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Identification and classification of commercially relevant per- and poly-fluoroalkyl substances (PFAS)

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Abstract

Per- and poly-fluoroalkyl substances (PFAS) are a universe of fluorinated organic substances with very different physical, chemical, and biological properties including polymers and non-polymers; solids, liquids, and gases. Commercial PFAS-based products have been used in a wide variety of industrial and consumer applications because they have unique performance properties of significant socioeconomic value. The PFAS definition has evolved and expanded over the years. Numerous lists of PFAS, some with thousands of entries, have been compiled, but none have clearly identified which of the substances are commercially relevant. This study is the first to use a bona-fide “bottom up” approach to identify how many of the 4730 PFAS substances listed in a 2018 OECD/UNEP Report are directly connected to commercial products based on input from three major global producers. This study provides new and valuable insight into the 2018 OECD/UNEP Report list of PFAS substances. The results show that 256, less than 6%, of the 4730 PFAS substances presented in the 2018 OECD/UNEP Report are commercially relevant globally. This study suggests that grouping and categorizing PFAS using fundamental classification criteria based on composition and structure can be used to identify appropriate groups of PFAS substances for risk assessment, thereby dispelling assertions that there are too many PFAS chemistries to conduct proper regulatory risk assessments for the commercially relevant substances. *Integr Environ Assess Manag* 2021;17:1045–1055. © 2021 The Chemours Company, Beach Edge Consulting, LLC, AGC Chemicals Americas Inc., Daikin America Inc. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Commercially relevant, OECD list, PFAS

INTRODUCTION

An OECD/UNEP work group commissioned and issued in 2007 a report entitled “Lists of PFOS, PFAS, PFOA, PFCA, related compounds and chemicals that may degrade to PFCA” listing 982 substances (OECD, 2007). Concurrently, regulations on these substances emerged (European Parliament, 2006; OECD, 2015). Also in 2006, eight major global manufacturers committed to and terminated the manufacture of “long-chain” per-fluoroalkyl acids (PFAAs) such as perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and related

substances by year-end 2015 (USEPA, 2020a). Replacements, including fluorinated alternatives with more favorable environmental and toxicology profiles, were registered and commercialized, for example, “short-chain” alternatives such as perfluorobutane sulfonyl products and 6:2 fluorotelomer products, fluorinated ether carboxylic acid polymerization aids, and oligomeric fluoropolyethers (Buck, 2015; KEMI, 2015; Wang et al., 2013, 2020).

Nomenclature and terminology for per- and poly-fluoroalkyl substances (PFAS) detected in the environment, wildlife, and humans was first presented by a multi-stakeholder group (Buck et al., 2011). The Buck et al. (2011) paper provided clear, specific, and descriptive terminology, names, and acronyms to unify and harmonize communication on PFAS by offering terminology for use by the global scientific, regulatory, and industrial communities. The substances included as PFAS focused on long-chain (OECD, 2020a) PFAAs such as PFOS, PFOA, long chain homologues of these two substances, “related substances” (substances that may degrade to form long-chain PFAAs), and substances made using

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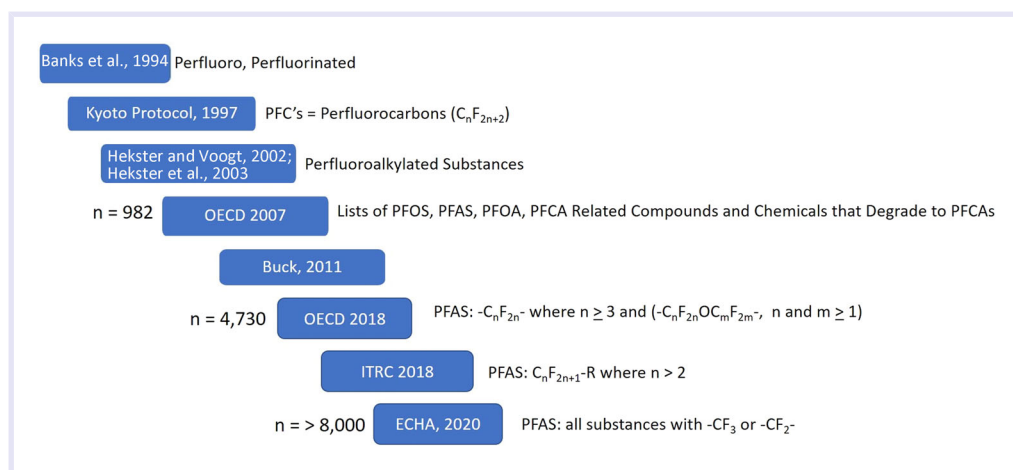


FIGURE 1 The evolution of the term per- and poly-fluoroalkyl substances (PFAS)

them. PFAS were defined by structure and composition, use, and their relationship to PFAAs. Noting the fundamental property differences amongst PFAS, the authors strongly encouraged the use of clear, specific, and descriptive nomenclature and terms—those provided in the paper—and the use of the acronym PFAS only when truly addressing all the substances defined as PFAS (see Supporting Information for PFAS terminology usage discussion). The acronym PFAS as defined and described included named categories, families, subfamilies, and specific substances by name and CAS number. The paper stated that the acronym “PFAS” was not intended to be used to encompass all substances with carbon-fluorine bonds. Substances already regulated by authorities or the subject of multi-stakeholder agreements should be excluded (e.g., The Montreal Protocol, The Kigali Amendment).

PFAS (Buck et al., 2011) defined a specific universe of fluorinated organic substances with very different physical, chemical and biological properties, including polymers and non-polymers; solids, liquids, and gases; highly reactive and inert substances; soluble and insoluble substances; and volatile and involatile substances. Commercial products that fall within the PFAS definition have been used in a wide variety of industrial and consumer applications because they have unique performance properties of significant socio-economic value (Ebnesajjad, 2013; Fluoropolymers Product Group, 2018; Moffett et al., 2020; Performance Fluoropolymer Partnership, 2018). The evolution of the term PFAS over time is depicted in Figure 1.

In 2018, an updated report commissioned by OECD/ UNEP entitled “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)” was issued (OECD, 2018). The report utilized publicly accessible information sources, including PFAS lists compiled by national or international regulatory bodies, public national and regional inventories (including pre-registration), public

national and regional inventories of chemicals subject to specific regulations, and a scientific database. The report used an expanded definition for identifying a substance as a PFAS (see Supporting Information); 4730 PFAS-related CAS numbers were identified. Each substance was assigned to a structure category. Eight structure categories were defined including several new groups of PFAS (Table 1). Each structure category was assigned a code (e.g., 100), and sub-codes were assigned to identify different sub-categories (e.g., 103) and sub-sub categories (e.g., 103.03) (see details in the Supporting Information).

The 2018 OECD/UNEP Report did not determine or identify the commercial relevance of the 4730 substances. It did not exclude substances never commercialized, phased-out of production, or made in very small research quantities (e.g., <1 kg). In addition, the report did not explicitly exclude substances already regulated by authorities or the subject of multi-stakeholder agreements such as refrigerants, blowing agents, and propellants subject to the Montreal Protocol (United Nations, 2020a) and Kigali Amendment (United Nations, 2020b) or pharmaceuticals (Wang et al., 2014) and pesticides, many of which contain per- or poly-fluoroalkyl moieties. The “large” number of compounds, “nearly 5000,” identified in the 2018 OECD/ UNEP Report, has been suggested to be “unmanageable” for regulatory risk assessment and has been used to justify a “regulate all PFAS” approach as exemplified in the recent European Chemicals Agency (ECHA) call for evidences by five European states, which expanded the definition of “PFAS to its broadest definition ever described (Figure 1)” (European Chemicals Agency [ECHA], 2020).

Commercial manufacture of fluorinated organic substances continues to be of high interest, and there is a desire by regulators, the public, academics, and NGOs to better understand what substances are, or have been, actually made and are commercially relevant (Johnson et al., 2020). It is important to reiterate that the 2018 OECD/UNEP Report created a list of substances and their CAS numbers with no recognition of what substances were of commercial

TABLE 1 2018 OECD/UNEP Report: 4730 PFAS substances assigned to eight structure categories

Series	Structure category	No.	%
100	Perfluoroalkyl carbonyl compounds	514	11
200	Perfluoroalkane sulfonyl compounds	629	13
300	Perfluoroalkyl phosphate compounds	23	1
400	Fluorotelomer-related compounds	1872	40
500	Per- and poly-fluoroalkyl ether-based compounds	365	8
600	Other PFAA precursors and related compounds—perfluoroalkyl ones	314	7
700	Other PFAA precursors or related compounds—semifluorinated	746	16
800	Fluoropolymers	267	6
		4730	100

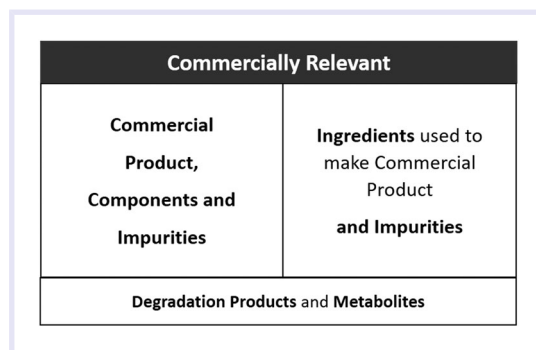
Abbreviations: PFAA, perfluoroalkyl acid; PFAS, per- and poly-fluoroalkyl substances.

relevance, the amount (e.g., tonnage), or the use. Therefore, the 2018 OECD/UNEP Report list does not speak to commercial importance, amount, or socioeconomic benefit. The three major global producers participating in this study recognized it would be useful to identify what substances on the 2018 OECD/UNEP Report list are of commercial relevance today.

This study used a “bottom up” approach to identify how many of the 4730 substances listed in the 2018 OECD/UNEP Report are directly connected to products actually in commerce globally (“commercially relevant”) as of December 2019, from three major global fluorotechnology producers: AGC Chemicals Company, The Chemours Company, and Daikin Industries. The study participants are manufacturers of fluoropolymers, perfluoropolyether polymers, and short-chain (aka C6) fluorotelomer-based products. This is the first study to identify commercially relevant substances and thereby a subset of the 4730 listed substances that are related to current commercial manufacturing (aka commercially relevant). For the purpose of this assessment, commercially relevant is defined to include substances on the 2018 OECD/UNEP Report list that are present in a commercial product offered for sale, including product components and impurities, ingredients used to make a commercial product and impurities, and degradation products (aka metabolites) (see Figure 2).

MATERIALS AND METHODS

AGC Chemicals Company, Daikin Industries, and The Chemours Company participated in this study. The 2018 OECD/UNEP Report entitled: “(new comprehensive) Global Database of Per- and Polyfluoroalkyl Substances (PFAS)” provides a database listing 4730 PFAS-related CAS numbers (OECD, 2018). As noted earlier, the report does not determine or identify the commercial

**FIGURE 2** Substances included in commercially relevant list

relevance, commercial quantity, or socioeconomic benefit of the 4730 substances, and it does not exclude substances never commercialized or made in research quantities (e.g., <1 kg) to identify or differentiate substances that are presently commercially relevant globally.

The study participants' product knowledge experts queried individual company databases and company subject matter experts to identify the commercially relevant (see Figure 2) substances on the list based on commercial products made and processes operating in December 2019.

To assist the participating companies, the American Chemistry Council (ACC) contracted an external independent consultancy, IAL, a division of BRG, that has over 40 years of experience delivering proprietary consulting projects to the world's leading chemical companies, to confidentially gather and collate the participants' data (IAL, a Division of BRG, 2020). IAL contacted each participating company individually to collect their input. Individual company results were blinded and aggregated and not shared among the companies. IAL compiled the participants' input into a summary of commercially relevant substances on the 2018 OECD/UNEP Report list summed by structure category.

STUDY METHODOLOGY

1. The ACC provided IAL with a list of study participant companies. IAL contacted each company independently and offered two options for completing the survey. Companies could complete the survey and return the completed documents to IAL or they could arrange a telephone interview with IAL to collaboratively complete the survey.
2. For the purposes of this survey “commercially relevant” substances were defined to include:
 - Commercial product
 - (a) Component in a commercial product;
 - (b) Impurity, an unintended substance, present in a commercial product (including those known or highly believed to be present, created during the synthesis and/or manufacture of the commercial product).

- Ingredient—used or added to manufacture the commercial product
 - (c) Impurity an unintended substance, present in the Ingredient.
 - Degradation product—a substance known, or highly believed, to be formed from abiotic or biotic degradation of a commercial product, component, impurity or ingredient (aka metabolites).
- Each company independently submitted its survey results to IAL, which then compiled the data into one list of commercially relevant PFAS substances, with no distinction made between commercial product, component, ingredient, impurity, or degradation product.
 - As part of this assessment, participants did not limit themselves to the OECD compound list and also reported additional “commercially relevant” substances not present on the 2018 OECD/UNEP Report 4730 compound database list.
 - IAL then provided the companies with a composite list of PFASs used commercially for further analysis.
 - No production amount or volume data, commercial product names, uses (such as articles that may contain PFAS substances), functionality information, or alternatives information were requested and none were provided for any compound.
 - This research was conducted on a confidential basis, and no information is attributed to individuals or organizations.

RESULTS

The study results were gathered and categorized first according to the PFAS definition and substance classes set forth in Buck et al. (2011). Following the study methodology described above, 241 commercially relevant substances were reported that met the PFAS definition set forth in 2011. An additional 15 substances reported did not meet the 2011 definition because they are either hydrofluoroethers (HFEs), hydrofluoroolefins (HFOs), refrigerants, or contain an aromatic ring, all of which were excluded in the 2011 definition. Therefore, a total of 256 substances were identified in this bottom up survey. The data were sorted using fundamental structure and composition criteria, first as non-polymer or polymer, and second in to the five classes presented in 2011. The results are presented in Table 2 and pictorially presented in Figures S1 and S2. Most of the substances reported, 189, are non-polymer, 78% of the total. Of the non-polymer substances, 111 are non-polymer polyfluoroalkyl substances and 78 are non-polymer perfluoroalkyl substances. Twenty-two percent of the reported substances are polymer including 38 fluoropolymers, 8 perfluoropolyether polymers, and 6 side-chain fluorinated polymers.

Second, using the expanded PFAS definition set forth in the 2018 OECD/UNEP Report, a total of 256 distinct commercially relevant substances were reported by the study participants. The data were reported as sum totals in each of

TABLE 2 Commercially relevant substances from three major global producers by substance class using Buck et al. (2011) PFAS definition

	Substance class	No.	%
Non-polymer (NP)	1 NP perfluoro	78	32
	2 NP polyfluoro	111	189 46 78%
Polymer	3 Fluoropolymer	38	16
	4 Perfluoropolyether polymer	8	52 3.3 22%
	5 Side-chain fluorinated polymer	6	2.5
		241	100

Abbreviation: PFAS, per- and poly-fluoroalkyl substances.

the eight structure categories set forth in the report. The results are presented in Table 3. The three structure categories containing the most substances are, in descending order: per- and polyfluoroalkyl ether-based compounds (series 500), fluorotelomer-related compounds (series 400), and fluoropolymers (series 800), constituting 77% of the total number of substances.

Last, to provide perspective on the “bottom-up” list of commercially relevant substances, this study compared the 2018 OECD/UNEP Report category classifications with the currently available US EPA TSCA Active List (USEPA, 2019). The US EPA TSCA Active List contains 370 non-CBI PFAS compounds and 236 CBI-classified PFAS compounds for a total of 606 active PFAS compounds on the USEPA TSCA Inventory (see Supporting Information). For the 370 non-CBI compounds, 26 did not meet the 2018 OECD/UNEP Report's PFAS definition, leaving 344 compounds to slot into the 8 structure categories. These classifications are shown in Table 4. It is also noteworthy that of the 344 compounds that did meet the 2018 OECD/UNEP Report's PFAS definition, approximately 149, or 43% of these compounds, could be classified as legacy long-chain substances.

DISCUSSION

The 2018 OECD/UNEP Report was an update of the 2007 OECD/UNEP Report that listed 982 substances. The 13-month effort from January 2017 to February 2018 conducted to compile the 2018 OECD/UNEP Report identified 4730 substances by CAS number and assigned them to eight structure categories, each containing a number of sub-categories (Table 1). It was acknowledged in the 2018 OECD/UNEP Report that there were many challenges, limitations, and gaps in this very large categorization process. In addition, the report did not determine or identify the commercial relevance of the 4730 substances, or exclude substances never commercialized or substances made in very small research quantities (e.g., <1 kg). Moreover, the report did not explicitly exclude substances already subject to unique, specific regulatory frameworks and multi-

TABLE 3 2018 OECD/UNEP Report: Commercially relevant substances by structure category and percent (%) and number (n) of substances in each structure category

Series	Structure category	This study		2018 OECD/UNEP Report	
		%	n	%	n
100	Perfluoroalkyl carbonyl compounds	5	14	10.9	514
200	Perfluoroalkane sulfonyl compounds	1	2	13.3	629
300	Perfluoroalkyl phosphate compounds	0	0	0.5	23
400	Fluorotelomer-related compounds	28	71	39.6	1872
500	Per- and poly-fluoroalkyl ether-based compounds	34	87	7.7	365
600	Other PFAA precursors and related compounds—perfluoroalkyl ones—for example, PF Alka(e)nes	8	20	6.6	314
700	Other PFAA precursors or related compounds—semifluorinated—for example, HFC's/HFE's	9	24	15.8	746
800	Fluoropolymers	15	38	5.6	267
		100	256	100	4730

Abbreviations: HFE, hydrofluoroether; PFAA, perfluoroalkyl acid.

stakeholder efforts such as refrigerants, blowing agents, and propellants subject to the Montreal Protocol (United Nations, 2020a) and Kigali Amendment (United Nations, 2020b) or pharmaceuticals and pesticides, many of which contain per- or poly-fluoroalkyl moieties (United Nations, 2020a, 2020b; Wang et al., 2014).

Using the PFAS definition set forth in the 2018 OECD/UNEP Report, this is the first study to conduct an in-depth assessment of the substances listed in this report by global commercial manufacturers that identified a total of 256 commercially

relevant substances, less than 6% of the 4730 (Table 3). Looking at the results by structure category or series, only a small number of substances of commercial relevance were reported in series 100–300, non-polymer perfluoroalkyl substances: perfluoroalkyl carbonyl compounds (14), 200—perfluoroalkyl sulfonyl compounds (2), and none in series 300—perfluoroalkyl phosphate compounds. The three major global producers who participated in the study have few series 200 (perfluoroalkyl sulfonyl compounds), because the participants do not practice electrochemical fluorination (ECF), the primary process that is the origin of many of these substances. The majority, 77%, of the commercially relevant substances were in three structure categories: series 500: per- and polyfluoroalkyl ether-based compounds, series 400: fluorotelomer-related compounds, and series 800: fluoropolymers. As expected, the commercially relevant substances identified in this study align with the commercial products manufactured by the study participants: fluoropolymers, perfluoropolyether polymers, and short-chain fluorotelomer-based products. The data from this study compared to the 2018 OECD/UNEP list is presented in Table 3 (see also the Supporting Information). In addition, whilst specific substances input by the study participants are confidential, 26 examples of commercially relevant substances from the three major producers who participated in the study that are present on the 2018 OECD/UNEP Report List and/or the USEPA non-CBI List are provided in structure categories in Table 5. Two confidential substances, not able to be recited, were reported for series 200, perfluoroalkane sulfonyl compounds, and no substances were reported for series 300, perfluoroalkyl phosphate compounds.

How these 256 commercially relevant substances fit into the 2018 OECD/UNEP Report's structure categories and how they compare with the OECD List of 4730 substances in

Table 4 USEPA non-CBI TSCA Active List assigned to 2018 OECD/UNEP Report structure categories

Series	Structure category	No.	%
100	Perfluoroalkyl carbonyl compounds	36	10.5
200	Perfluoroalkane sulfonyl compounds	90	26.2
300	Perfluoroalkyl phosphate compounds	2	0.6
400	Fluorotelomer-related compounds	103	29.9
500	Per- and poly-fluoroalkyl ether-based compounds	39	11.3
600	other PFAA precursors and related compounds—perfluoroalkyl ones—for example, PF Alka(e)nes	30	8.7
700	other PFAA precursors or related compounds—semifluorinated—for example, HFC's/HFE's	2	0.6
800	Fluoropolymers	42	12.2
		344	100

Abbreviations: HFE, hydrofluoroether; PFAA, perfluoroalkyl acid.

TABLE 5 Examples from the 2018 OECD/UNEP Report list and/or current USEPA TSCA non-CBI list of commercially relevant substances

Series	Structure category	Name	CAS No.
100	Perfluoroalkyl carbonyl compounds	Perfluorobutanoic acid—PFBA	375-22-4
		Perfluorohexanoic acid—PFHxA	307-24-4
		Perfluorooctanoic acid—PFOA	335-67-1
200	Perfluoroalkane sulfonyl compounds	None	Two substances, CBI
300	Perfluoroalkyl phosphate compounds	None	No substances
400	Fluorotelomer-related compounds	Perfluorohexyl iodide—PFHxI	355-43-1
		6:2 fluorotelomer iodide—6:2 FTI	2043-57-4
		6:2 fluorotelomer alcohol—6:2 FTOH	647-42-7
		6:2 fluorotelomer acrylate—6:2 FTAC	17527-29-6
		6:2 fluorotelomer methacrylate—6:2 FTMAC	2144-53-8
		6:2 fluorotelomer sulfonic acid—6:2 FTSA	27619-97-2
		6:2 fluorotelomer carboxylic acid—6:2 FTCA	53826-12-3
		6:2 fluorotelomer unsaturated carboxylic acid—6:2 FTUCA	70887-88-6
		5:3 acid	914637-49-3
500	Per- and poly-fluoroalkyl ether-based compounds	Propanoic acid, 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-	13252-13-6
		Propanoic acid, 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-, ammonium salt (1:1)	62037-80-3
		Propanoic acid, 3-[1-[difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoro-, methyl ester	63863-43-4
		Propanoic acid, 3-[1-[difluoro[1,2,2,2-tetrafluoro-1-(fluorocarbonyl)ethoxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoro-, methyl ester	69116-73-0
600	Other PFAA precursors and related compounds—perfluoroalkyl ones	Perfluorohexane	355-42-0
		Perfluorooctane	307-34-6
700	Other PFAA precursors or related compounds—semifluorinated	Butane, 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-	163702-07-6
		Propane, 2-(difluoromethoxymethyl)-1,1,1,2,2,3,3,3-heptafluoro-	163702-08-7
800	Fluoropolymers	Polytetrafluoroethylene—PTFE	9002-84-0
		Fluorinated ethylene propylene—FEP	25067-11-2
		Ethylene tetrafluoroethylene—ETFE	68258-85-5
		Propane, 1,1,1,2,2,3,3-heptafluoro-3-[(1,2,2-trifluoroethenyl)oxy]-, polymer with 1,1,2,2-tetrafluoroethene	26655-00-5
		Ethene, 1,1,1,2,2-tetrafluoro-, polymer with 1,1,2-trifluoro-2-(1,1,2,2,2-pentafluoroethoxy)ethene	31784-04-0
		Propanoic acid, 3-[1-[difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoro-, methyl ester, polymer with 1,1,2,2-tetrafluoroethene	63863-44-5

TABLE 6 Comparison of classification/categorization approaches

Buck et al. (2011)				2018 OECD/UNEP Report	
Class ^a				Series	Structure category
1	Non-polymer perfluoro			100	Perfluoroalkyl carbonyl compounds
1	Non-polymer perfluoro			200	Perfluoroalkane sulfonyl compounds
1	Non-polymer perfluoro			300	Perfluoroalkyl phosphate compounds
1	2	5	Non-polymer & polymer ^b	400	Fluorotelomer-related compounds ^b
1	2	4	Non-polymer & polymer ^b	500	Per- and poly-fluoroalkyl ether-based compounds ^b
1	Non-polymer perfluoro			600	Other PFAA precursors and related compounds—perfluoroalkyl ones
1	2		Non-polymer Perfluoro & polyfluoro ^c	700	Other PFAA precursors or related compounds—semifluorinated ^c
		3	Polymer	800	Fluoropolymers

^aFrom Table 1: 1 = non-polymer perfluoroalkyl; 2 = non-polymer polyfluoroalkyl; 3 = fluoropolymer; 4 = perfluoropolyether polymer; 5 = side-chain fluorinated polymer.

^bIncludes both non-polymer and polymer substances as well as perfluoroalkyl and polyfluoroalkyl non-polymer substances.

^cIncludes both perfluoroalkyl and polyfluoroalkyl non-polymer substances.

presented in Table 3. The number and percentage of total substances identified in this study as commercially relevant when compared to the 2018 OECD/UNEP Report list is shown. The fluorotelomers (series 400) was significantly smaller at 28% for this study versus the 2018 OECD/UNEP Report list at nearly 40%. The data for Ethers (series 500; 34%) and Fluoropolymers (series 800; 15%) were significantly higher than those in the 2018 OECD/UNEP Report List at nearly 8% and nearly 6%, respectively. This is consistent with the study participants' principal commercial products as noted earlier. A comparison of the USEPA non-CBI TSCA list categorization to both this study and the 2018 OECD/UNEP Report is presented in the Supporting Information.

A challenge arises when trying to compare the results of this study using the Buck et al. (2011) PFAS definition and classification and using the 2018 OECD/UNEP Report definition and classification. As shown in Table 6, the 2018 OECD/UNEP Report structure categories 400, 500, 600, and 700 combine and overlap polymer and non-polymer substances as well as perfluoro- and polyfluoro- non-polymer substances. The fundamental classification criteria, polymer and non-polymer, perfluoro- and polyfluoro-, distinguish substances using chemical structure distinction concepts based on basic structure and atomic composition. Unfortunately, these fundamental classification criteria were not used to differentiate and categorize substances in the 2018 OECD/UNEP Report methodology. Thus, the structure categories contain substance types that have fundamentally different structure and composition (e.g., non-polymer and polymer) and do not belong together. One may dig into the detailed structure sub-categories and sub-sub-categories provided, but these do not facilitate sorting substances based on fundamental properties. Starting to sort substances based on fundamental classification criteria first makes sense, followed by useful

articulation of structure categories and subcategories using well-established structure and composition criteria that are the basis to differentiate and categorize organic chemicals. We suggest this approach to sorting PFAS should be applied to identify and group commercially relevant PFAS for regulatory assessment.

Uncertainties need to be acknowledged regarding the results reported in this study. Analytical tools, techniques, and methods are rapidly evolving and advancing to identify PFAS substances in product matrices (which can be very challenging) at parts-per-billion and perhaps lower levels that is, parts-per-trillion (European Parliament, 2006; OECD, 2020b). Therefore, there are possibly more substances not yet identified. Work will need to continue on identification and defining concentration levels of unintentional impurities in products. Second, polymers registered and reported with CAS numbers may vary up to 2% with additional monomers and still have the same CAS number. This means that there are likely more fluoropolymers and more fluorotelomer-based side-chain fluorinated polymers than the numbers in this the study identified. Third, all study participants participated in the 2010/15 USEPA PFOA Stewardship Program (USEPA, 2020a). As such, as of December 2019, short-chain (aka C6) fluorotelomer-based substances were being manufactured and no manufacture or use of PFOA, longer-chain homologues, or their potential precursors is occurring. The results of this study reflect this noteworthy commercial reality for the participants in the survey. The outcome of this study does clearly show that the actual number of commercially relevant substances is substantially smaller than the 4730 substances listed in the 2018 OECD/UNEP Report. This study shows that there are a few hundred PFAS commercially relevant chemistries, not thousands.

Since its publication, the 2018 OECD/UNEP Report list of 4730 PFAS chemistries has been cited widely in the press

and scientific literature as a list of commercial PFAS substances (e.g., Glüge et al., 2020), which it is not. This study suggests these statements are likely incorrect. The number of commercially relevant substances, not including substances made for research purposes in small quantities, which may constitute a large number of the substances on the list, is significantly smaller. Further, the 2018 OECD/UNEP Report has been cited as justification for grouping all PFAS as one (Cousins et al., 2020; ECHA, 2020) and not conducting proper complete risk assessments, thus abandoning over 100 years of accepted regulatory practice based on the development of sound societal use decisions anchored in scientifically developed risk versus benefit assessments (Paustenbach, 2002; UNEDSA, 2010; UNEP/IPCS, 1999; USEPA, 2020c). Likewise, the misuse of the 2018 OECD/UNEP Report has served as the catalyst and justification for pursuing such subjective approaches to regulation and de-regulation as assigning essential or non-essential use classifications in place of more definitive approaches driven by data (Cousins et al., 2019, 2020). Thus, the assertion that there are too many of these substances (4700, aka “thousands”) and the number is “unmanageable” for regulatory risk assessment used to justify a “regulate all PFAS” approach (ECHA, 2020) to conduct proper risk assessments is incorrect.

The acronym PFAS describes a universe of fluorinated organic substances with vastly different physical, chemical, and biological properties, including polymers and non-polymers; solids, liquids, and gases; highly reactive and inert substances; soluble and insoluble substances; and volatile and involatile substances. No one would assert that the organic chemicals polyethylene (a solid polymer), ethanol (a liquid, used in hand sanitizer), and propane (a flammable gas) should be “grouped together” because they all have $-CH_2-$ in them. Likewise, polytetrafluoroethylene (a solid, incredibly stable polymer), short-chain 6:2 fluorotelomer

alcohol (a liquid), and HFC-134a (a refrigerant gas) should not be grouped together because they have $-CF_2-$ in them; they have completely different properties, hazards, and risk based on how they are used (Figures 3 and 4).

Hundreds of substances can be appropriately categorized and grouped for risk assessment. It works for the organic chemical universe, and it can and should similarly be applied for the universe of fluorinated organic substances based on the composition and properties of the substances and their use(s).

Furthermore, there has been a move to expand the definition of PFAS to include substances containing only an isolated $-CF_2-$ group in the carbon backbone (ECHA, 2020; USEPA, 2020b). We suggest this is not a prudent approach, as organic substances containing a $-CF_2-$ group adjacent to a hydrocarbon moiety, $-CH_2-$, would not be expected to lead to persistent fluorinated substances upon degradation. These specific substances would be readily susceptible to biodegradation leading to breaking of the carbon-fluorine bonds and elimination of the fluorine atoms. For example, this has been well demonstrated in the biodegradation pathways of fluorotelomer alcohols, $F(CF_2)_n-CH_2-CH_2OH$, which have a $-CF_2-$ group adjacent to a $-CH_2-$ group is readily degraded, breaking both $-CF_2-$ carbon-fluorine bonds (Liu & Mejia Avendaño, 2013). Thus, without the presence of a CF_3- in the substance, there would not be the possibility of degradation leading to a persistent fluorinated carboxylic acid as an end-product. Therefore, we submit that substances containing only an isolated $-CF_2-$ group in the carbon backbone should not be classified as PFAS.

The present study shows that the number of commercially relevant PFAS manufactured by the authors' companies is 256, which is small when compared to the total number of substances (4730) on the OECD list by individual CAS number, roughly 5.5%. The breakdown of commercial

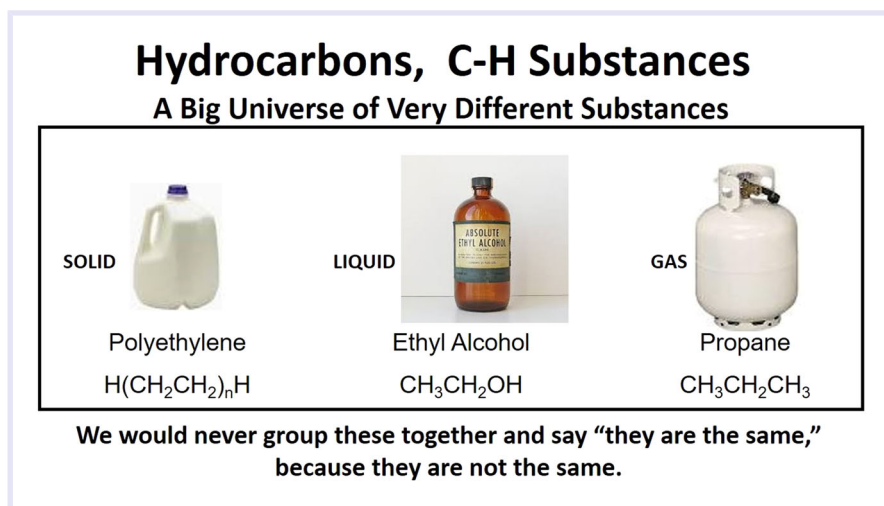


FIGURE 3 Hydrocarbons: A big universe of very different substances

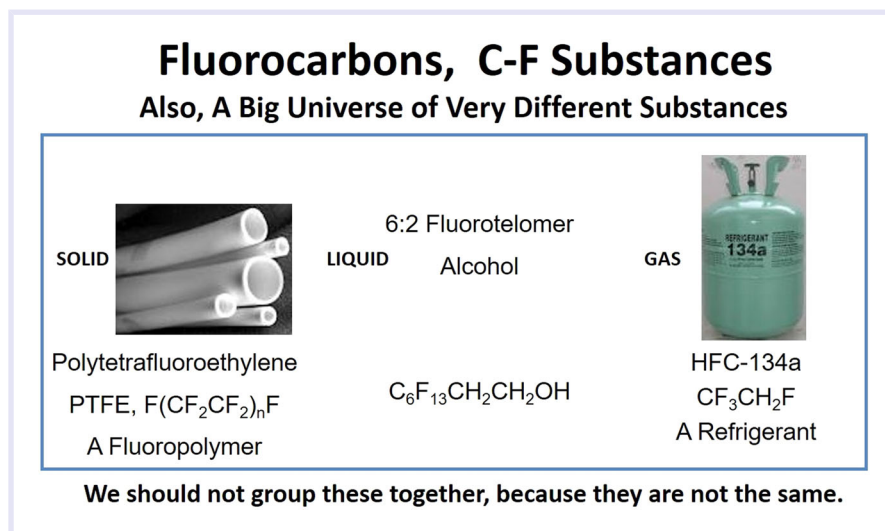


FIGURE 4 Fluorocarbons: Also, a big universe of very different substances

substances by class is shown in Table 3. There are 189 non-polymer versus 52 polymer substances (plus 15 not classified). This means the number of substances needing evaluation is significantly reduced and should be manageable. The commercially relevant PFAS chemistries can be classified into the following five sub-classes: non-polymer perfluoroalkyl, non-polymer polyfluoroalkyl, fluoropolymers, perfluoropolyether polymers, and side-chain fluorinated polymers. In fact, these five classes of substances possess very different physical–chemical properties and toxicological profiles, and they should not be grouped together when evaluating their risk to humans and the environment. For example, fluoropolymers are high molecular weight, water-insoluble, inert polymers that are not bioavailable (Henry et al., 2018). Further, the toxicological properties within a given class can vary greatly depending on structure as demonstrated by the dramatic toxicological property differences between the two perfluorocarboxylic acids (PFCAs), perfluorohexanoic acid and PFOA (Anderson et al., 2019; Luz et al., 2019).

FUTURE WORK

A unique and critical attribute of this study is that it was done by a bona-fide “bottom-up” approach by three major global producers to identify commercially relevant substances. The results of this study contain information from three major global producers. To obtain a more complete global picture of commercially relevant substances, we strongly encourage other producers to weigh in. The methodology presented in this study provides a ready-to-use template for further study with participation from additional global producers. A reminder that highly detailed information such as specific CAS numbers and production amounts were not gathered in this study to ensure confidentiality.

The 2018 OECD/UNEP Report list is not the only list of PFAS substances (USEPA, 2020b; Williams et al., 2017). Future work may endeavor to overlay assessment and data

gathered with multiple lists and seek to align stakeholders on criteria that provide a clear, understandable, and sound scientific basis for grouping and categorizing PFAS substances as a basis for their assessment.

SUMMARY AND CONCLUSIONS

Numerous lists of PFAS, some with thousands of entries, have been compiled from database searches, but none have clearly identified which of the substances on these lists are in commercial use that is, commercially relevant. Moreover, the structural definition of what constitutes a substance as a PFAS has evolved and changed over time, leading to confusion and a lack of clarity that conflicts with the desired purpose and intent of the original multi-stakeholder paper that first defined PFAS (Buck et al., 2011). The purpose of this study was to identify the commercially relevant PFAS substances on the 2018 OECD/UNEP Report list in global commerce today based on input from three major global producers: AGC Chemicals Company, Chemours, and Daikin Industries. This study provides new and valuable insight to the limited number of substances of commercial relevance on the 2018 OECD/UNEP Report list of PFAS substances. The study identified and classified 256 commercially relevant PFAS. The results show that a small subset, 256, roughly 5.5%, of the 4730 PFAS substances presented in 2018 OECD/UNEP Report are commercially relevant. Further, the study highlights that how classification criteria are applied matters by comparing the results when the original 2011 definition and categorization for PFAS is applied to the results and when the definition and categorization presented in the 2018 OECD/UNEP Report are applied. The comparison suggests that grouping and categorizing PFAS using fundamental classification criteria based on composition and structure provided in Buck et al. (2011) first is the best practice and makes sense. This approach can be used to identify appropriate groups of PFAS

substances for risk assessment thereby dispelling assertions that there are too many PFAS chemistries (“thousands”) and the number is “unmanageable” to conduct regulatory risk assessments for the commercially relevant substances.

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CONFLICT OF INTEREST

The study authors are employed by companies that commercially manufacture fluorinated substances of many types (e.g., fluoropolymers, perfluoropolyether polymers, and short-chain fluorotelomer-based products). S. H. K. is an independent fluorotechnology consultant working for AGC Chemicals Americas, Inc. and principal of BeachEdge Consulting, LLC.

DATA AVAILABILITY STATEMENT

Data gathered for this paper is presented in the paper itself and the Supporting Information.

SUPPORTING INFORMATION

FIGURE S1. Number of commercially relevant substances identified in this study that meet the Buck et al. (2011) PFAS definition.

FIGURE S2. Commercially relevant substances ($n = 256$) on the 2018 OECD/UNEP Report list—Pictorial.

FIGURE S3. 2018 OECD/UNEP Report list pictorial.

FIGURE S4. USEPA TSCA active non-CBI list by 2018 OECD/UNEP list category—Pictorial.

TABLE S1. 2018 OECD/UNEP Report structure category names and codes.

TABLE S2. Comparison of 2018 OECD/UNEP Report list and USEPA TSCA non-CBI list.

TABLE S3. USEPA TSCA active non-CBI list.

TABLE S4. USEPA TSCA active CBI list.

TABLE S5. Comparing the USEPA active CBI list with this study.

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