully fluorinated alkyl side chain."

The Subgroup agrees there are inconsistencies and uncertainties associated with inclusion of cyclic compounds. The Subgroup has not adopted the Buck et al. 2011 definition due to exclusion of chemicals with one fully fluorinated carbon that are attached to more than one but less than three fluorines. For example, structures with the formula C_nF_{2n+1} such as CF_3-R and CF_3-CF_2-R or C_2F_5-R are considered PFAS, whereas R-CF_2-R' and R-CF_2-CF-R'(R''), where R is not fluorine or hydrogen, are not considered PFAS according to this definition.

Additional Detail on Cyclic Compounds

The MPART Executive Director requested the Human Health Workgroup (HHWG) develop a whitepaper on perfluoroethylcyclohexane sulfonate (PFECHS). PFECHS (Figure 1) was analyzed for and detected in Great Lakes fish (De Silva et al., 2011) and it wasn't clear at the time if PFECHS should be considered PFAS because of its cyclic structure.

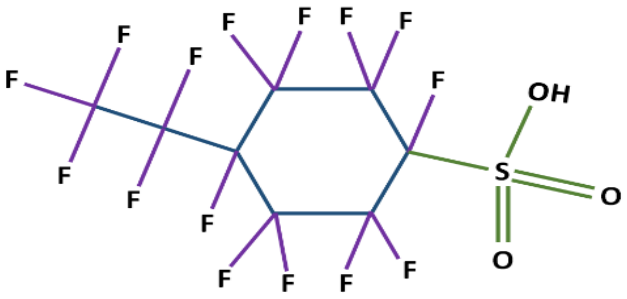


Figure 1. Structure of the neutral form of PFECHS. Adapted from "Emerging poly- and perfluoroalkyl substances in the aquatic environment: A review of current literature," by Xiao F. 2017, *Water Res, 124: p. 482-495*.

Excerpt from the MPART PFECHS Whitepaper:

PFECHS is an 8-carbon cyclic PFAS that is an analog of PFOS (meaning that the molecules share structural similarity) (MPART 2020). Commercially, PFECHS has been used as a replacement for PFOS in various formulations and has been reported in environmental media around the world. Since the 1940s, PFECHS has been used in aircraft hydraulic fluids, and studies have linked environmental contamination to aviation use (de Solla et al. 2012 and Macinnis et al. 2017).

The similarities of PFOS and PFECHS were examined using chemoinformatic tools. These compounds were found to have similar physicochemical properties such as molecular weight, boiling point, melting point, Henry's Law constant, octanol/air partition coefficient, vapor pressure, water solubility and structure[2]. Therefore, PFECHS is thought to have similar persistence in the environment and toxicokinetics (i.e., uptake and distribution) in humans and animals as PFOS (Liu et al. 2019, and Xiao et al. 2017).

Because of the similarities of PFECHS to PFOS, the Human Health Workgroup recommended that "MPART consider cyclic compounds, like PFECHS, as included structures when defining PFAS. This will allow MPART agencies to characterize the extent and concentrations of PFECHS in Michigan. Equipped with that information, the eventual emergence of reliable toxicological data will leave MPART agencies well-positioned to develop screening and health-based criteria for PFECHS" (MPART 2020).

2. National Defense Authorization Act (NDAA)

The NDAA Fiscal Year 2020 (FY2020) bill authorizes appropriations and sets forth policies for Department of Defense program and activities. Included in the FY2020 bill are policies for PFAS in which the NDAA defines "PFAS" as "perfluoroalkyl and polyfluoroalkyl substances that are man-made chemicals with at least one fully fluorinated carbon atom."

NDAA further defines the term "fully fluorinated carbon atom" as "a carbon atom on which all the hydrogen substituents have been replaced by fluorine."

[2] https://www.michigan.gov/-/media/Project/Websites/PFAS-Response/Workgroups/Human-Health/White-Paper-Physiochemical-Properties-Environmental-Contamination-Toxicity-PFECHS.pdf?rev=b86a48ec037549b29dbbace62c98fec8

This is a regulatory definition used for –

a. Reporting of PFAS in impacted media, such as surface water and groundwater, due to military activities;

b. Ban of PFAS in firefighting foam and equipment; and

c. Biomonitoring of PFAS in military personnel

A few other States also broadly define PFAS as class of chemicals containing at least one fully fluorinated carbon for reporting and eventual ban of PFAS in varied applications as listed below –

a. **California:** firefighting foam and equipment

b. **Washington:** firefighting foam and food contact materials

c. **Vermont:** firefighting foam and products used in rugs/carpets/food packaging/ski wax

d. **Maine:** any product containing intentionally added PFAS

The Subgroup did not adopt this definition because it was too broad and included chemicals such as CF_4, CF_3COOH, CF_3-CHF_2 that may already be regulated under existing protocols.

3. The Organization for Economic Co-operation and Development (OECD)

The OECD is an intergovernmental organization of 35 industrialized countries in North and South America, Europe, and the Asia and Pacific region, as well as the European Commission, that convene to discuss issues of mutual concern and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialized committees composed of member country delegates (OECD, 2018). This document discusses both the OECD 2018 and OECD 2021 PFAS reports. The 2018 OECD PFAS report[3] summarizes efforts by nine OECD/United Nations Environment Programme (UNEP) Global Per- and polyfluorinated chemical (PFC) Groups. Between January 2017 and February

[3] Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs): Summary report on updating the OECD 2007 list of per- and polyfluoroalkyl substances (PFASs)

2018, the Groups updated the OECD "Lists of Perfluorooctanesulfonic acid (PFOS), PFAS, Perfluorooctanoic acid (PFOA), Perfluoroalkyl carboxylic acids (PFCA), Related Compounds and Chemicals That May Degrade to PFCA," which had last been updated in 2007. The Group's goal was to provide a comprehensive list of PFAS that may have been on the global market (OECD, 2018).

Their definition broadens the list of compounds to include PFAS with both ends of the perfluoroalkyl moiety (i.e., $– C_nF_{2n}–$, n ≥ 3) (see Figure 2), or a perfluoroalkyl ether moiety with two or more carbons (i.e., $–C_nF_{2n}OC_mF_{2m}–$, n and m ≥ 1) (see Figure 3) connected to a functional group such as carboxyl (– COOH), carbonyl (– CO), etc. Functional groups are chemical motifs, or patterns of atoms that display consistent function, such as properties and reactivity, regardless of the exact compound in which they are found.

Figure 2. Structure of Hexafluoropentanedioic Acid (CAS # 376-73-8); Source: PubChem

Figure 3. Structure of Perfluoromethoxypropionyl fluoride (CAS # 425-38-7); Source: PubChem

The definition also includes cyclic compounds that are analogues of linear PFAS (OECD, 2018). The study identified 4,730 PFAS CAS numbers utilizing this definition (OCED, 2018). The Subgroup thought this definition to include more compounds than Buck et al. (2011); however, the definition was extended to only 3 or more carbons for compounds with the $-C_nF_{2n}-$ structural formula. This implies $-C_2F_4-$ and $-CF_2-$ are not considered PFAS according to this definition, which would

otherwise be considered fully fluorinated if either of the carbons are not directly attached to hydrogen atoms.

The more recent 2021 OECD report[4] compiles efforts between June 2018 and March 2021 of the OECD/UNEP Global PFC Group to revise the PFAS definition and provide recommendations and practical guidance to all stakeholders concerning PFAS terminology. As per the new OECD report:

> 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 ($–CF_3$) or a perfluorinated methylene group ($–CF_2–$) is a PFAS.

The rationale provided by OECD (2021) for their 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 PFAS and non-PFAS, by both experts and non-experts. 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.

According to the OECD 2021 definition, tetrafluoromethane (CF_4) (Figure 4) is considered PFAS based on its chemical structure; i.e., tetrafluoromethane contains one fully fluorinated methyl ($–CH_3$) carbon atom that is not attached to H/Cl/Br/I. The Subgroup believes this definition is too broad and may include chemicals already regulated under the existing protocols such as Kyoto and Montreal.

Figure 4. Structure of Tetrafluoromethane (CAS # 75-73-0); Source: PubChem

[4] https://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV/CBC/MONO(2021)25&docLanguage=en

While the OECD 2021 definition does not recommend all chemicals identified be regulated or subject to voluntary actions, it is recommended that users utilizing this definition should establish their own working scope according to their specific needs. Although the definition significantly broadens the number of compounds that may be considered PFAS, it allows flexibility for users to shape their working scope to focus efforts on compounds of interest.

4. United States Environmental Protection Agency (EPA)

The EPA has developed specific definitions to best address PFAS under different programs detailed below –

(i) EPA CompTox Chemicals Dashboard

EPA researchers within the National Center for Computational Toxicology curated and structure-annotated several registered and public PFAS lists, both from within and outside EPA. These public PFAS lists encompass PFAS of potential interest based on –

a. Manufacturing process data, which was procured for testing within EPA research programs; and
b. Environmental occurrence, either through literature reports or analytical detection.

An EPA representative with the Center for Computational Toxicology and Exposure, EPA, Research Triangle Park, North Carolina, gave a presentation to MPART staff on February 25, 2021, on the CompTox Database. The presentation detailed the use of substructures, shown below (Figure 5), to consolidate a list of PFAS of current interest to researchers and regulators worldwide. The "PFAS Master List of PFAS Substances," on the CompTox Chemicals Dashboard, currently lists 12,034 chemicals[5].

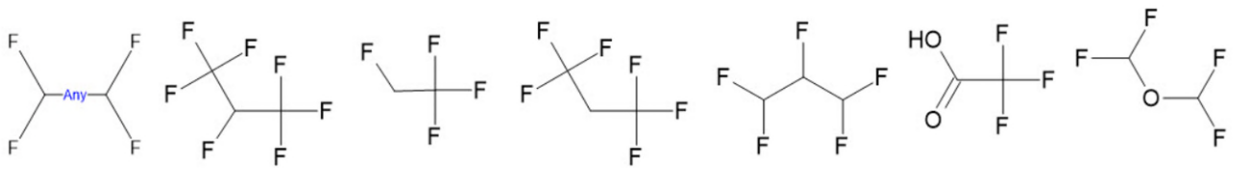


Figure 5. Substructures used to consolidate master list of PFAS; EPA's CompTox Chemicals Dashboard

[5] CompTox Chemicals Dashboard (epa.gov)

While there is not a specific definition for EPA CompTox, the substructures shown in Figure 5 were used to generate a list of 12,034 PFAS. This list includes chemicals with partially fluorinated carbons; i.e., carbon attached to one or more hydrogen atoms that have not been replaced by fluorine, that can be categorized as PFAS under EPA CompTox.

Based on OECD 2021 definition, only the following EPA substructures (Figure 6) meet the proposed definition for PFAS; i.e., any chemical with at least a perfluorinated methyl group (–CF_3) or a perfluorinated methylene group (–CF_2–), without any H/Cl/Br/I atom attached to the carbon atom.

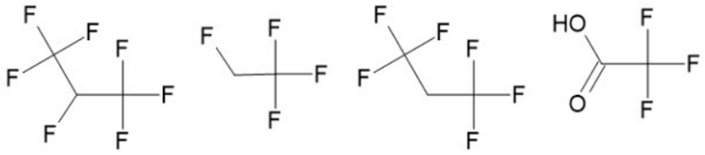


Figure 6. Substructures that meet OECD 2021 definition for PFAS. EPA's CompTox Chemicals Dashboard

(ii) Toxic Substances Control Act (TSCA)

In July 2022, EPA issued its final rule for PFAS reporting and recordkeeping requirements under TSCA. In accordance with obligations under TSCA, as amended by the NDAA for FY2020, EPA proposes to require any persons that manufacture (including import) or have manufactured these chemical substances in any year since January 1, 2011, to electronically report information regarding PFAS uses, production volumes, disposal, exposures, and hazards. EPA is requesting public comment on all aspects of this proposed rule and has also identified items of particular interest for public input. In addition to fulfilling statutory obligations under TSCA, this document will enable EPA to better characterize the sources and quantities of manufactured PFAS in the United States.

For the purposes of this proposed action, the structural definition of PFAS includes per- and polyfluorinated substances that structurally contain the unit R-(CF_2)-C(F)(R') R." Both the CF_2 and CF moieties are saturated carbons and none of the R groups (R, R' or R") can be hydrogen. See examples shown below in Figures 7 and 8.

Figure 7. Structure of Dichlorotetrafluoroethane (CAS # 76-14-2); Source: PubChem

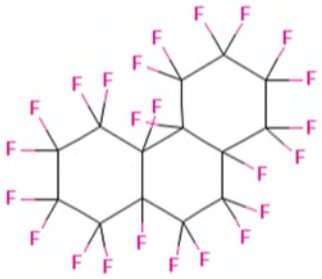


Figure 8. Structure of Perfluoroperhydrophenanthrene (CAS # 306-91-2); Source: PubChem

This is a provisional, not official, definition for the proposed PFAS Reporting Rule under TSCA and it should be noted that this structural definition of PFAS is a working description, which has been used by EPA's Office of Pollution Prevention and Toxics when identifying PFAS on the TSCA inventory. This definition may not be identical to other definitions of PFAS used within EPA.

The Subgroup considered this definition to be appropriate since it excludes a lot of chemicals with just one fully fluorinated carbon that may already be regulated under existing protocols.

5. Gluge et al. (2020)

In their paper, "An overview of the uses of per-and polyfluoroalkyl substances (PFAS)," Gluge et al. (2020) provide a broad, but not exhaustive, overview of the uses of PFAS and individual substances associated with each of them. These individual substances account for more than 1,400 PFAS in total. Gluge et al. used a working definition of PFAS to define the scope of PFAS considered in their study.

The study focuses on polymeric PFAS with $–CF_2–$ moiety (Figure 9), and non-polymeric PFAS with the $–CF_2–CF_2–$ moiety. It does not include non-polymeric

substances that only contain a $–CF_3$ or $–CF_2–$ moiety, with the exception of perfluoroalkyl ethers and per- and polyfluoroalkylether-based substances. For these two PFAS groups, substances with a $–CF_2OCF_2–$ or $–CF_2OCFHCF_2–$ moiety are also included (Figure 10).

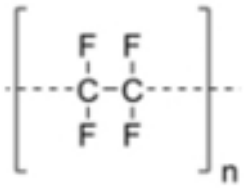


Figure 9. Example of polymeric PFAS. Polytetrafluoroethylene (PTFE) (CAS # 9002-84-0); Source: PubChem

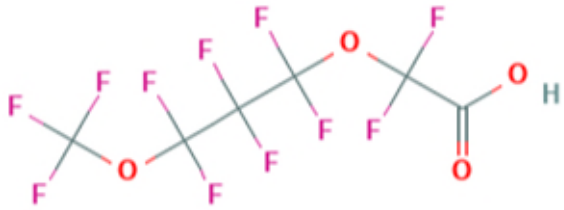


Figure 10. Structure of Perfluoro-2-[3-(methoxy) propoxy] acetic acid (CAS # 919005-51-9); Source: PubChem

The Gluge et al. definition differs from TSCA by requiring non-polymeric perfluorolalkyl substance to have at least a $-CF_2-CF_2-$ moiety as opposed to $-CF_2-CF-$ moiety according to TSCA. The Subgroup did not adopt this definition since it excluded chemicals with two adjacent carbon atoms associated with just three fluorines, as mentioned earlier under Buck et al.

6. European Chemical Agency (ECHA)

The ECHA is a body of the European Union (EU), established to act as an independent body in the context of the implementation of the regulation (No. 1907/2006) on the **R**egistration, **E**valuation, **A**uthorization and Restriction of **Ch**emicals (REACH), concerning chemicals and their safe use. ECHA aims to improve the protection of human health and the environment through a system of REACH; i.e., restriction on the manufacture, placing on the market, and use of PFAS.

In 2020, PFAS in the scope of this restriction intention had the following structural formula:

> X– (–CF_2–)n–X' with n equal to or larger than 1 and X, X' not being H (thus including X-CF_3), meaning fluorinated substances that contain at least one aliphatic carbon atom that is both saturated and fully fluorinated; i.e., any chemical with at least one perfluorinated methyl group (– CF_3) or at least one perfluorinated methylene group (–CF_2–), including branched fluoroalkyl groups and substances containing ether linkages, fluoropolymers and side chain fluorinated polymers.

Figure 11. Structure of Dichlorotetrafluoroethane (CAS # 76-14-2); Source: PubChem

In 2021, REACH adopted the OECD 2021 definition for the scope of this restriction intention. According to this, PFAS is any chemical with at least a perfluorinated methyl group (–CF_3) or a perfluorinated methylene group (–CF_2–), without any H/Cl/Br/I atom attached to the carbon atom. The chemical example shown in Figure 11 is not PFAS according to the OECD 2021 definition since Cl is attached to the carbon atom.

7. Toxics Use Reduction Act (TURA)

Adopted in 1989, the Toxics Use Reduction Act (TURA) is designed to protect public health and the environment while enhancing the competitiveness of Massachusetts businesses. Under TURA, facilities that use large amounts of toxic chemicals are required to report on their chemical use, conduct toxics use reduction planning every two years, and pay a fee. The fees paid by TURA filers support the work of the TURA implementing agencies and are used to provide a wide variety of services, including training, grant programs, and technical assistance.

TURA reporting requirements are affected by continual updates to the Toxics Release Inventory (TRI) under the 2020 NDAA. PFAS can be reported under TURA either individually or as part of a category.

"PFAS are reportable individually under TURA either when a) they are individually listed under TRI, or b) if they were already reportable under TURA."

PFAS are reportable as part of a category as part of:

a. C1-C4 Halogenated Hydrocarbons Not Otherwise Listed (NOL) Category, or
b. Certain PFAS NOL Category, or
c. Both.

Certain PFAS NOL Category is defined as those PFAS that contain a perfluoroalkyl moiety with three or more carbons (e.g., $–C_nF_{2n}–$, n ≥ 3; or $CF_3–C_nF_{2n}–$, n ≥ 2) or a perfluoroalkyl ether moiety with two or more carbons (e.g., $–C_nF_{2n}OC_mF_{2m}–$ or $– C_nF_{2n}OC_mF_m–$, where n and m ≥ 1). This is same as OECD 2018 definition.

Facilities can use OECD Portal on Per and Poly Fluorinated Chemicals[6] as an important first step to see whether the facility uses PFAS by checking CAS numbers in the comprehensive database. Note, there are PFAS that are not in the OECD's database and alternatively, not all PFAS in the OECD database are reportable under TURA. In addition, it is important to check with the suppliers about products that contain less than 1 percent[7] PFAS and are not listed in the Safety Data Sheet (SDS) or claimed as Confidential Business information.

[6] OECD Portal on Per and Poly Fluorinated Chemicals - OECD Portal on Per and Poly Fluorinated Chemicals

[7] See *de minimis* exemption (40 CFR 372.38). Currently, the EPA is proposing to add PFAS to the List of Lower Thresholds for Chemicals of Special Concern. The EPA is additionally proposing to remove the availability of this exemption for chemicals on this list (Proposed Rule as of 12/5/2022).

MPART Working Descriptions of PFAS Structure

1. Previous Versions of the Working Description

In 2020, the Subgroup offered the following first draft of a PFAS working description:

> The basic chemical structure is a chain (or tail) of two or more adjacent carbon atoms with a charged functional group head attached at one end. The tail may be linear or branched, or contain a cyclic portion, but it always contains adjacent fluorinated carbon atoms in a C_nF_{2n+1} – moiety (with n ≥2). The functional groups commonly are carboxylates or sulfonates, but other forms are also detected in the environment. For a linear or branched aliphatic tail, this structure can be written as: **C_nF_{2n+1}-R** where "C_nF_{2n+1}" defines the length of the perfluoroalkyl chain tail, "n" is ≥2, and "R" represents the attached functional group head.

In 2021, the Subgroup revised their working description, taking into consideration newly available definitions or descriptions for PFAS from peer-reviewed literature, government agencies, and non-government organizations, such as EPA TSCA, OECD 2021, and TURA. The following is the revised 2021 working description of PFAS:

> PFAS contain the chemical structure unit **R–(CF_2)–C(F)(R') R**," with two adjacent, fully fluorinated carbons where R, R', and R" represent any functional group or atom except H/Cl/Br/I; i.e., with a few noted exceptions. This description also includes substances with R–CF_2–CF_2–R' and CF_3–CF_2–R units. Note, R, R', R" can be the same or different atoms.

The revised MPART working description reflects the latest scientific information made available since 2020. For example, the initial MPART description (2020) was written to include linear, branched, and cyclic portions of the aliphatic tail, with at least two or more adjacent and fully fluorinated carbons on one end, and a functional group head on the other end. Listed below are major changes made to broaden the initial MPART working description from 2020, thereby covering a greater number of PFAS:

- Refined the structural representation of perfluoroalkyl moieties to include C_2F_3 and C_2F_4, which was previously restricted to C_2F_5 based on the moiety C_nF_{2n+1} where n $\geq$2.

- Two adjacent fully fluorinated carbons need not always be towards one end of the structure.
- Two adjacent carbons are considered fully fluorinated when not directly attached to H/Cl/Br/I.
- Includes functional groups attached to either end of the carbon-fluorine skeleton (i.e., R–(CF_2)–C(F)(R') R").
- Carbon-fluorine skeleton can also be attached to group of atoms on either end or single atoms that are not H/Cl/Br/I.

Subsequently, in February 2022, based on newly available information from various literature and public sources, the Subgroup revised the working description again as per guidance provided by OECD (2021). The intent is to have a broader PFAS definition that is a combination of all available definitions or working descriptions. The revised MPART working description considers compounds with at least two fully fluorinated carbons, whereas compounds with just one fully fluorinated carbon that are excluded from the working description should be evaluated for specific toxicity traits to assess and manage health risks[8].

2. Current Version of Working Description

In 2022, based on further review, the Subgroup broadened the PFAS working description to include perfluoroalkyl ether moieties such as **–$C_nF_{2n}OC_mF_{2m}$–** or **–$C_nF_{2n}OC_mF_m$–** where n and m ≥ 1.

> PFAS means per- and polyfluoroalkyl substances that contain the perfluoroalkyl moiety with two adjacent fully fluorinated carbons, **R–(CF_2)–C(F)(R') R"** or perfluoroalkyl ether moiety, **R–(CF_2)–O–(CF)(R') R,"** where R, R', and R" represent any functional group or atom except hydrogen (H). This includes perfluoroalkyl substances with R–CF_2–CF_2–R' and CF_3–CF_2–R units or perfluoroalkyl ether substances with R–CF_2–O–CF_2–R' and CF_3–O–CF_2–R units.

Note, R, R', R" can be the same or different atoms. The current version of MPART working description includes carbon atoms attached to Cl, Br, and I atoms. OECD is the only organization that excludes carbon atoms attached to Cl, Br, and I

[8] As noted above, the MPART working description is based on the chemical structure of PFAS and does not provide specific information as to whether or not a compound is harmful to human health.

limiting the number of PFAS covered under their definition. The Subgroup wanted to broaden the working description to avoid excluding chemicals that are potentially PFAS despite the presence of Cl, Br, or I attached to carbon atom.

Figure 12. Structure of Difluoro(perfluoromethoxy)acetic acid (CAS # 674-13-5); Source: PubChem

This working description (2022) is an extension of the previous version (2021) and now includes the perfluoroalkyl ether moieties.

Buck et al., NDAA, and other states have considered substances containing a single fluorinated carbon as PFAS (an example is shown in Figure 13). However, the Subgroup did not consider substances with just a single fully fluorinated carbon as part of the current working description. As mentioned earlier in this document, this will be further evaluated in the next version of our working description.

An example of single fluorinated chemical that would be considered PFAS under the Buck et al. 2011, TURA and other state definitions:

Figure 13. Structure of Trifluoroacetic acid (CAS # 76-05-1); Source: PubChem

Appendix B shows some structural examples of substances that the Subgroup selected to demonstrate how each substance is or is not classified as PFAS, according to the various descriptions. It is important to note this is the Subgroup's application and interpretation of the referenced description that resulted in the

yes/no identifier for PFAS. Bolded text from Appendix A can be used to compare examples to see if they meet those criteria for each description. If an example meets all criteria, the substance is considered to be PFAS. If one or more criteria are not met, the substance is not considered to be PFAS. For EPA CompTox, use the dashboard link provided in footnote 8 to search for examples using CAS numbers. If the result depicts the substance for which the search was performed, this indicates it is part of the PFAS database containing 12,039 members and thus is classified as PFAS. If there are no search results, it is not considered as being PFAS within EPA's CompTox.

Toxicological Considerations

The Subgroup has acknowledged that some fluorinated chemicals do not meet PFAS classification under the current working description based on chemical structure alone. However, they may have modes of action similar to most-studied PFAS. While chemical structure alone can be a first step in identifying a chemical as PFAS, as documented in this paper, both chemical structure and activity should be used as lines of evidence to support the screening of candidate substances (SOT, Undated; EPA, 2022).

Challenges or Data Gaps

1. Individual PFAS and PFAS mixtures with incomplete or no available toxicological data make regulation challenging.
2. Chemicals claimed as confidential business information cannot be reviewed.
3. Reviewing each individual chemical could be time-consuming.

4. Epidemiological studies have revealed associations between exposure to specific PFAS and a variety of health effects; however, modes of action and adverse outcome pathways must be expanded.[9]

Summary

For policy and future regulatory decisions, it is imperative to understand which fluorinated chemicals get classified as PFAS. The MPART PFAS working description provides some clarity in understanding what is meant when discussing the PFAS group of chemicals. The Subgroup will continue to evaluate new peer-reviewed publications and evaluate further PFAS definitions to determine if this working description should be revised in the future. The Subgroup will continue discussing lesser studied/unknown chemicals without sufficient toxicological information.

[9] Fenton, et al., 2020. Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environmental Toxicology and Chemistry*—Volume 40, Number 3—pp. 606–630, 2021.

References

Buck, Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., & van Leeuwen, S. P. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management*, *7*(4), 513–541. https://doi.org/10.1002/ieam.258

Buck, Korzeniowski, S. H., Laganis, E., & Adamsky, F. (2021). Identification and classification of commercially relevant per- and poly-fluoroalkyl substances (PFAS). *Integrated Environmental Assessment and Management*, *17*(5), 1045–1055. https://doi.org/10.1002/ieam.4450

Current Knowledge of Physiochemical Properties, Environmental Contamination and Toxicity of PFECHS Whitepaper (michigan.gov)

De Silva, Spencer, C., Scott, B. F., Backus, S., & Muir, D. C. G. (2011). Detection of a Cyclic Perfluorinated Acid, Perfluoroethylcyclohexane Sulfonate, in the Great Lakes of North America. *Environmental Science & Technology*, *45*(19), 8060–8066. https://doi.org/10.1021/es200135c

de Solla, De Silva, A. O., & Letcher, R. J. (2012). Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada. *Environment International*, *39*(1), 19–26. https://doi.org/10.1016/j.envint.2011.09.011

EFCTC (2020). Per- and Polyfluoroalkyl Substances: HFCs and HFOs a distinct subset. Retrieved December 8, 2022, from https://www.fluorocarbons.org/wp-content/uploads/2020/03/2020-02-07_EFCTC_PFAS-Position-Paper_F-02.03.pdf

EPA (2022). Persistent, Bioaccumulative, and Toxic (PBT) Chemicals under TSCA Section 6(h). Retrieved December 8, 2022, from https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/persistent-bioaccumulative-and-toxic-pbt-chemicals

Freeling, Scheurer, M., Koschorreck, J., Hoffmann, G., Ternes, T. A., & Nödler, K. (2022). Levels and Temporal Trends of Trifluoroacetate (TFA) in Archived Plants: Evidence for Increasing Emissions of Gaseous TFA Precursors over the Last Decades. *Environmental Science & Technology Letters*, *9*(5), 400-405. https://doi.org/10.1021/acs.estlett.2c00164

Generalized Read-Across (GenRA) | US EPA. (2023, April 3). US EPA. https://www.epa.gov/chemical-research/generalized-read-across-genra

Glüge, Scheringer, M., Cousins, I. T., DeWitt, J. C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C. A., Trier, X., & Wang, Z. (2020). An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science--Processes & Impacts*, *22*(12), 2345–2373. https://doi.org/10.1039/d0em00291g

Guo, Y., Zhao, L., Zhang, X., & Zhu, H. (2019). Using a hybrid read-across method to evaluate chemical toxicity based on chemical structure and biological data. *Ecotoxicology and Environmental Safety*, *178*, 178–187. https://doi.org/10.1016/j.ecoenv.2019.04.019

Hammel, Webster, T. F., Gurney, R., & Heiger-Bernays, W. (2022). Implications of PFAS definitions using fluorinated pharmaceuticals. *iScience*, *25*(4), 104020–104020. https://doi.org/10.1016/j.isci.2022.104020

ITRC (2022). Per- and Polyfluoroalkyl Substances Technical and Regulatory Guidance Document. https://pfas-1.itrcweb.org/wp-content/uploads/2022/09/PFAS-Guidance-Document-9-2022.pdf

Kleinstreuer, N., Tetko, I. V., & Tong, W. (2021). Introduction to Special Issue: Computational Toxicology. *Chemical Research in Toxicology*, *34*(2), 171-175. https://doi.org/10.1021/acs.chemrestox.1c00032

Liu, Zhang, Y., Li, J., Wu, N., Li, W., & Niu, Z. (2019). Distribution, partitioning behavior and positive matrix factorization-based source analysis of legacy and emerging polyfluorinated alkyl substances in the dissolved phase, surface sediment and suspended particulate matter around coastal areas of Bohai Bay, China. *Environmental Pollution (1987)*, *246*, 34–44. https://doi.org/10.1016/j.envpol.2018.11.113

MacInnis, French, K., Muir, D. C. G., Spencer, C., Criscitiello, A., De Silva, A. O., & Young, C. J. (2017). Emerging investigator series: a 14-year depositional ice record of perfluoroalkyl substances in the High Arctic. *Environmental Science--Processes & Impacts*, *19*(1), 22–30. https://doi.org/10.1039/c6em00593d

OECD (2018). *Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs).* Retrieved December 8, 2022, from https://fluoridealert.org/wp-content/uploads/endicott-legal.oecd-report.may-4-2018.pdf

OECD (2021). *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance (No. 61).* Retrieved December 8, 2022, from https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/terminology-per-and-polyfluoroalkyl-substances.pdf

Patlewicz, G. *A Framework to Build Scientific Confidence in Read-across.* Presented at Chinese Society of Toxicology Webinar, RTP, NC, March 29, 2019. https://doi.org/10.23645/epacomptox.8291774

REACH. (n.d.). *Annex XIII: Criteria for the Identification of Persistent, Bioaccumulative and Toxic Substances, and Very Persistent and Very Bioaccumulative Substances.* Retrieved December 8, 2022, from https://reachonline.eu/reach/en/annex-xiii.html

Rovida, C., Barton-Maclaren, T. S., Benfenati, E., Caloni, F., Chandrasekera, P. C., Chesne, C., Cronin, M. T. D., De Knecht, J., Dietrich, D. R., Escher, S., Fitzpatrick, S., Flannery, B. M., Herzler, M., Bennekou, S. H., Hubesch, B., Kamp, H., Kisitu, J., Kleinstreuer, N., Kovarich, S., . . . Hartung, T. (2020). Internationalization of read-across as a validated new approach method (NAM) for regulatory toxicology. *Alternatives to Animal Experimentation*. https://doi.org/10.14573/altex.1912181

S.1059 - 106th Congress (1999-2000): National Defense Authorization Act for Fiscal Year 2000. (1999, October 5). https://www.congress.gov/bill/106th-congress/senate-bill/1059

State of Michigan (2020). *Current Knowledge of Physiochemical Properties, Environmental Contamination and Toxicity of PFECHS Whitepaper.* Current Knowledge of Physiochemical Properties, Environmental Contamination and Toxicity of PFECHS Whitepaper (michigan.gov)

TURA (2022). *Guidance for Reporting Per- and Poly-Fluoroalkyl Substances (PFAS) under the Toxics Use Reduction Act (TURA), including Individually Listed PFAS and the Certain PFAS Not Otherwise Listed (NOL) Category.* Retrieved December 8, 2022, from https://www.turi.org/content/download/13942/220270/file/Guidance+for+Reporting+of+PFAS+under+TURA+April+2022.pdf

USEPA (n.d.). *CompTox Chemicals Dashboard* [Dataset]. https://comptox.epa.gov/dashboard/

Wang, Buser, A. M., Cousins, I. T., Demattio, S., Drost, W., Johansson, O., Ohno, K., Patlewicz, G., Richard, A. M., Walker, G. W., White, G. S., & Leinala, E. (2021). A New OECD Definition for Per- and Polyfluoroalkyl Substances.

Environmental Science & Technology, *55*(23), 15575–15578. https://doi.org/10.1021/acs.est.1c06896

Xiao. (2017). Emerging poly- and perfluoroalkyl substances in the aquatic environment: A review of current literature. *Water Research (Oxford)*, *124*, 482–495. https://doi.org/10.1016/j.watres.2017.07.024

Appendix A

Comparison of Available Descriptions of PFAS from 2011 to 2022

Source and date	Definition/working description	Number of PFAS covered
Buck et al. (2011)	A subset of fluorinated substances is the highly fluorinated **aliphatic** substances that contain **1 or more C** (carbon) atoms on which all the H (hydrogen) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by F (fluorine) atoms, in such a manner that they contain the perfluoroalkyl moiety **C_nF_{2n+1}–**	The Supplemental Data lists **42 families and subfamilies** of PFASs and **268 selected individual compounds**
OECD (2018)	Broadens the PFAS compounds to include PFAS with both ends of the perfluoroalkyl moiety (i.e., **–C_nF_{2n}–, n ≥ 3**) or a perfluoroalkyl ether moiety with two or more carbons (i.e., **–$C_nF_{2n}OC_mF_{2m}$–, n and m ≥ 1**) connected to a functional group such as carboxyl (– COOH), carbonyl (– CO), etc.	**4,730** (includes chemicals covered under Buck et al, 2011)
MPART (2020)	For a linear or branched aliphatic tail, this structure can be written as: **C_nF_{2n+1}–R** where "**C_nF_{2n+1}**" defines the length of the perfluoroalkyl chain tail, **"n" is ≥2**, and "R" represents the attached functional group head. The tail may be linear or branched, or contain a cyclic portion, but it always contains adjacent fluorinated carbon atoms in a **C_nF_{2n+1} –** moiety (with **n≥2**).	
Gluge et al. (2020)	The study focuses on **polymeric PFAS** with the **–CF_2–** moiety and **non-polymeric PFAS** with the **–CF_2–CF_2–** moiety. It does not include non-polymeric substances that only contain a –CF_3 or –CF_2– moiety, with the exception of perfluoroalkyl ethers and per- and polyfluoroalkyl ether-based substances. For these two PFAS groups, substances with a **–CF_2OCF_2–** or **–$CF_2OCFHCF_2$–** moiety are also included.	
EPA TSCA (2021)	For the purposes of this proposed action, the structural definition of PFAS includes per- and polyfluorinated substances that structurally contain the unit **R–(CF_2)–C(F)(R')R"**. Both the CF_2 and CF moieties are saturated carbons and none of the R groups (R, R' or R") can be hydrogen. R can be any halogen (F, Cl, Br, I)	**6,504** (based on structure) **1,346** (active chemicals known to be in commerce from June 2006 – April 2021)
OECD (2021)	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 (**–CF_3**) or a perfluorinated methylene group (**–CF_2–**) is a PFAS.	

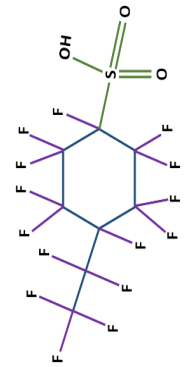
REACH/ECHA (2021)	PFAS in the scope of this restriction intention have the following structural formula: **X– (–CF_2–)$_n$–X'** with **n equal to or larger than 1** and **X, X' not being H** (thus **including X-CF_3**), meaning fluorinated substances that contain at least one aliphatic carbon atom that is both, saturated and fully fluorinated; i.e., any chemical with at least one perfluorinated methyl group (– **CF_3**) or at least one perfluorinated methylene group (–**CF2**–), including branched fluoroalkyl groups and substances containing ether linkages, fluoropolymers and side chain fluorinated polymers.	
EPA CompTox	The consolidated list contains a number of PFAS CAS-name substances, with **a subset represented with defined chemical structures**. There is no precisely clear definition of what constitutes a PFAS substance given the inclusion of partially fluorinated substances, polymers, and ill-defined reaction products on these various lists. Hence, PFASMASTER[10] serves as a consolidated list of substances defining a practical boundary of PFAS chemical space (within DSSTox) of current interest to researchers and regulators worldwide. This PFAS Master List will continue to expand as component lists grow.	**12,034**
MPART WD Revised (2022)	PFAS contain the perfluoroalkyl moiety with two adjacent fully fluorinated carbons, **R–(CF_2)–C(F)(R') R"** or perfluoroalkyl ether moiety, **R–(CF_2)–O–(CF)(R') R,"** where **R, R', and R" represent any functional group or atom except hydrogen (H)**. This includes perfluoroalkyl ether substances with **R–CF_2–CF_2–R'** and **CF3–CF2–R** units or perfluoroalkyl ether substances with **R–CF_2–O–CF_2–R'** and **CF_3–O–CF_2–R** units. **Note:** R, R', R" can be the same or different atoms	Estimated to be more than **4,730** but less than **12,034**
TURA	Companies covered by TURA are required to report on **Certain Per- and Polyfluoroalkyl Substances Not Otherwise Listed** (Certain PFAS NOL). Certain PFAS NOL Category is defined as those PFAS that contain a perfluoroalkyl moiety with three or more carbons (e.g., **–C_nF_{2n}–, n ≥ 3**; or **CF_3–C_nF_{2n}–, n ≥ 2**) or a perfluoroalkyl ether moiety with two or more carbons (e.g., **–$C_nF_{2n}OC_mF_{2m}$– or –$C_nF_{2n}OC_mF_m$–, where n and m ≥ 1).** This is same as OECD 2018 definition.	

Note: Bolded text is only for added emphasis on key words within each definition or description

[10] CompTox Chemicals Dashboard (epa.gov)

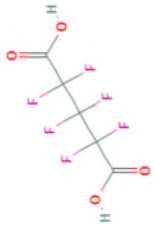
Appendix B

Walkthrough of Some Examples to Identify if it is PFAS or not According to the Various Definitions and the Current MPART PFAS Working Description (2022)

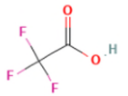
	Buck et al 2011	OECD 2018	MPART (ITRC Tech Reg) 2020	Gluge et al. Oct 2020	EPA TSCA June 2021	OECD July 2021*	REACH/ECHA July 2021	EPA CompTox	MPART WD Revised 2022*
 [11]	**Unclear** Fits general description with C_nF_{2n+1}– moiety with n≥1 but there are inconsistencies regarding understanding of inclusion of cyclics under Buck et al.	**Yes** Cyclics of linear analogs are included; PFECHS is linear analog of PFOS and has C_nF_{2n+1}– moiety with n≥1	**Yes** Includes cyclics and fits general description of C_nF_{2n+1}– R with n ≥2 and R= SO_3H	**Yes** Non-polymeric and has $–CF_2–CF_2–$ moiety	**Yes** Fits general description of R–(CF_2)–C(F)(R') R"	**Yes** Cyclics are included and has the basic $CF_3–$ or $–CF_2–$ structure that is not attached to H/Cl/Br/I	**Yes** Does not mention cyclics but has the basic $CF_3–$ or $–CF_2–$ structure that is both saturated and fully fluorinated[12]	**Yes** Included within PFASMASTER list	**Yes** Fits general description of R–(CF_2)–C(F)(R') R" where R groups are any functional groups or atom except H

[11] Perfluoroethylcyclohexane sulfonate (PFECHS); CAS # 646-83-3

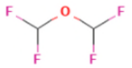
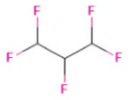
[12] Saturated carbon is surrounded by four single bonds, no single or triple bonds; fully fluorinated carbon is one that is not directly attached to H/Br/Cl/I

	Buck et al 2011	OECD 2018	MPART (ITRC Tech Reg) 2020	Gluge et al. Oct 2020	EPA TSCA June 2021	OECD July 2021*	REACH/ECHA July 2021	EPA CompTox	MPART WD Revised 2022*
 13	**No** There is no C_nF_{2n+1}– moiety	**Yes** Has –C_nF_{2n}– moiety with n≥3	**No** There is no C_nF_{2n+1}– where n≥2 moiety	**Yes** Non-polymeric and has –CF_2–CF_2– moiety	**Yes** Fits general description of R–(CF_2)–C(F)(R′) R″	**Yes** Has the –CF_2– moiety that is not attached to H/Cl/Br/I	**Yes** Has the –CF_2– moiety that is both saturated and fully fluorinated	**Yes** Included within PFASMASTER list	**Yes** Fits general description of R–(CF_2)–C(F)(R′) R″
 14	**Yes** Has C_nF_{2n+1}– moiety with n≥1	**Yes** Has C_nF_{2n+1}– moiety with n≥1	**No** Has C_nF_{2n+1}– moiety with n≥2 but does not have R or functional group	**Yes** Non-polymeric and has –CF_2–CF_2– moiety	**Yes** Fits general description of R–(CF_2)–C(F)(R′) R″ where R groups can be anything except hydrogen	**Yes** Has the CF_3– or –CF_2– structure that is not directly attached to H/Cl/Br/I	**Yes** Has the basic CF_3– structure that is both saturated and fully fluorinated	**Yes** Included within PFASMASTER list	**Yes** Has R–(CF_2)–C(F)(R′) R″ structure
 15	**Yes** Has C_nF_{2n+1}– moiety with n≥1	**Yes** Has C_nF_{2n+1}– moiety with n≥1	**No** Has C_nF_{2n+1}– moiety with n≥2 but does not have R or functional group	**Yes** Non-polymeric and has –CF_2–CF_2– moiety	**Yes** Fits general description of R–(CF_2)–C(F)(R′) R″ where R groups can be anything except hydrogen	**Yes** Has the –CF_2– moiety that is not directly attached to H/Cl/Br/I	**Yes** Has the basic CF_3– or –CF_2– structure that is both saturated and fully fluorinated	**Yes** Included within PFASMASTER list	**Yes** Fits general description of R–(CF_2)–C(F)(R′) R″

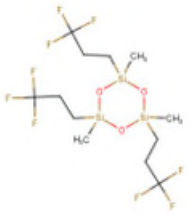
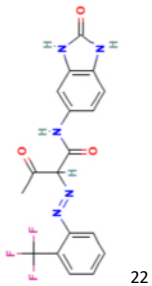
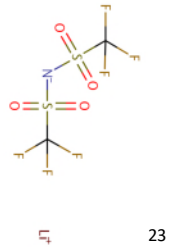
[13] Hexafluoropentanedioic Acid; CAS # 376-73-8
[14] Chloropentafluoroethane; CAS # 76-15-3
[15] Decafluorobutane; CAS # 355-25-9

	Buck et al 2011	OECD 2018	MPART (ITRC Tech Reg) 2020	Gluge et al. Oct 2020	EPA TSCA June 2021	OECD July 2021*	REACH/ECHA July 2021	EPA CompTox	MPART WD Revised 2022*
 [16]	**Yes** Have C_nF_{2n+1}– moiety with n≥1	**Yes** Has C_nF_{2n+1}– moiety with n≥1	**No** There is no C_nF_{2n+1}– where n≥2 moiety	**No** Does not have $–CF_2–CF_2–$ moiety	**No** Fits the general description of $R–(CF_2)–C(F)(R')\ R''$ but one of the R groups is a hydrogen	**Yes** Has the $–CF_2–$ moiety that is not directly attached to H/Cl/Br/I	**Yes** Has the basic $CF_3–$ structure that is both saturated and fully fluorinated	**Yes** Included within PFASMASTER list	**No** Has $R–(CF_2)–C(F)(R')\ R''$ structure but one of the R groups is hydrogen
 [17]	**Yes** Have C_nF_{2n+1}– moiety with n ≥1	**Yes** Has C_nF_{2n+1}– moiety with n ≥1	**No** There is no C_nF_{2n+1}– where n ≥2 moiety	**No** Does not have $–CF_2–CF_2–$ moiety	**No** Does not meet general description of $R–(CF_2)–C(F)(R')\ R''$	**Yes** Has the $–CF_2–$ moiety that is not directly attached to H/Cl/Br/I	**Yes** Has the basic $CF_3–$ structure that is both saturated and fully fluorinated	**Yes** Included within PFASMASTER list	**No** Does not have $R–(CF_2)–C(F)(R')\ R''$ structure
 [18]	**Yes** Has C_nF_{2n+1}– moiety with n≥1	**Yes** Has C_nF_{2n+1}– moiety with n≥1	**No** There is no C_nF_{2n+1}– where n≥2 moiety	**No** Does not have $–CF_2–CF_2–$ moiety	**No** Does not meet general description of $R–(CF_2)–C(F)(R')\ R''$	**Yes** Has the $–CF_2–$ moiety that is not directly attached to H/Cl/Br/I	**Yes** Has the basic $CF_3–$ structure that is both saturated and fully fluorinated	**No** (EPA used this as an example but not part of PFASMASTER list)	**No** Does not have $R–(CF_2)–C(F)(R')\ R''$ structure

[16] Tetrafluoroethane; CAS # 811-97-2
[17] Hexafluoropropane; CAS # 690-39-1
[18] Trifluoroacetic acid; CAS # 76-05-1

	Buck et al 2011	OECD 2018	MPART (ITRC Tech Reg) 2020	Gluge et al. Oct 2020	EPA TSCA June 2021	OECD July 2021*	REACH/ECHA July 2021	EPA CompTox	MPART WD Revised 2022*
 [19]	**No** There is no C_nF_{2n+1}– moiety	**No** Has –$C_nF_{2n}OC_mF_{2m}$– moiety with n and m ≥ 1 but carbons attached to one hydrogen each and not functional group(s) per description	**No** There is no C_nF_{2n+1}– where n ≥2 moiety	**Yes** Has –CF_2OCF_2– moiety and does not exclude carbons attached to hydrogen	**No** Does not meet general description of R–(CF_2)–C(F)(R') R"	**No** Has the –CF_2– moiety but is directly attached to hydrogen	**No** Has the basic–CF_2– rstructure that is saturated but not fully fluorinated because carbon is directly attached to H	**Yes** Included within PFASMASTER list	**No** Has R–(CF_2)–O–(CF)(R') R" but carbon atoms are attached to hydrogen.
 [20]	**No** There is no C_nF_{2n+1}– moiety	**No** There is no C_nF_{2n+1}– moiety with n ≥1 OR –C_nF_{2n}– moiety with n ≥3	**No** There is no C_nF_{2n+1}– where n ≥2 moiety	**No** Does not have –CF_2–CF_2– moiety	**No** Fits the general description of R–(CF_2)–C(F)(R') R" but one of the R groups is a hydrogen	**No** Has the –CF_2– moiety but is directly attached to Hydrogen	**No** Has the basic–CF_2– rstructure that is saturated but not fully fluorinated because carbon is directly attached to H	**Yes** Included within PFASMASTER list	**No** Has R–(CF_2)–C(F)(R') R" structure but one of the R groups is hydrogen

[19] Tetrafluorodimethylether; CAS # 1691-17-4
[20] Pentafluoropropane; CAS # 24270-66-4

	Buck et al 2011	OECD 2018	MPART (ITRC Tech Reg) 2020	Gluge et al. Oct 2020	EPA TSCA June 2021	OECD July 2021*	REACH/ECHA July 2021	EPA CompTox	MPART WD Revised 2022*
 21	**Yes** Considering Si-O ring is not aromatic and has C_nF_{2n+1}– moiety	**Yes** Has C_nF_{2n+1}– moiety with n ≥1	**No** There is no C_nF_{2n+1}– where n ≥2 moiety	**No** Does not have $–CF_2–CF_2–$ moiety	**No** Does not meet general description of $R–(CF_2)–C(F)(R')R''$	**Yes** Has the basic CF_3–structure that is not attached to H/Cl/Br/I	**Yes** Has the basic CF_3– structure that is both saturated and fully fluorinated	**No** Not included within PFASMASTER list	**No** Does not have $R–(CF_2)–C(F)(R')R''$ structure
 22	**Yes** has C_nF_{2n+1}– moiety	**Yes** Has C_nF_{2n+1}– moiety with n ≥1	**No** There is no C_nF_{2n+1}– where n ≥2 moiety	**No** Does not have $–CF_2–CF_2–$ moiety	**No** Does not meet general description of $R–(CF_2)–C(F)(R')R''$	**Yes** Has the basic CF_3–structure that is not attached to H/Cl/Br/I	**Yes** Has the basic CF_3– structure that is both saturated and fully fluorinated	**No** Not included within PFASMASTER list	**No** Does not have $R–(CF_2)–C(F)(R')R''$ structure
 23	**Yes** has C_nF_{2n+1}– moiety	**Yes** Has C_nF_{2n+1}– moiety with n ≥1	**No** There is no C_nF_{2n+1}– where n ≥2 moiety	**No** Does not have $–CF_2–CF_2–$ moiety	**No** Does not meet general description of $R–(CF_2)–C(F)(R')R''$	**Yes** Has the basic CF_3–structure that is not attached to H/Cl/Br/I	**Yes** Has the basic CF_3– and is saturated and fully fluorinated	**No** Not included within PFASMASTER list	**No** Does not have $R–(CF_2)–C(F)(R')R''$ structure

[21] Cyclotrisiloxane; CAS # 2374-14-3

[22] 2-(2-Trifluoromethylphenylazo)-N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxobutanamide; CAS # 68134-22-5

[23] Lithium bis[(trifluoromethyl)sulfonyl]azanide; CAS # 90076-65-6