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# Synthesis Report on Understanding Perfluoropolyethers (PFPEs) and Their Life Cycle

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# Synthesis Report on Understanding Perfluoropolyethers (PFPEs) and Their Life Cycle

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# Executive Summary

Developed within the framework of the OECD/UNEP Global PFC group, this report presents recent efforts in gathering and synthesizing publicly available information on PFPEs, with the aim of elucidating the identities of PFPEs on the global market and analyzing their life cycle (including production and use, presence of other PFASs as impurities in commercial formulations, degradation mechanisms, and environmental releases of PFPEs and other PFASs present in commercial formulations).

Despite the abundance of knowledge and data gaps identified, the following key points can be concluded from the analysis. A variety of structurally diverse PFPEs exist on the global market, and their use in various industrial applications and consumer products is extensive. Most, if not all, PFPEs belong to four main families and are differentiated based on their brand names and synthesis processes. Notably, many PFPEs have rather low molecular weight, even below 1000 Da in some cases, and may warrant further examination. Production volumes of PFPEs are often reported as confidential business information. Some evidence demonstrates that other PFAS may be present in PFPE commercial formulations from different origins, but further investigation is needed to capture this comprehensively.

PFPEs are generally considered to be stable, demonstrating elevated thermal stability. However, they are vulnerable to Lewis acid-catalyzed decomposition. During use, several degradation mechanisms may take place, and the fate of PFPEs depends largely on the nature of the industrial application or process. Possible mechanisms of degradation for PFPE lubricants include thermal decomposition, catalytic decomposition, mechanical scission and triboelectric decomposition. A variety of degradation products have been identified for various PFPEs, including per-/polyfluoroalkylether carboxylic acids. Evidence of environmental releases of PFPEs remains limited, although efforts to identify PFPEs in New Jersey (United States) soil and water samples have shown that PFPEs have been detected in varying concentrations across several environmental matrices, and may undergo transformation and degradation.

These findings are only a first step towards understanding the life cycle of PFPEs and the extent of their use on the global market. The gaps in knowledge and data clearly demonstrate how little is known about these substances and why concern may be warranted. Concerted action by all stakeholders is needed to address PFPEs efficiently and effectively. This includes allocating time, funding, and research efforts towards addressing the critical knowledge and data gaps identified in this report, especially those most relevant for sound management of PFPEs. Researchers, government officials, and other stakeholders may consider the following actions as possible priorities when addressing critical knowledge and data gaps:

- Develop and/or utilize additional chemical identifiers for PFPEs beyond CASRNs and CAS names, to communicate more comprehensive information with respect to their chemical identities and structural characteristics.
- Collaborate with manufacturers to gain public access to relevant information such as production and use, presence of other PFAS impurities in commercial formulations, degradation during the use phase, and environmental releases from manufacturing sites, where applicable.
- Expand the scope of analysis of this report by including safety data sheets and patents, which were not actively searched in this report due to time and resource constraints.

- Continuously gather new data and synthesize them for a better understanding of PFPEs on the global market and their life cycles.

In addition to addressing critical knowledge and data gaps, parallel action can be taken to promote stewardship programmes and regulatory action on both national and international levels, with the aim of reducing PFPE emissions and exposure.

# List of Acronyms

| | |
|---|---|
| CAS | Chemical Abstracts Service |
| CASRNs | CAS Registry Numbers |
| CAGR | Compound Annual Growth Rate |
| CDR | Chemical Data Reporting |
| ECHA | European Chemicals Agency |
| EU | European Union |
| FCN | Inventory of Effective Food Contact Substance Notifications |
| ICCM | International Conference on Chemicals Management |
| MFA | Perfluoromethylalkoxy copolymers |
| N.A. | Not available |
| n.d. | No date |
| OECD | Organisation of Economic Co-operation and Development |
| PAPs | Fluorotelomer phosphate esters |
| PFA | Perfluoroalkoxy alkanes |
| PFASs | Per- and polyfluoroalkyl substances |
| PFECAs | Per-/polyfluoroalkylether carboxylic acids |
| PFCAs | Perfluoroalkylcarboxylic acids |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctanesulfonic acid |
| PFPEs | Perfluoropolyethers |
| PFPMIEs | Perfluoropolymethylisopropyl ethers |
| PFSAs | Perfluoroalkanesulfonic acids |
| REACH | Registration, Evaluation, Authorization and Restriction of Chemicals |
| SDS | Safety data sheets |
| SPIN | Substances in Preparations in Nordic Countries |
| t | Tonnes |
| UN | United Nations |

| | |
|---|---|
| UNEP | United Nations Environment Programme |
| US | United States |
| US EPA | US Environmental Protection Agency |
| US FDA | US Food & Drug Administration |
| WWTP | Wastewater Treatment Plant |

# Table of contents

## Tables

## Figures

# 1

# Background, motivation, scope

The OECD/UNEP Global PFC Group was created to address Resolution II/5 passed at the second session of the UN International Conference on Chemicals Management (ICCM 2) in 2009. Resolution II/5 called on various organizations, governments, and additional stakeholders to develop national and international stewardship programs as well as regulatory approaches, with the aim of reducing the presence of certain perfluorinated chemicals in products and, if feasible, eliminate them entirely. This was reaffirmed in Resolution III/3 during the third session of the conference in 2012, which recognized that more work was needed to implement the original resolution. Additional information about the group and its efforts can be found on the OECD PFAS web portal (https://oe.cd/).

Developed within the framework of the Global PFC Group, this report provides a summary of recent efforts from October 2022 to December 2023 in collecting and synthesizing publicly available scientific and technical information on perfluoropolyethers (PFPEs), a subset of per- and polyfluoroalkyl substances (PFASs). The objective of the report is to provide a comprehensive overview of the identities of PFPEs on the global market and to illustrate their life cycle, including their production and use, the presence of other PFASs in commercial formulations, degradation/stability during use and end-of-life, and environmental releases of PFPEs and other PFASs in commercial formulations. The report is founded upon a review of peer-reviewed scientific literature, regulatory reports, databases, and technical documents. It aims to be comprehensive, but not exhaustive. Due to time and resource limitations, the report does not include a thorough examination of safety data sheets or patents. Moreover, additional critical knowledge gaps exist regarding PFPEs beyond those outlined in this report.

PFASs are a class of anthropogenic chemicals 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 (OECD, 2021). They are known for their typical technical properties such as oil- and water-repellency, chemical and thermal stability, and others. This class comprises thousands of chemical substances (OECD, 2018; US EPA, n.d.), with numerous applications in industrial processes and consumer products (Glüge et al., 2020).

Although many PFASs have been manufactured and used since the 1950s (Lyons, 2007; Richter et al., 2018), concerns regarding their environmental persistence, ubiquitous occurrence, and health-related risks started to gain attention in the early 2000s. At the time, two long-chain PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), were at the forefront of attention, leading to an expansion of research and risk management measures for a plethora of different PFASs over time.

On the whole, PFASs can be divided into two major categories: non-polymeric and polymeric. Research on identities, life cycles, hazards, occurrences, exposures, and risks has historically focused on non-polymeric PFASs. While some research has been conducted for polymeric PFASs, including side-chain fluorinated polymers, fluoropolymers, and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2021), much of them has been fragmented and scattered over the public domain.

The Global PFC Group has established the understanding of the life cycle of polymeric PFASs as a key priority of its activities. This report complements the previous Synthesis Report on Understanding Side-

Chain Fluorinated Polymers and Their Life Cycle (OECD, 2022), with a new focus on perfluoropolyethers (PFPEs). PFPEs are defined as “ether polymer backbone with F atoms directly attached” (Buck et al., 2011), i.e., polymers that contain perfluorinated ether moieties such as $–CF_2–O–CF_2–$ as repeating units directly in the polymer backbone chain. It should be noted that certain PFPEs, used as intermediates to produce larger side-chain fluorinated polymers (e.g., under the brand Fluorolink$^{TM}$), have been included in the previous Synthesis Report, and thus, are not necessarily repeated here.

PFPEs should not be confused with certain other polymeric PFASs, such as perfluoroalkoxy alkanes (PFA) and fluorinated ionomers including Nafion$^{TM}$ and CASRN 111173-25-2[1]. This is because the latter are fluoropolymers—defined as “carbon-only polymer backbone with F directly attached to backbone C atoms” (Buck et al., 2011). While such fluoropolymers also contain perfluorinated ether moieties, these moieties are located on the side chains that attach to the polymer backbone chain instead of being part of the polymer backbone chain (see Figure 1). Such structural differences result in some distinct properties between PFPEs and fluoropolymers. For example, the rigidity of the perfluorinated carbon chain is reduced in PFPEs by the ether linkages (C–O–C), resulting in PFPEs that may remain liquid at ambient temperature even at molecular weights as high as 10,000 Dalton or more (Chittofrati et al., 1989a). Fluoropolymers will be separately elaborated in a future synthesis report of the series.

Furthermore, PFPEs should not be confused with discrete perfluoroalkylether-based compounds. The latter are individual chemical compounds, whereas PFPEs are always a mixture of compounds (see Figure 1), in accordance with the OECD definition of polymers (OECD, 1991):“a substance consisting of molecules characterized by the sequence of one or more types of monomer units and comprising a simple weight majority of molecules containing at least three monomer units which are covalently bound to at least one other monomer unit or other reactant and consists of less than a simple weight majority of molecules of the same molecular weight. Such molecules must be distributed over a range of molecular weights wherein differences in the molecular weight are primarily attributable to differences in the number of monomer units.” Discrete perfluoroalkylether-based compounds are not a focus of this series of synthesis report on the life cycle of polymeric PFASs; more information on these compounds can be found at Wang et al. (2020) and references therein[2].

PFPEs share many of the same properties as other (polymeric) PFASs, including oil- and water-repellency, and chemical and thermal stability (Sansotera et al., 2016). Individual properties can vary greatly depending on unique chemical structure and functional groups (Banks et al., 1994; Sansotera et al., 2016; Sianesi et al., 1971). In contrast to other polymeric PFASs, PFPEs have drawn little public attention. Nevertheless, they are of interest due to many having low molecular weight and even <1000 Dalton in some cases (see Table 1), ongoing and historic production, widespread use, presence of other PFAS impurities in commercial formulations, and environmental releases of PFPEs and other related PFASs. Additionally, PFPEs may be used in ways which results in direct human and ecosystem exposure and potential adverse effects on the environment and human health[3].

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[1] Ethanesulfonic acid, 1,1,2,2-tetrafluoro-2-[(1,2,2-trifluoroethenyl)oxy]-, polymer with 1,1,2,2-tetrafluoroethene

[2] Additional examples include Chemical Abstracts Service Registry Numbers (CASRNs) 127003-77-4 [1,1,1,2,2,3,3,5,6,6,8,9,9,11,12,14,14,15,15,16,16,16-Docosafluoro-5,8,11,12-tetrakis(trifluoromethyl)-4,7,10,13-tetraoxahexadecane], 61098-00-8 [1,1,1,2,2,3,3,5,6,6,8,9,11,11,12,14,14,15,15,16,16,16-Docosafluoro-5,8,9,12-tetrakis(trifluoromethyl)-4,7,10,13-tetraoxahexadecane] and 61098-01-9 [1,1,1,2,2,3,3,5,6,6,8,9,9,11,12,14,14,15,17,17,18,20,20,21,21,22,22,22-Octacosafluoro-5,8,11,12,15,18-hexakis(trifluoromethyl)-4,7,10,13,16,19-hexaoxadocosane].

[3] The adverse effects of PFPEs on the environment and human health are not reviewed in this report. Nevertheless, during the preparation of this report, it is noted that DuPont employees shared unpublished data with some scientists regarding the toxicology of a PFPE surfactant that had an average molecular weight of 740 and was similar to $CF_3O(CF_2CF(CF_3)O)_3CF_2COO^-NH_4^+$: they found that the PFPE surfactant can cause decrease in body weights and

The report will first introduce the identities of PFPEs on the global market in Chapter 2, which provides an overview of general PFPE structural categorization based on typical synthesis methods, a closer analysis of the identities of some individual PFPEs, and challenges and opportunities in the identification and characterization of PFPEs. Chapter 3 follows with an investigation of the life cycle of PFPEs, with a focus on (1) historical and ongoing production and uses, (2) presence of other PFASs in commercial formulations, (3) degradation of PFPEs during use and after end-of-life, and (4) environmental releases of PFPEs and related impurities.

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increase in liver weights in rats (Johnston et al., 1996a,b). The New Jersey Department of Environmental Protection established an interim specific ground water quality criterion of 0.002 µg/L for Cl-PFECAs, which is considerably lower than those for PFOA (0.014 µg/L) and PFOS (0.013 µg/L) (see New Jersey Register, vol. 54, iss. 2, 54 N.J.R. 185(a)). Cl-PFECAs that have been detected in the environment are discrete components of some PFPEs. In addition, a commercial PFPE mixture containing perfluoropolymethylisopropyl ethers (PFPMIEs) demonstrated an instantaneous radiative forcing of 0.65 W $m^{-2}$ $ppb^{-1}$, equivalent to a global warming potential of 9000 relative to $CO_2$ on a 100 year time scale (Young et al., 2006).Thus, the adverse effects of PFPEs on the environment and human health may warrant future review.

# 2 Identities of PFPEs on the Global Market

**Chapter summary:**

- 153 PFPEs are identified, 134 have an assigned Chemical Abstracts Service Registry Numbers (CASRNs), and only 23 have structures available on SciFinder. They belong to four main families of PFPEs, based on the brand names and their respective unique synthesis methods.
- While detailed information on the chemical identities of many PFPEs are not readily accessible in the public domain, a vast range of PFPEs have been noted, with distinct chain lengths, types and numbers of end-groups, and other functional modifications. In some cases, the average molecular weight can be even lower than 1000 Dalton.
- Additional PFPEs on the global market may exist; however, their identities, chemical structures, and properties remain unknown.
- Several factors contribute to the challenges in identifying and characterising PFPEs based on publicly accessible information. These include confidential-business-information claims and that CASRNs and CAS names alone are not sufficient in communicating the diversity and complexity of PFPEs on the market.
- Future efforts could expand the review scope by including a search of safety datasheets, patents, and other technical documents.
- Collaboration with chemical manufacturers is recommended to gain a comprehensive understanding of existing commercial formulations and chemical identities. This information should be made readily and easily accessible to the public, including a need for improved naming conventions and novel comprehensive chemical identifiers.

A wide range of PFPEs have been commercialized by several manufacturers since the 1960s, including those under the brands Krytox™ (Chemours, formerly DuPont), Fomblin™, Fluorolinks™, Galden™, Solvera™,[4], (Solvay, formerly Montedison and Ausimont), Demnum™ (Daikin), Afluid™ (Asahi), Aflunox™ (NOK CORPORATION, formerly Nippon Mektron), Hostinert™ (formerly Hoechst), Topda™ (Topda) (Sianesi et al. 1994; Okazoe, 2015; Topda, n.d.). Building upon the previous Nordic Council Report (Wang et al., 2020)[5], the US EPA ChemView database[6], and some other sources, a non-exhaustive list of 153

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[4] According to the manufacturer, Solvera® was phased out in 2022.

[5] Briefly, this Nordic report compiled information on per- and polyfluoroalkylether substances (PFAEs) through an extensive review of regulatory inventories of industrial chemicals, with a dedicated section specific to PFPEs

[6] United States Environmental Protection Agency ChemView Database: https://chemview.epa.gov/chemview/

PFPEs that have been or may have been on the global market is identified. The list of PFPEs and additional information, including chemical structures and registration status in national/regional chemical inventories, can be found in Table S1 and Table S2 in the Annex (an Excel sheet file provided separately).

## An overview of PFPEs on the global market

Overall, four main families of PFPEs can be identified on the global market, based on their respective typical synthesis methods, while various categorization schemes have been used in the literature.

PFPE-K are prepared via anionic polymerization of hexafluoropropylene epoxide (HFPO) at low temperatures (Figure 1, A1; Ameduri & Boutevin, 2004; Costello et al., 2004; Dams & Hintzer, 2016; Moffett et al., 2020). The intermediate polymers are stabilized by reaction with water, followed by reaction with elemental fluorine (Moffett et al., 2020). The range of average molecular weight are reported to be 1,000–13,500 Daltons for PFPE-K (Hoshino and Morizawa, 2017; Moffett et al., 2020).

PFPE-Y are prepared by photochemical catalyzed polymerization of hexafluoropropylene at low temperatures in the presence of oxygen, also termed the photooxidation of hexafluoropropylene (Figure 1, A2; Ameduri & Boutevin, 2004; Costello et al., 2004; Dams & Hintzer, 2016; Moffett et al., 2020). The average molecular weight of PFPE-Y can range from 1,000 to 10,000 Daltons (Hoshino and Morizawa, 2017; Moffett et al., 2020). PFPE-Z are prepared using the same process as for PFPE-Y, but using tetrafluoroethylene as the starting material (Figure 1, A2; Moffett et al., 2020). The range of average molecular weight for PFPE-Z is reported to be 3000–25,000 Dalton (personal communication from the manufacturer; Solvay, 2014a; Hoshino and Morizawa, 2017). A typical production of Galden$^{TM}$ is a mixture having molecular weights 350–8000, and an average molecular weight of ca. 690 (Chittofrati et al., 1989b).

PFPE-D are produced by Lewis-acid catalyzed or fluoride ion ring-opening polymerization of 2,2,3,3,-tetrafluorooxetane, followed by direct fluorination with elemental fluorine (Figure 1, A3; Ameduri & Boutevin, 2004; Costello et al., 2004; Dams & Hintzer, 2016; Moffett et al., 2020). The range of average molecular weight for PFPE-D is reported to be 2000–10,000 Dalton (Hoshino and Morizawa, 2017).

PFPE-A[7] may start with the esterification of polyethylene glycol with a perfluoroacyl fluoride to give partially fluorinated polymers, which are then undergo direct fluorination with F2 to give perfluorinated polymers, with over a conversion rate of over 99%. The perfluorinated polymers may be further reacted to produce desired PFPE-A (Figure 1, A4; Okazoe, 2015). It is reported that the molecular weight distribution from this synthesis route is narrow, and that this synthesis route allows for branched structures having three or more terminal functional groups per molecule (Okazoe, 2015; Hoshino and Morizawa, 2017). Information on the range of average molecular weight is not identified during the preparation of this report.

Despite a limited number of general structures known as described above, a large variety of PFPE derivatives can be synthesized through modification of the terminal functional groups on the polymer backbone chain (i.e., end-groups), with possible end-groups including silanes, amines, esters, alcohols, and phosphates (Dimzon et al., 2015; Sansotera et al., 2016; Hoshino and Morizawa, 2017). Due to many possible chain lengths, various end-groups, and other functional modifications, a vast range of PFPE

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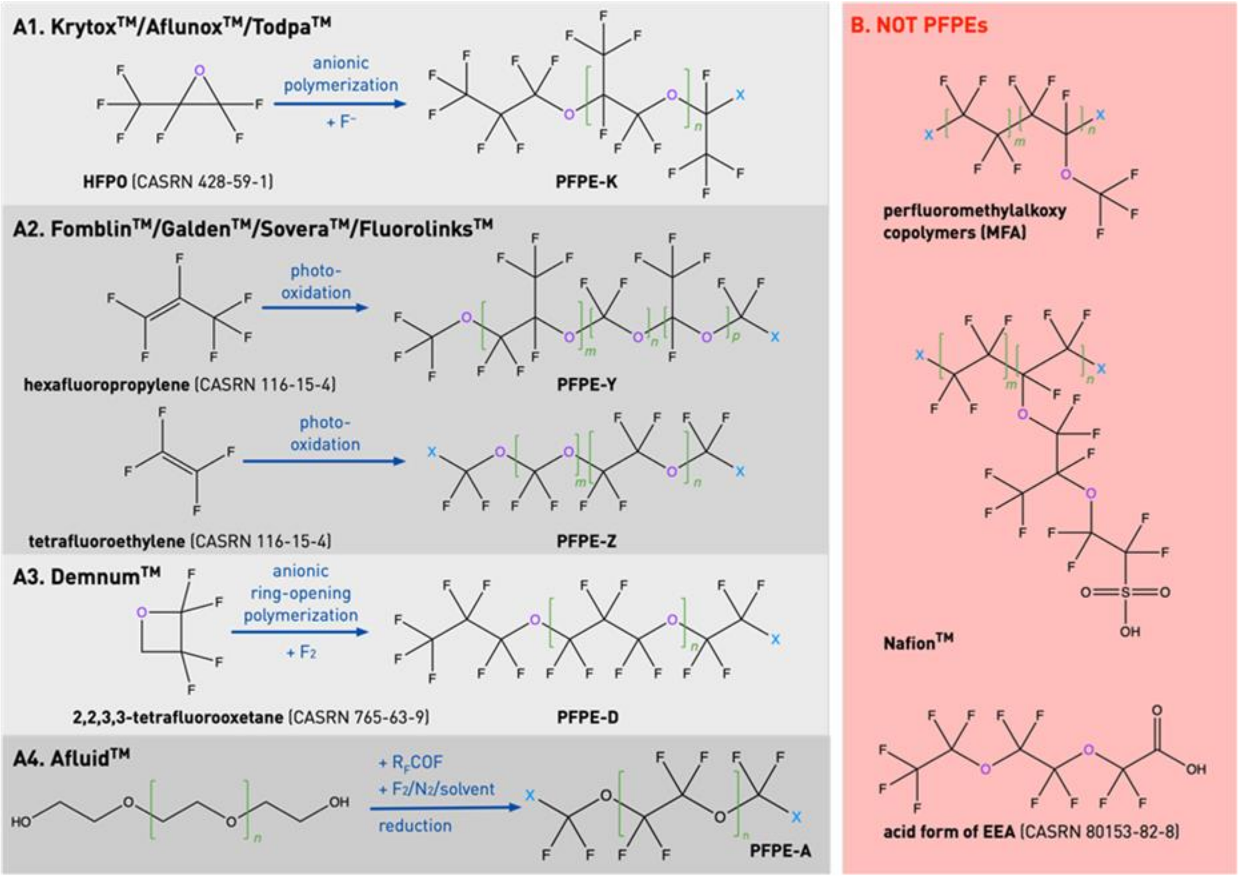
[7] Note that PFPE-A to describe a PFPE family is first introduced in this report, mimicking the style of other PFPE families. Meanwhile, it should be noted that the acronym of “PFPE-A” has been used in previous studies to described individual PFPEs, such as perfluoropolyether quaternary ammonium salt (Dou et al., 2023), perfluoropolyether amide propyl dimethyl ammonium iodide (Zhang et al., 2019). Readers are advised to pay attention to the acronym, particularly whether it is used to describe a PFPE family or a specific PFPE.

structures are possible and many of them have been commercialized, as demonstrated by the 153 PFPEs identified during the preparation of this report.

Figure 1. A) Synthesis routes of the four main families of PFPEs, where X represents an end-group. B) PFASs that are not PFPEs (MFA, which belong to the family of PFA, and NafionTM are fluoropolymers, and the acid form of EEA is a discrete perfluoroalkylether-based compound).



Note: Oxygen atom (O) in the ether linkage is highlighted in violet, repeating units on the polymer backbone chain are highlighted using square brackets in green, and end-groups (X) are highlighted in blue.

## Challenges in the identification and characterization of individual PFPEs

It is critical to have a comprehensive understanding of specific characteristics of individual polymers, including the range of molecular weights, and the type and number of functional groups, in order to assess their hazards (Wang et al., 2021; Groh et al., 2023). While much is known about the general categorization of PFPE families, it is challenging to characterise the multitude of the polymer identities and structures of individual PFPEs on the global market. Of the 153 PFPEs identified, 134 have their assigned CASRNs identified, and only 23 have structures available on SciFinder[8] (see Table S1 and Table S2 in the Annex).

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[8] It is noted that SciFinder is not the only source that have information on the structures of chemicals, while being the largest chemical database. For example, the structure of CASRN 161075-00-9 is not available on SciFinder, but is

This lack of structural understanding in the public domain is largely because much of the information on the polymer identities and structures has been claimed as confidential business information or has simply not been made publicly accessible (Wang, 2022).

Meanwhile, the current naming conventions of polymers for public use are often ambiguous, posing major challenges in determining the chemical structure based solely off the names (Wang et al., 2021). For example, CASRN 161075-00-9 is assigned the name “1-Propene, 1,1,2,3,3,3-hexafluoro-, oxidized, polymd., reduced, fluorinated” without any structure reported on SciFinder. Similarly, CASRN 161075-08-7 is assigned the name “Oxirane, (chloromethyl)-, reaction products with reduced Me esters of reduced polymd. oxidized tetrafluoroethylene” without any structure reported on SciFinder. It is feasible to identify the general family of such PFPEs based on the general synthesis routes as elaborated above (e.g., CASRN 161075-00-9 may well be a PFPE-Y, whereas CASRN 161075-08-7 may well be a PFPE-Z; see Figure 1). However, as the exact structures depend on specific reaction conditions and other reagents present, which are not reported in their names, it is hard to draw conclusions on the exact structures of these PFPEs. Also, while the four main families of PFPEs in Figure 1 are based on the major manufacturers, this categorization and identification approach is not necessarily a comprehensive representation of all PFPEs on the global market. Other PFASs which meet the definition of a PFPE, but which are synthesized by using alternative methods, are not effectively captured with this categorization and identification approach.

In some cases, the assigned chemical name for some PFPEs are specific for determining the chemical structures, e.g., CASRN 1033385-42-0, “Poly[oxy[trifluoro(trifluoromethyl)-1,2-ethanediyl]], α-[1,2,2,2-tetrafluoro-1-[[(2-hydroxyethyl)amino]carbonyl]ethyl]-ω-[tetrafluoro(trifluoromethyl)ethoxy]-, ether with α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (2:1)”. However, even in such cases, critical information such as the range of molecular weights is still missing.

Furthermore, it is noted that in the public literature, additional structural details for PFPEs and other polymers are rarely available, and when they are, they are often ambiguous. For example, Wolfberger et al. (2021) studied different PFPE lubricants and greases used in space applications using their trade names, “Fomblin™ Z25”, “Brayco™ 815Z” and “MAPLUB™ PF 100-B,” without disclosing the associated CASRNs, chemical names, and complete structures. Similarly, Tao and Bhushan (2005b) conducted experimental work on the use of PFPE lubricants without revealing the chemical structures and identities.

External analytical studies may be helpful in determining the structural details of individual PFPEs. For example, Dimzon et al. (2016) used a high-resolution mass spectrometry to elucidate the molecular structures in Solvera PT5045: $(HO)_2(O)P–O–(C_2H_4O)_n–CH_2CF_2O–(C_2F_4O)_p–(CF_2O)_q–P(O)(OH)_2$, where the repeating units $–C_2F_4O–$ and $–CF_2O–$ per molecule range from 2 to 7, and 2 to 3, respectively, and the

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available at https://echa.europa.eu/de/substance-information/-/substanceinfo/100.105.997. This report did not conduct a systematic search of all sources to locate chemical-identity information of the individual PFPEs identified.

total number of $–CF_2–$ per molecule ranges from 6 to 17. But such analytical studies are time- and resource-consuming, and challenging due to a number of factors[9] including lack of access to analytical standards[10].

It should be further noted that, CASRN has been used as a main identifier in this report to look for chemical information. However, this approach has its limitations. For example, CASRN 161075-00-9 has the assigned CAS name "1-Propene, 1,1,2,3,3,3-hexafluoro-, oxidized, polymd., reduced, fluorinated" on SciFinder, with "polymd." (i.e., polymerized) indicating it being a polymer. The same CASRN has another name "Hexafluoropropene, oxidized, oligomers, reduced, fluorinated" in the EU REACH database, which is likely linked to a non-polymeric mixture (as polymers are not required to register under the EU REACH). This raise the question whether this CASRN has been used for different substances, which has been shown in other cases (Wang et al., 2021; OECD, 2022). This shortcoming may lead to an underestimate of PFPEs on the global market, which could have distinct hazardous properties, bioavailability, environmental fate, degradation pathways, and risks to human health (Wang et al., 2021; Groh et al., 2023). In addition, 12 PFPEs identified have deleted CASRNs, i.e., those CASRNs replaced by the active CASRNs. Such merge of CASRNs is generally not well-documented and problematic, as it can pose challenges in tracking information of the substances over different time periods and from different sources.

## Structural characteristics and properties of known individual PFPEs

Still, available information suggests that the chemical makeup of these substances, including their molecular weights and end-groups, can vary significantly between different types of PFPEs on the market. For example, as shown in Section 2.1, Figure 1 above and Table 1 below, individual PFPEs may have distinct ranges of molecular weights and numbers of end-groups. Also, while many PFPEs are linear, many others have –CF3 side chains attaching to the polymer backbone. Noticeably, some PFPEs have rather low molecular weight, even below 1000 Da (see Table 1). It may be recommended to reflect on these low-molecular-weight substances (OECD, 2021).

In addition, Karis et al. (2002) reported that most commercial PFPEs have a fairly broad and asymmetrical molecular-weight distribution: PFPE-Zs with $–CF_3$ end-groups have a polydispersity index[11] (a measure of the heterogeneity of a sample based on size) in the range of 1.3–2, and the polydispersity index of PFPE Zdol (a commercial PFPE from the PFPE-Z family, see Table 1) is typically in the range of 1.5–1.7. Karis et al. (2002) further reported that polydisperse PFPE Zdol is often processed in supercritical $CO_2$, which separates by molecular weight, to obtain fractions with a narrow range of molecular weight. The variation of the chemical makeup, including molecular weights and end-groups, can have significant impacts on the

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[9] Dimzon et al. (2016) noted the analytical challenges in elucidating the structures of the individual species present in a formulation of PFPEs and other polymers. In general, studying polymeric structures includes understanding the different features that contribute to their diversity such as (1) molecular weight distribution; (2) nature of the repeating units; (3) presence of end-groups, side chains, and other functionalities. The study also noted that the next challenges in the mass spectrometry of polymers would include the development of ionization techniques to enable analyzing of hardly ionizable types, for example, the PFAS-based polymers. The study further noted that the development of a better mass spectral data processing tool is another challenge. This would be essential in the post-analysis of the mass spectra of highly complex and diverse polymer formulations like the PFPEs on the market.

[10] Ng et al. (2021) noted that high-quality analytical reference standards that enable targeted analysis with reliable quantification are expensive and still unavailable for many PFASs that commercial standard providers cover only about 80 different PFASs.

[11] Polydispersity index (PI) = weight-average molecular weight / number-average molecular weight. International Standards Organizations (ISOs) have established that PI values <0.05 are more common to monodisperse samples, while values >0.7 are common to a broad size distribution of particles (ISO 22,412:2017).

physicochemical properties, and thus, the fate and behavior of PFPEs in the environment and biota (Table 1 and Figure 2). For example, for PFPEs with the same functional end-groups, their vapour pressure (i.e., the volatility) decreases as the number of repeating units increases (see blue dots in Figure 2) or the molecular weight/size increases (see both blue and green dots in Figure 2). A more in-depth review of the impact of the chemical makeups, including the presence of –CF3 side chains and different functional end-groups, on the physicochemical properties, fate and behaviour of PFPEs is warranted

## Options for way forward

Obtaining comprehensive data about the chemical identities of commercial PFPEs on the global market, including various structural characteristics such as molecular weights and end-group compositions, remains a challenge, while such data have a critical role in understanding the hazards, exposure and risks of the various PFPEs on the market. Moreover, additional PFPE identities and their properties are yet to be identified, and emerging substances may not fit into any of the four families of PFPEs mentioned above.

To confront these critical knowledge and data gaps, future efforts could expand the scope of the literature review by including a search of company safety datasheets, patents, and other technical documents to compile as much existing information as possible. Moreover, it is advisable to cooperate with chemical manufacturers to get a better understanding of commercial PFPEs being currently or historically used. Manufacturers could share more information on existing commercial formulations, including their chemical identities and structural characteristics; priority may be given to PFPEs actively being produced and sold on the global market with high production volumes.

Additionally, chemical identities and structural characteristics of commercial PFPEs should be made readily and easily accessible to the public. In particular, CASRNs and CAS names alone are not sufficient in communicating the diversity and complexity of PFPEs on the market as elaborated above, calling for improved naming conventions and novel more comprehensive chemical identifiers. Developing more comprehensive unique identifiers beyond CASRNs and CAS names may enable a better understanding of the fate and behaviour of individual unique PFPEs. Such better understanding may also support development of predictive models for property estimation to support uncertainty and data gaps.

### Table 1. Additional structural characteristics and physico-chemical properties of multiple commercial PFPEs

| PFPE category | Commercial PFPEs | End-groups | Average molecular weight (Da) | Boiling point ℃ | Water solubility | Vapour pressure at 20 ℃ (mm Hg) | References |
|---|---|---|---|---|---|---|---|
| PFPE-Y | Fomblin™ Y LVAC 06/6 | | 1800 | | | $8 \times 10^{-7}$ | Solvay, 2023 |
| PFPE-Y | Fomblin™ Y LVAC 14/6 | | 2500 | | | $1 \times 10^{-7}$ | |
| PFPE-Y | Fomblin™ Y LVAC 16/6 | | 2700 | | | $9 \times 10^{-8}$ | |
| PFPE-Y | Fomblin™ Y LVAC 25/6 | | 3300 | | | $6 \times 10^{-8}$ | |
| PFPE-Y | Fomblin™ Y | | 6600 | | | | |

| PFPE category | Commercial PFPEs | End-groups | Average molecular weight (Da) | Boiling point ℃ | Water solubility | Vapour pressure at 20 ℃ (mm Hg) | References |
|---|---|---|---|---|---|---|---|
| | HVAC 140/13 | | | | | | |
| PFPE-Y | Galden™ LS200 | $CF_3$ | 870 | 200 | | 0.16 | Solvay, 2022 |
| PFPE-Y | Galden™ LS215 | $CF_3$ | 950 | 215 | | 0.09 | |
| PFPE-Y | Galden™ LS230 | $CF_3$ | 1020 | 230 | | 0.03 | |
| PFPE-Y | Galden™ HS240 | $CF_3$ | 1085 | 240 | | 0.01 | |
| PFPE-Y | Galden™ HS260 | $CF_3$ | 1210 | 260 | | 0.01 | |
| PFPE-Y | Galden™ SV55 | $CF_3$ | | 55 | <10 ppm | 228 | Solvay, 2015 |
| PFPE-Y | Galden™ SV70 | $CF_3$ | | 70 | <10 ppm | 141 | |
| PFPE-Y | Galden™ SV80 | $CF_3$ | | 80 | <10 ppm | 62 | |
| PFPE-Y | Galden™ SV110 | $CF_3$ | | 110 | <10 ppm | 17 | |
| PFPE-Y | Galden™ SV135 | $CF_3$ | | 135 | <10 ppm | 8 | |
| PFPE-Y | Galden™ D02TS | $CF_3$ | 750 | 165 | | | Solvay, 2014b |
| PFPE-Y | Galden™ D03 | $CF_3$ | 870 | 203 | | | |
| PFPE-Y | Galden™ D02 | $CF_3$ | 760 | 175 | | | |
| PFPE-Y | Galden™ D05 | $CF_3$ | 1020 | 230 | | | |
| PFPE-Y | Galden™ DET | $CF_3$ | 430 | 81 | | | |
| PFPE-Y | Galden™ HT55 | $CF_3$ | 340 | 55 | <10 ppm | 225 | Solvay, 2014c |
| PFPE-Y | Galden™ HT70 | $CF_3$ | 410 | 70 | <10 ppm | 141 | |
| PFPE-Y | Galden™ HT80 | $CF_3$ | 430 | 80 | <10 ppm | 105 | |
| PFPE-Y | Galden™ HT110 | $CF_3$ | 580 | 110 | <10 ppm | 17 | |

| PFPE category | Commercial PFPEs | End-groups | Average molecular weight (Da) | Boiling point ℃ | Water solubility | Vapour pressure at 20 ℃ (mm Hg) | References |
|---|---|---|---|---|---|---|---|
| PFPE-Y | Galden™ HT170 | $CF_3$ | 760 | 170 | <10 ppm | 0.8 | |
| PFPE-Y | Galden™ HT230 | $CF_3$ | 1020 | 230 | <10 ppm | 0.03 | Solvay, 2014c |
| PFPE-Y | Galden™ HT270 | $CF_3$ | 1550 | 270 | <10 ppm | $<10^{-2}$ | |
| PFPE-Y | Galden™HT-135 | $CF_3$ | 610 | 135 | <10 ppm | 5.8 | Pompili et al., 1994; Solvay, 2014c |
| PFPE-Y | Galden™HT-200 | $CF_3$ | 870 | 200 | <10 ppm | 0.2 | |
| PFPE-Z | H-Galden™ ZT | $CF_2H$ | 328; 480; 641$^{F}$ | 88; 133; 178 | | | Marchionni et al., 2004 |
| PFPE-Z | Z03 | $CF_3$ | 6810$^{E}$ | | | | Karis et al., 2002 |
| PFPE-Z | Zdol | $CH_2OH$ | 1190; 1050; 1810; 1360; 4740; 5450; 2270; 2420$^{E,G}$ | | | | |
| PFPE-Z | Zdeal | $COOCH_3$ | 2070$^{E}$ | | | | |
| PFPE-Z | Ztetrol | $CH_2OCH_2OCH(OH)CH_2OH$; 2300$^{E}$ | | | | | Karis et al., 2002 |
| PEPF-Z | Zdiac | COOH | 2310$^{E}$ | | | | |
| PFPE-Z | Ztx | $CH_2(OCH_2CH_2)_{15}OH$; 2230$^{E}$ | | | | | |
| PFPE-D | Demnum™ SA2, SA 2000 | $CH_2OH$ | 3080; 2080$^{E}$ | | | | |
| PFPE-D | Demnum™ S100 | $CF_3$ | 5230$^{E}$ | | | | |
| PFPE-K | Krytox™ 143 AD | $CF_3$ | 6580$^{E}$ | | | | |
| PEPE-D | Demnum™ SH$^{D}$ | COOH | ca. 3000$^{E}$ | | | | Doan et al., 1997 |
| PFPE-Z | Fomblin™ Z-DIAC$^{D}$ | COOH | ca. 2000$^{E}$ | | | | Doan et al., 1997 |
| PFPE-Y | Fomblin™ HC/01$^{A}$ | $CF_3$ | 650 | | | 10 | Malinverno et al., 1996 |
| PFPE-Y | Fomblin™ HC/04$^{A,B}$ | $CF_3$ | 1500 | | | $10^{-3}$ | |
| PFPE-Y | Fomblin™ HC/25$^{A,B}$ | $CF_3$ | 3200 | | | $10^{-5}$ | |

| **PFPE category** | **Commercial PFPEs** | **End-groups** | **Average molecular weight (Da)** | **Boiling point ℃** | **Water solubility** | **Vapour pressure at 20 ℃ (mm Hg)** | **References** |
|---|---|---|---|---|---|---|---|
| PFPE-Y | Fomblin™ HC/R[A,B] | $CF_3$ | 6250 | | | $10^{-7}$ | |
| PFPE-Y | D-40 | $CF_3$ | 2000 | 400 | | <0.01 (25 ℃) | Pompili et al., 1994 |
| PFPE-Y | Fomblin™ Y/04 | $CF_3$ | 1500 | | | N.R. | Caporiccio, 1986 |
| PFPE-Y | Fomblin™ Y/25 | $CF_3$ | 2800 | | | $2 \times 10^{-5}$ | |
| PFPE-Y | Fomblin™ Y/R | $CF_3$ | 6000 | | | N.R. | |
| PFPE-Z | Fomblin™ Z/03[C] | $CF_3$ | 4000 | | | N.R. | |
| PFPE-Z | Fomblin™ Z/15[C] | $CF_3$ | 8500 | | | $2 \times 10^{-6}$ | |
| PFPE-Z | Fomblin™ Z/25[C] | $CF_3$ | 10000 | | | $2 \times 10^{-12}$ | |
| PFPE-K | Krytox™ 157FSL[D,H] | | 2500[E] | | | | Personal communication from a PFPE manufacturer |
| PFPE-K | Krytox™ 157FSM[D,H] | | 5000[E] | | | | |
| PFPE-K | Krytox™ 157FSH[D,H] | | 7250[E] | | | | |

A. According to the manufacturer, the phase-out of Fomblin™ HC series completed in 2022.

B. The content of low-molecular-weight molecules in these commercial PFPEs is <0.1% (Malinverno et al., 1996).

C. Fomblin™ PFPE-Zs nominally have two identical end-groups.

D. In Demnum™-SH and Krytox™-157FSL, 157 FSM and 157FSH, the acid end-group is present only at the propagation end (the ethoxy side) of the chain, whereas Fomblin™ Z-DIAC has acid end-groups at both ends.

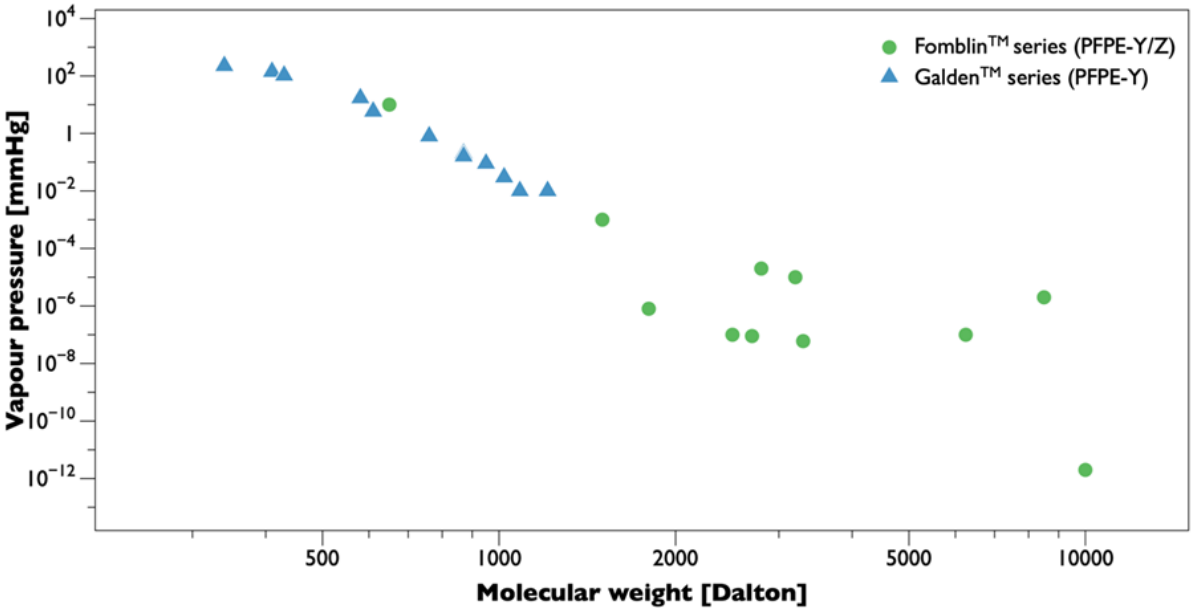
E. These are number-averaged molecular weight. For the others, no information is available whether they are number- or weight-averaged molecular weight.

F. Three samples were obtained by fractional distillation of a polydisperse mixture having boiling points from 35 to 200 ℃.

G. Several Zdol products and fractions of the same products were reported in the study.

H. According to the manufacturer, Krytox™ 157FSM was discontinued in circa 2020, while Krytox™ 157FSL and 157 FSH remain commercially available.

### Figure 2. Vapour pressure vs. molecular weight of Fomblin™ and Galden™ PFPEs with $-CF_3$ on both ends



# 3 The Life Cycle of PFPEs

**Chapter summary:**

- The production and use volumes of PFPEs remain largely unknown. It is noted that some information has been claimed confidential.
- PFPEs are used in at least 29 different industry branches, primarily as greases and lubricants, but also as additives, processing aids, surface treatments, etc. Examples of industries which use PFPEs include aerospace, automotive, electronics, food packaging, medical equipment, and textiles.
- Other PFAS are present in commercial PFPE formulations from different origins, but limited information is available in the public domain to provide a comprehensive overview of PFAS impurities in various PFPE formulations. More information from manufacturers is needed on the presence and concentrations of impurities in commercial formulations.
- PFPEs are considered to be generally chemically inert with high thermal stability under natural conditions (while certain transformation may take place at hetero-atom reaction centers and/or functional end-groups). However, they may be subject to degradation under technical conditions and possibly forming perfluoroalkylether-based carboxylic acids.
- The mechanism and rate of PFPE degradation depends on the application for which it is being used. Causes of degradation for PFPE lubricants include thermal decomposition, catalytic decomposition, mechanical scission, and triboelectric decomposition. PFPE degradation also varies depending on the molecular weight and end-groups of the polymer, while the presence of Lewis acids can reduce the thermal stability of certain PFPEs.
- Information on PFPE degradation during end-of-life treatment remains scarce, and incineration and open burning may need to be investigated, given their instability at high temperature observed under technical conditions.
- Studies on environmental releases of PFPEs are limited, with the exception of a series of studies related to PFPEs detected in New Jersey, United States soil and water samples. Several different chloroperfluoropolyether carboxylic acids were identified in various environmental matrices, one of which has also been identified in the Bormida di Spigno River, Italy.
- A deeper understanding of the flows and fates of PFPEs throughout their life cycle is needed, including developing substance flow analyses.

## Historical and ongoing production and uses

PFPEs were reportedly first synthesized by DuPont in the late 1950s and later publicly presented at a lubrication conference in the fall of 1965 (Lawson, 1986; Moffett et al., 2020). This first generation of PFPEs were based on hexafluoropropylene oxide (Moffett et al., 2020). Immediate interest arose for PFPE use in military and aerospace applications, given their high chemical and thermal stability, very low surface energies and friction coefficients, and their non-miscibility with organic solvents (Moffett et al., 2020; Kirsch, 2004). PFPEs later found use where conventional lubricants gave marginal performance, especially in high-temperature applications (Lawson, 1986). At the time, DuPont, the U.S. military, and NASA collaborated to produce specialized PFPE greases for aerospace applications (Moffett et al., 2020). Popularity of PFPEs rose rapidly in the 1980s. Banks et al. (1994) report that from 1985 to 1989, PFPE citations in the literature doubled, and the world market for PFPEs increased to 700 tonnes (t) per annum. Over time, the use of PFPEs expanded to a plethora of different applications beyond the initial implementation in military and aerospace. Moffett et al. (2020) further discuss the uses of PFPEs, which includes valve and o-ring lubrication, aircraft instrument bearings lubrication, seal lubrication in reactive chemical environments, extreme high/low temperature greases, and others. Today, significant applications of PFPEs include vacuum pump fluids (VPF) for semiconductor manufacturing and electronics production, automotive uses, and the corrugator industry[12] (personal communication from a PFPE manufacturer).

To acquire further information on the production volumes and uses of individual PFPEs, several databases, including the US TSCA CDR (2020)[13], SPIN[14], US FDA FCN[15], and EU REACH[16], were screened for all CASRNs identified in Table S1 in the Annex, along with a brief literature review. Production and uses of PFPEs, both historical and current, are highlighted below.

## Historical and Ongoing Production and Use Volumes

Information regarding PFPE production and use volumes in the public domain is limited. Table 2 summarizes the production or use volumes of specific PFPEs which could be found through the public databases. Most of the CASRNs searched for in each database yielded limited or no results (summarized in Table S3 in the Annex). For substances which were successfully found in one or more of the databases, the vast majority values were reported as confidential.

Despite the general lack of information, certain PFPEs (e.g., CAS 60164-51-4 and CAS 69991-67-9) have reportedly been used historically over the last 2 decades in varying volumes and in several European countries, as recorded in the SPIN database. One PFPE (CASRN 200013-65-6) produced by Solvay was listed in the US TSCA CDR, but production volumes were claimed as confidential business information. Recently, a PFAS restriction proposal under the EU REACH regulation provides more insight into some relevant use volumes of PFPEs in certain industrial sectors in the EEA region (see Table 3).

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[12] The corrugator industry refers to the sector involved in the manufacturing of corrugated cardboard and boxes (a type of packaging material that consists of a fluted corrugated sheet sandwiched between two flat liner sheets); for more details, see spirax sarco, n.d.

[13] United States Toxic Substances Control Act Chemical Data Reporting Data (2020): https://www.epa.gov/chemical-data-reporting/access-cdr-data

[14] Substances in Products in the Nordic Countries Database: http://spin2000.net/

[15] United States Food and Drug Administration Inventory of Effect Food Contact Substance Notifications: https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN

[16] European Union Registration, Evaluation, Authorisation, and Restriction of Chemicals Regulation, Registered Substance Factsheets: https://echa.europa.eu/information-on-chemicals/registered-substances

## Table 2. Reported PFPE production or use volumes in public databases.

Only the most recent statistics are listed here.

| CASRN | PFPE category | Country | Year | Production or Use Volumes [t] | Source |
|---|---|---|---|---|---|
| 161075-02-1 | PFPE-Z | Sweden | 2020 | Confidential | SPIN (2022) |
| 161075-14-5 | PFPE-K and/or PFPE-Y | Sweden | 2020 | Confidential | SPIN (2022) |
| | | Finland | 2015 | Confidential | SPIN (2022) |
| 161212-22-2 | PFPE-K and/or PFPE-Y | Sweden | 2003 | Confidential | SPIN (2022) |
| 162492-15-1 | PFPE-Z | Denmark | 2020 | Confidential | SPIN (2022) |
| | | Sweden | 2020 | Confidential | SPIN (2022) |
| 200013-65-6 | PFPE-Z | Sweden | 2017 | Confidential | SPIN (2022) |
| | | USA | 2019 | National aggregated production volume was <454 t, confidential | US TSCA CDR (2020) |
| 51798-33-5 | PFPE-K | Finland | 2020 | Confidential | SPIN (2022) |
| 60164-51-4 | PFPE-K and PFPE-Y[A] | Sweden | 2020 | 0.3 | SPIN (2022) |
| | | Norway | 2020 | 0 | SPIN (2022) |
| | | Finland | 2020 | 0 | SPIN (2022) |
| | | Denmark | 2020 | Confidential | SPIN (2022) |
| 69991-61-3 | PFPE-Z | Sweden | 2020 | Confidential | SPIN (2022) |
| 69991-67-9 | PFPE-K and/or PFPE-Y | Sweden | 2020 | 0.3 | SPIN (2022) |
| | | Denmark | 2020 | 0.1 | SPIN (2022) |
| | | Norway | 2020 | Confidential | SPIN (2022) |
| | | Finland | 2020 | Confidential | SPIN (2022) |

Note:
Source:

A. On SciFinder, the CASRN is assigned to Aflunox 606, Fomblin 225, Krytox 143, Krytox 16350, Krytox 293R, Krytox 335R, Krytox 39R, Krytox AD, and Krytox TLF 8996.

## Table 3. Tonnages of PFPEs used in different industries in EEA in 2020 (Germany et al., 2023)

| Industry [tonnes/year] | Low Estimate | Mid Estimate | High Estimate |
|---|---|---|---|
| TULAC (textile, upholstery, leather, apparel and carpets) | 786 | 1235 | 1683 |
| Electronics and Semiconductors | 9 | 281 | 552 |
| Energy | 2 | 3 | 3 |
| Lubricants (base oils) | 300 | 550 | 800 |

## Historical and Ongoing Uses

PFPEs have been reportedly used in a variety of industrial applications and consumer products. Here, at least 29 different industry branches were identified, which reportedly use PFPEs primarily as greases and lubricants, but also as additives, processing aids, surface treatments, and others. Examples of industries which use PFPEs include aerospace, automotive, electronics, food packaging, medical equipment, and textiles. Table 4 summarizes the detailed findings of PFPE commercial applications.

Notably, specific PFPE identities, structures, usage volumes, or formulations were seldom provided[17]. For this reason, the extent of specific PFPEs used in these applications remains unclear[18]. Some specific PFPEs for which CASRNs are known were linked to specific applications, as reflected in Table S3 in the Annex. In contrast, certain specific PFPEs reported to be used as lubricants or greases did not have any additional information with respect to application-specific uses. These miscellaneous or unspecified lubricants and greases include CASRNs 156559-18-1, 161075-00-9, 161075-02-1, 161075-14-5, 370097-12-4, 51798-33-5, 60164-51-4, 69991-67-9, and 76415-97-9. Other broad use areas (i.e., industrial sectors or applications) of PFPEs include “washing and cleaning products”, “heat transfer fluids”, “plastic product and machinery and vehicles”, “finishing agent”, “paints and coatings”, and others. Detailed information regarding reported uses for specific PFPEs and sources can be found in Table S3 in the Annex.

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[17] For example, in *Daikin Fluorochemical Products: Product Overview*, it reported that PFPE-Ds are used as lubricating oil, vacuum pump oil, sealing liquid, heating medium, and lubricants (for high-temperature, for high-vacuum, in chemical plants and in clean rooms), without giving further details on specific PFPE-Ds.

[18] Doan et al. (1997) reported that PFPE fractions employed in lubricant applications have molecular weight of 2000–10,000 Da, corresponding to the number of monomer units in each chain of 12–60. No further details were provided.

## Table 4. Overview of the identified historical and ongoing use categories of PFPEs. Noting that some uses may have been phased out in some parts of the world, or entirely[19]

| Industry / Application | Functional Use | Description of PFPE Function | Source |
|---|---|---|---|
| Aerospace | Additive | Additive in phosphate ester-based brake and hydraulic fluids in aircrafts. | (Banks et al., 1994; Glüge et al., 2020) |
| | Lubricant | Used in bearings, seals for valves and pumps, o-rings, oxygen systems, rocket engines, turbines, gimbals, pumps, gears, valves, actuators, spline hafts, control linkages, antenna pointing mechanisms, solar array drive mechanisms, hinges, hold down and release mechanisms, reaction wheels, deployable booms and antennae, instrument mechanisms, and de-spin mechanisms.<br>Desirable properties suitable for aerospace applications: reliability, long-lasting, reduced maintenance requirements, temperature tolerance, contact with fuel and oxidizers, robust resistance to harsh environmental conditions, good frictional properties, compatibility with other materials, and very low vapor pressure and outgassing over a wide temperature range, particularly at low temperatures. | (Glüge et al., 2020; Hoshino & Morizawa, 2016; Chemours, 2015a; Wolfberger et al., 2021) |
| Analytical Instruments | Lubricant | PFPE lubricants used as oil and grease in laboratory equipment and pumps. CASRN 156559-18-1 used in the production of Immersol-W (Zeiss), which is an immersion oil used to increase the resolving power of microscopes. | (Cousins et al., 2019; Glüge et al., 2020; Wang et al., 2020) |
| Architecture | Coatings | Used as an additive in paint coatings applied to the surfaces of buildings and bridges, including anti-graffiti coatings. Helps with resistance against corrosion, UV, weather, and flame. | (Germany et al., 2023) |
| Automotive | Lubricant | Used in emission controls such as EGR (exhaust gas recirculation) valves, throttle bodies, turbocharger and supercharger systems, and to reduce noise and vibration in vehicles. For example, metal-on-plastic squeak, leather-on-leather itch, window lace, convertible top seals, sliding door seals, steering column gaskets, weather stripping.<br>Used as a lubricant in fan clutch bearings, emission air pumps, spark plug boots, clutch release bearings, antilock brake systems, windshield wiper motors, belt pulleys, oil pressure sensors, alternator | (Germany et al., 2023; Glüge et al., 2020; Chemours, 2015a,b; Moffett et al., 2020) |

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[19] According to the manufacturer, the H-Galden™ series were discontinued in 2012, the Solvera™ was phased-out in 2022, the phase-out of the Fomblin™ series completed in 2022, and the ADV series was discontinued in 2021 with additional information that may be found at https://www.solvay.com/en/press-release/solvay-phase-out-use-fluorosurfactants-globally. For the ADV series, another member of the Global PFC Group reported that in 2022, the Solvay company announced to dismiss their production in the Italian plant from June 2023.

| Industry / Application | Functional Use | Description of PFPE Function | Source |
|---|---|---|---|
| | | bearings, and sintered bearings in motors, wheel bearings, CV/universal joints, weather stripping, sunroof seals, window lift mechanism, leather seats, consoles and trim, flocked and unflocked window seals and channels, door handles, switches, air vents, controls, and airbag covers. Desirable properties include wide temperature range, resistance to harsh environments, no compatibility issues with other automotive components. | |
| Batteries | Heat transfer fluid | PFPEs used as a heat transfer fluid in lithium-ion battery production. | (Glüge et al., 2020) |
| Box Board Corrugating | Lubricant | Corrugator equipment typically operates in the range of 170 to 200 ºC and PFPEs are used for extended relubrication intervals on heated rolls in single facers. Lubricate bearing on heated rolls in single facers and other equipment, can protect bearings, up to 399 ºC (in the case of the additionally processed Krytox™ XHT). | (Chemours, 2015a; spirax sarco, n.d.) |
| Electronics | Antifouling agent | Anti-fingerprint agent used in touch panel displays, gives smudge resistance and easy wiping over fingerprints. Also used in camera lenses and sensor surfaces. | (Germany et al., 2023; Hoshino & Morizawa, 2016; Min et al., 2018)<br>Databases: EPA Chemview (2023) |
| | Coating | Hard disk drive coating, used to protect the magnetic material from friction and scratches. | (Hoshino & Morizawa, 2016) |
| | Inert fluid | Used as inert fluids in electronics testing applications, including liquid burn-in testing, thermal shock testing, gross and fine leak testing. CASRN 69991-67-9 used in immersion cooling of electronics. H-Galden™ PFPEs were developed to be implemented as heat transfer medium (i.e., coolant) in critical conditions. | (Banks et al., 1994; Germany et al., 2023; Glüge et al., 2020) |
| | Lubricant | Used in semiconductor and electronics manufacturing wet and dry vacuum pumps, vacuum system sealants, bearings, valves, seals, o-rings, chains, compressors, gearboxes. | (Chemours, 2015a; Moffett et al., 2020) |
| | Miscellaneous | Used in wire and cable insulation.<br>H-Galden™ PFPEs are used in front-end semiconductor manufacturing tools such as dry etchers, ion implanters, lithography steppers, etc. | (Germany et al., 2023) |
| Electroplating | Additive | Fluorinated surfactants prevent the evaporation of chromium (VI) vapor in chrome plating baths. By lowering the surface tension of the electrolyte solution, the surfactants diminish the size of the gas bubbles. | (Glüge et al., 2020; Kissa, 2001) |
| Fluoropolymer Manufacture | Processing aid | Used as fluorinated alternatives to ammonium or sodium perfluorooctanoate (APFO and NaPFO), as emulsifiers in the production of fluoropolymers, e.g., | (EFSA Panel on food contact materials, enzymes, |

| Industry / Application | Functional Use | Description of PFPE Function | Source |
|---|---|---|---|
| | | CASRN 329238-24-6 (ADV series). Also used as dispersing agents in fluoropolymer production. Example of a fluoropolymer produced: polytetrafluoroethylene (PTFE). | flavourings and processing aids (CEF), 2010, 2011; Gordon, 2011; Wang et al., 2013, 2020) |
| Food packaging | Treatment | Used in food packaging and food contact paper to help confer grease and water repellency.<br>CASRN 200013-65-6 used as a finishing agent in food packaging, liquid form (maximum concentration 90% +).<br>CASRN 200013-65-6 used as a water and oil repellant, lubricant, and finishing agent in the manufacture of food-contact paper and paper board.<br>CASRN 69991-62-4 (Solvera$^{TM}$) used as an oil and water repellent employed in the manufacture of food-contact paper and paperboard either prior to the sheet-forming operation or at the size press, approved by US FDA[20]. | (Dimzon et al., 2016; EFSA Panel on food contact materials, enzymes, flavourings and processing aids (CEF), 2010; Glüge et al., 2020; Trier et al., 2011; Wang et al., 2013, 2020; Westbury & Michitsch, 2013)<br>Databases: US TSCA CDR (2020), US FDA FCN (2020) |
| Food Processing Equipment | Lubricant | Many PFPE oils and greases are registered as NSF-H1 for incidental food contact and are used in oven applications, lubrication of production line equipment, including bearings, valves, seals, o-rings, chains, compressors, gear boxes, and pumps. | (Dimzon et al., 2016;Chemours, 2015a; Moffett et al., 2020; NSF, n.d.) |
| Fuel cells | Coating | Used as a coating to confer hydrophobicity to the gas diffusion layers of proton exchange membrane fuel cells.[21] | (Sansotera et al., 2016) |
| Glass | Surface treatment | Glass surfaces are treated with functionalized PFPEs (silanes, acrylates, etc.) to acquire permanent water and stain repellence. Helps improve visibility. | (Germany et al., 2023) |
| Leather | Impregnation | Used to impregnate leather against water, grease, and dirt.[22] | (Glüge et al., 2020; Kissa, 2001) |
| Magnetic Disk Drives | Lubricant | A layer of liquid PFPE lubricant is used at | (Dimzon et al., |

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[20] When applied prior to the sheet-forming operation the FCS is to be used at a level not to exceed 1 percent by weight of the finished dry paper and paperboard to be used in contact with all food types. When applied at the size press the total use level of the FCS is not to exceed 0.5 percent by weight of the finished dry paper and paperboard to be used in contact with aqueous foods and 1 percent by weight of the finished dry paper and paperboard to be used in contact with all other food types. (US FDA Inventory of Effective Food Contact Substance (FCS) FCN No. 538).

[21] According to the industry's feedback, this use may have remained in the state of research and development without commercialization.

[22] Note that this use is mainly linked with PFPEs under the brand name Fluorolink$^{TM}$, which is included in the previous synthesis report as noted above.

| Industry / Application | Functional Use | Description of PFPE Function | Source |
|---|---|---|---|
| | | the head-media interface of magnetic recording media to reduce friction and wear. PFPEs offer desirable lubricant properties including chemical inertness, low surface tension, low volatility, high thermal oxidative stability. PFPE functional end-groups are critical to bonding the lubricant and overcoat. | 2016; Gellman, 1998; Kasai & Raman, 2003; Li, Jones, & Hsia, 2004; Li, Jones, Merzlikine, et al., 2004; Spada & Basov, 2000; Tao & Bhushan, 2005b) |
| Medical Equipment | Lubricant | Used in oxygen systems and respirators. | (Chemours, 2015a) |
| | Miscellaneous | Medical and silicone tapes and wound dressings use PFPE-enabled release liners. PFPEs used as coating for ophthalmic lenses. Also used in ophthalmoscopy, and in cardiovascular implants. | (ECHA, 2023) |
| Metal Processing | Lubricant | Used in rod mills, smelters, acid, steel, foundry, aluminum, copper, and gold. | (Chemours, 2015a) |
| Personal Care Products | Additive | PFPEs have been detected in cosmetic products, e.g., used as an antistick and anti-irritant in lipsticks, creams, hair conditioner. For example, Fomblin™ HC products have a primary application in the prevention and treatment of irritant dermatitis, but are also widely used in rinse-off and longer term skin-contact cosmetic products. | (Costello et al., 2004; Glüge et al., 2020; Trier et al., 2011) |
| Petrochemical | Lubricant | Non flammable and non reactive. | (Chemours, 2015a) |
| Polymer | Medium | PFPE used as medium in resin, elastomers, and adhesives cross-linking by vapour or liquid immersion techniques. CASRN 200013-65-6 used in plastics material and resin manufacturing. | Polymer |
| | Additives | Fomblin™ Y45 provides a lower Coefficient of Friction (COF) and reduced wear. In addition, it delivers stain resistance and improves production throughput without modifying the mechanical properties of the host polymer. Typical applications of such polymers: polymer gear/bushings, auto weather stripping and interiors, shoe soles and cleats, o-rings/seals, polymer films, processing aids, and cable liners. The recommended loading of Fomblin™ Y45 is 0.1–1.0 %, depending on the base polymer matrix and desired final performance.<br>Fomblin™ DA305 and DA306/VAC, functionalized PFPEs, as anti-rust additives in Fomblin™ PFPE lubricants and Fomblin™ Y-LVAC fluids, respectively. | |
| Power Generation | Lubricant | Turbine auxiliary systems, gearboxes, dampers, valves, gaskets, high voltage circuit breakers, seals. | (Chemours, 2015a) |

| Industry / Application | Functional Use | Description of PFPE Function | Source |
|---|---|---|---|
| | Coating | PFPEs used in the front and back sheets of photovoltaic modules, part of the electric insulator. | (ECHA, 2023) |
| Printing | Lubricant | PFPEs used in lubricants for typewriters and photocopy machines. | (Banks et al., 1994; Glüge et al., 2020) |
| Pulp and Paper | Lubricant | Turbine auxiliary systems, gearboxes, dampers, valves, gaskets, seals, and other components.<br>Used to decrease frequency of lubrication and withstand extreme production environments. | (Chemours, 2015a) |
| Reactive Gas Service | Lubricant | Prevents auto-ignition in oxygen at high temperatures, or under high pressures. | (Chemours, 2015a) |
| Siliceous surfaces | Oil- and water-repellent treatment | PFPE silanes applied to siliceous surfaces, including shower panels and bathroom ceramics, to help impart water repellency. PFPE silanes applied in dilution with alcohol and catalytic amounts of acid. PFPE layer provides repellency and easy-to-clean properties, durability against harsh chemicals and mechanical abrasion. | (Dams & Hintzer, 2016) |
| Soldering | Vapour phase fluid | Used vapor phase fluids/heat transfer in soldering applications. | (Banks et al., 1994; Glüge et al., 2020; Solvay, 2022) |
| Textile | Lubricant | Enhance function of textile machinery, including tenter frame cross screw boxes, steamer and dryer bearings, lifter reel bearings in dye machines, tenter frame chains and gear boxes, high-speed motors, and guiding rails and clips for fabric and film stretching. | (Chemours, 2015a) |
| Tires | Lubricant | Used in electrical- and steam-heated tire molds. | (Chemours, 2015a) |
| Watchmaking | Lubricant | Used as a lubricant in Rolex watches. | (Banks et al., 1994; Glüge et al., 2020) |

## Presence of other PFASs in commercial formulations

Existing information shows evidence of the presence of other PFASs during the production of PFPEs, as described below. However, a comprehensive overview of which other PFASs may be present in different commercial formulations and at what levels is not available, hampering a comprehensive understanding of the environmental releases and degradation pathways of such PFASs.

**Reaction by-products**: Impurities in the final PFPE product may arise from monomers used in the synthesis of PFPEs. For instance, HFPO is used as a monomer unit for the production of commercial PFPE-K (DuPont, 2008). HFPO supplied by DuPont (later Chemours) was claimed to have a minimum purity of 98.6 weight% with impurities such as hexafluoropropene (HFP; key chemical precursor to HFPO; up to 1 weight%) and potential impurities such as hexafluoroacetone (HFA; a potential reproduction hazard) (DuPont, 2008; Chemours, 2018). HFA is an isomer of HFPO and is generated by a metal catalyzed mechanism that can be initiated by improper storage and handling methods (e.g., due to the presence of Lewis acids such as $SbF_5$, HF or $ACl_xF_{3-x}$ with x = 0.05–0.3) (DuPont, 2008; Chemours, 2018).

It is unclear how these impurities in the reagents used to synthesize PFPEs can affect the impurities present in final PFPE products.

**Unreacted reaction intermediates**: A non-peer reviewed master's thesis from the University of Toronto aimed to characterize, identify, and quantify several PFPE homologues through chromatographic, mass spectral, and nuclear magnetic resonance techniques (Di Lorenzo, 2012). They suggest that PFPE-diols (precursor of the phosphate) may be present within the technical PFPE-diphosphates, since all samples spiked with the PFPE-diphosphates showed chromatographic signals of PFPE-diols, even at time = 0.

A study by Monduzzi et al. (1994) investigating the phase behavior in water of the ammonium salts of three different PFPE carboxylic acids briefly mentions impurities. The chemical identities and structures of the PFPEs were vague, and substances were referred to as S1, S2, and S3. The study claims that the acids may contain residual amounts of PFPE oil with similar molecular weight and the levels of impurities in the surfactants were none, 1 weight %, and 4 weight % for S1, S2, and S3, respectively.

**Unclear origins**: A safety data sheet for Krytox™ 157FSH noted that perfluorooctanoic acid (PFOA) may be present as impurity at background (environmental) levels for a perfluoropolyether carboxylic acid-based lubricant with CASRN 51798-33-5 and maximum PFPE concentration between 90–100% (composition kept a trade secret) (Chemours, 2020). Similarly, Sianesi et al. (1994) reported that under favorable synthesis conditions, the yield of PFPE-Y exceeds 95% with the predominant by-products being $COF_2$ and $CF_3COF$ (which converts 100% to $CF_3COOH$, i.e., trifluoroacetic acid (TFA) through hydrolysis). The formation mechanism of such perfluorocarboxylic acids (PFCAs) during the PFPE production is not identified during the preparation of this report.

**Intentional addition**: It should also be noted that some commercial PFPE products may contain other types of PFASs as active ingredients. For example, Fomblin™ Grease RT 15 is a mixture of perfluoropolyethers (69991-67-9) and PTFE (9002-84-0).

## Degradation of PFPEs during use and after end-of-life

### *General stability of the perfluoroether chains under environmental conditions*

Early studies of physical and chemical properties describe PFPEs as chemically inert with high thermal stability (Sianesi et al. 1971). A critical review of studies on the degradation of perfluoroether-based non-polymeric PFASs (such as EEA, HFPO-DA or often referred to as "GenX™", and ADONA) shows that perfluoroether chains are highly resistant to both abiotic (photolysis[23], OH radical reaction, and hydrolysis) and biotic degradation under natural conditions (Wang et al., 2015).

This stability and persistence of the perfluoroether chain would be analogous in PFPEs. For example, Young et al. (2006) studied the atmospheric behavior of a commercial mixture containing perfluoropolymethylisopropyl ethers (PFPMIEs)[24]. They note low reactivity in the troposphere, and that the lifetime of the PFPE is limited by transport to the mesosphere where photolysis by Lyman-alpha radiation is efficient. A lower limit for total atmospheric lifetime is estimated to be at 800 years (degradation via C–C or C–O bond scission in $CF_3OCF(CF_3)$– or $CF_3OCF_2OCF_2$– moieties leads to 2 or 4 molecules of $COF_2$, respectively). In addition, in a response to a call for information on alternatives to PFOS under the

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[23] Malinverno et al. (1996) noted that for non-functionalized PFPEs, transmittance is close to 100% at the near-UV wavelengths, 200–380 nm, indicating photostability.

[24] The study reported that PFPMIEs are sold as mixtures according to their boiling point. The authors tested a fraction that boils at 70°C. The mixture was composed mainly of $CF_3OCF(CF_3)(CF_2O)_2CF_3$, with smaller amounts of $CF_3OCF(CF_3)(CF_2O)_3CF_3$ and longer-chain analogues. The fraction had an average molecular weight of 410 Dalton (using fractional distillation to remove any hydrogen-containing impurities).

Stockholm Convention, Solvay stated that Solvera (a PFPE for food packaging use) does not undergo biotic or abiotic degradation in the environment without further information provided. Furthermore, Evich et al. (2022) took extensive investigatory efforts with samples of soil contaminated by chloro-polyfluoroalkylether carboxylic acids (Cl-PFECAs)[25] and found no convincing evidence of scission at any ether linkages in the perfluoroether chain.

### *Use-Related Degradation*

A number of studies have investigated use-related degradation of PFPEs, particularly when used as lubricants in different industrial applications. Li, Jones, and Hsia (2004) describe the advantages of using PFPEs as lubricants in magnetic recording media due to their high performance and temperature stability. Marchionni et al. (2004) observed, after 8 hours of exposure to 160–230ºC, no evidence of degradation products of two PFPEs ($HCF_2O(CF_2O)_{0.28}(CF_2CF_2O)_{0.86}CF_2H$ with an average molecular weight of 328 Dalton and ($HCF_2O(CF_2O)_{0.74}(CF_2CF_2O)_{1.91}CF_2H$ with an average molecular weight of 480 Dalton). In contrast, degradation was observed with treatment at 300ºC, with CHF3 being the main degradation products in the gas phase and the formation of $R_FOCF_2COF$[26](precursors to perfluoroalkylether carboxylic acids upon hydrolysis) together with traces of HF and compounds with the chain ends of $–OCF_2CF_2H$[27] detected in the liquid phase (Marchionni et al., 2004). Marchionni et al. (2004) further observed that one PFPE, $HCF_2O(CF_2O)_{1.45}(CF_2CF_2O)_{3.67}CF_2H$ with an average molecular weight of 641 Dalton, can withstand about 30 hour at 250ºC, but details on the possible degradation are not available.

The decomposition of several different PFPE-Z lubricants with varying molecular weight and end-groups was investigated. Decomposition varied by molecular weight: lower-molecular-weight compounds evaporated, whereas loss of higher-molecular-weight compounds was driven by thermal oxidative decomposition. Moreover, end-groups also had a significant effect on decomposition: hydroxyl-end group compounds experience oxidative decomposition, whereas perfluoromethyl end-group compounds undergo a thermal depolymerization reaction. Li, Jones, Merzlikine et al. (2004) also describe how the thermal stability of PFPE lubricants depends largely on end-groups. For example, the thermal stability of certain PFPEs follows the sequence of PFPEs with $–CH_3$ end group(s) < PFPEs with $–CH_xF_{3-x}$ end groups < PFPEs with $–CF_3$ end groups (Marchionni et al., 2003, 2004).

Further studies have shown that presence of Lewis acids reduces the thermal stability of certain PFPEs (Caporiccio, 1986; Li, Jones, Merzlikine et al. 2004). Specifically, while investigating the decomposition of PFPE lubricants in the presence of aluminum oxides, Kasai (1992) concluded that the intra-molecular disproportionation process drives the decomposition. Pacansky and Waltman (1997) found that the presence of a Lewis acid catalyst reduces the activation energy needed for PFPE decomposition. Liu et al. (2003) also proposed that a free radical degradation loop mediates Lewis acid-catalyzed decomposition. Additionally, Sianesi et al. (1971) discuss that PFPE decomposition at 100ºC can be promoted by Lewis

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[25] Note that in Evich et al. (2022), the authors named the substances as “chloroperfluoropolyether carboxylic acids” or “Cl-PFPECAs”, which is also used by some other sources. In this report, the naming is changed to be in accordance with OECD (2021). In particular, the change from “polyether” to “alkylether” is because “polyether” is used to reflect “polymers” in this report, whereas “alkylether” is used to reflect “discrete compounds,” and the change from “perfluoro” to “polyfluoro” is due to the presence of chlorine atom on the fluorinated ether chain, in line with the revised PFAS definition in OECD (2021). Cl-PFECAs that have been detected in the environment are discrete components of some PFPEs.

[26] The proposed mechanism: $R_FCF_2OC_xH_yF_z \rightarrow R_FCOF + C_xH_yF_{(z+1)}$, where x = 1 or 2 and $R_F$ = a perfluoroether chain.

[27] Marchionni et al. (2004): The formation of the hydrogenated chain ends, $–OCF_2CFH$ and $COF_2$, observed at 300℃, is indicative of homolytic C–H bond breaking reactions, previously reported to be significant over 260℃.

acids including aluminum trichloride and antimony pentafluoride. Tiunova et al. (1999) observed the thermal stability of $CF_3O(CF_2CF_2O)_n(CF_2O)_mCF_3$ where n / (n+m) = 4%, in dependence on the material used, decrease according to the following sequence: ceramics > Ni > Pt > Al > Ni + Cu > stainless steel. It is further noted that the thermal degradation when using a stainless steel of 18H12X10T type[28] started at 192ºC with T50 (temperature at which 50% degradation was observed being 284ºC), about 100ºC lower than using ceramic (started at 329ºC and T50 at 375ºC). It is stipulated that the presence of metal interacting with the oxygen atom of difluoromethylenoxide chains ($–CF_2OCF_2–$) determines the kinetic parameters of the process of polymer thermal destruction.

In their investigation of PFPE lubricant Zdol used to coat magnetic layers of hard storage disks, Kasai and Raman (2003) found that degradation catalyzed by Lewis acid centers led to chain scission forming two distinct fragments: one terminated with a trifluoromethoxy ($CF_3O–$) end-group and the other with a fluorocarbonyl end-group (–RFOCOF). When in contact with humid air, the latter converts to a fluorinated carboxylic acid (–RFOCOOH), which readily reacts with alkali or alkaline earth metal ions.

To reduce Lewis acid-catalyzed decomposition, PFPE lubricants may contain additives such as bis(4-fluorophenoxy)tetrakis(3-trifluoromethylphenoxy)cyclotriphosphazene, [also known as X-1P, CASRN 134367-14-9, $(NP)_3(OC_6H_4CF_3)_4(OC_6H_4F)_2$] (Li, Jones, Merzlikine, et al., 2004). The triphosphazene ring acts as a Lewis base, ultimately slowing down or eliminating decomposition of the PFPE (Li, Jones, Merzlikine, et al. 2004).

Moreover, Spada and Basov (2000) investigated molecular changes in Fomblin™ Zdol, a PFPE surface lubricant used on magnetic media in disk drives, when exposed to direct current (DC) electric fields. They found that degradation primarily affected the functional end group rather than the acetal units in the polymer backbone chain, and identified a new spectral feature C=O group.

Beyond their use in magnetic recording media, PFPE lubricants may also be used in microelectromechanical/nanoelectromechanical systems. Tao and Bhushan (2005a) describe that the technical environment has a noticeable influence on lubricant performance, noting that it is weakened at high humidity. Potential causes of lubricant degradability include thermal decomposition, catalytic decomposition, mechanical scission, and triboelectric decomposition, with the latter two mechanisms deemed the most critical. The following degradation products for Zdol lubricant were identified: $CF_2CF_3$, $CF_2CFO$, $CF_3$, $CF_2O$, $HCF_2$, $CF_2$, and CFO. Additionally, the sliding of Si on Zdol films can lead to electron emission. Electron interaction with Zdol molecules could lead to the creation of various radicals, which in turn may decompose, react with one another, and/or react with other Zdol molecules. Ultimately, this leads to a large variety of potential decomposition products with unknown properties.

Tao and Bhushan (2005b) conducted an additional study where the degradation of PFPE lubricants with varying end-groups were compared when lubricants were applied onto a Si substrate. For Zdol and Ztetraol lubricants, degradation products included $CF_2CFO$, $CF_3$, $CF_2O$, $HCF_2$, $CF_2$, and CFO, whereas for A20H films, degradation products included $C_6H_4CF_3$, $C_6H_5CF_2$, $CF_3$, $HCF_2$, CFO, P, and $H_2$. Again, they found that degradation is mainly caused by triboelectric reaction and mechanical scission during the sliding of Si on PFPE films, and that various radicals may be created during this process.

Furthermore, PFPEs used in anti-fingerprint films in touch screen devices are prone to mechanical degradation, primarily due to shearing and frictional forces from daily finger rubbing. Min et al. (2018) found that the Si–C bond in the polymer chain is the weakest in terms of intrachain strength, and thus prone to dissociation and possibly formation of a C–O bond. With respect to interchain interactions, they found that increasing the chain length led to enhanced film mechanical properties. They propose that the configuration of the polymer chain and thus film structure can be optimized to prolong the lifespan of coated

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[28] It contains 12% of Cr, 18% of Ni, 10% of Ti, 60% of Fe.

films for touch screen devices. Interchain interaction in the film structure can be improved by first placing shorter chains to the silica surface, then followed by longer chains.

Recently, Wolfberger et al. (2021) described the relevance of liquid lubricant degradation in spacecraft reliability, since the loss of lubricating performance can have dire consequences for a multitude of spacecraft mechanisms where reapplication of lubricants is not feasible. PFPE-based lubricants are commonly used in such applications. They describe moisture uptake, separation of components, conformational changes, and contamination as key physical aging processes relevant to liquid lubricants. With respect to chemical aging, the following processes are deemed relevant for liquid lubricants: thermal degradation, mechano-chemical degradation, electron-mediated degradation, catalytic degradation, and oxidative degradation.

### *End-of-Life Degradation*

Limited information is available on the fate of PFPEs at their end-of-life. Di Lorenzo (2012), the aforementioned non-peer reviewed master's thesis from the University of Toronto, describes the potential relevance of PFPEs in WWTP biodegradation. They hypothesized that since fluorotelomer phosphate esters (PAPs) can be microbially hydrolyzed in WWTP sludge, there may be an analogous degradation pathway for PFPE-diphosphates, which share certain structural features with PAPs. They did not identify hydrolysis products in their experiment, but this may have been related to issues with PFPE solubility, sorption to bottle walls, or sorption to particulate matter in sewage sludge. Additionally, they propose that PFPE-diol may be a degradation product of PFPE-diphosphates. Such transformation of functional end-groups has been observed in other studies. For example, Evich et al. (2022) investigated potential environmental transformations of the Cl-PFECAs found in New Jersey soils. Transformation products were predicted based on analogous PFAS transformation pathways available in the literature, and were used as the basis for high-resolution mass-spectrometric suspect screening of soil samples. A number of suspected transformation products were observed in their analysis, including H-PFECAs, epox-PFECAs, and diOH-PFECAs[29]. Ultimately, it remains unclear to what extent, apart from transformation at hetero-atom reaction centers and/or functional end-groups, PFPEs are able to degrade in WWTP sludge, if at all. It is noted that a PFPE, Solvera XPH-723 used for paper coating [$(HO)_2(O)P–O–(C_2H_4O)_n–CH_2CF_2O–(C_2F_4O)_p–(CF_2O)_q–(C_2H_4O)_n–P(O)(OH)_2$], remained unchanged despite undergoing 12 weeks of thermophilic composting (Westbury and Michitsch, 2013; Westbury, 2014), in line with the general stability of perfluoroether chains as discussed above.

Furthermore, at least one company reported that they have developed a technology to regenerate PFPEs after their end-of-life, but no details are provided on their website[30]. No information on the degradation of PFPEs during incineration is identified during the preparation of this report. Nevertheless, given their instability at high temperature observed under technical conditions as elaborated above, the fate of PFPEs during incineration and open burning warrants further investigation.

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[29] Subject to the functional group connected to the fluorinated ether chain, the substances may be perfluorinated (e.g., when the functional group is epoxide functional group or –OH in diOH-PFECAs) or polyfluorinated (e.g., when the functional group is a hydrogen, –H, or chlorine, –Cl), following the definition in OECD (2021).

[30] https://www.umex-gmbh.de/en/products/regeneration-von-pfpe-fluiden/

## Environmental releases of PFPEs and other PFAS present in commercial formulations

Publicly available information regarding environmental releases of PFPEs and other associated PFASs is limited. In addition to the aforementioned thermal and Lewis acid-catalyzed degradation mechanisms, washout is another potential route of PFPE release to the environment. A US patent indicates that when used in underwater applications, PFPE-based grease is subject to displacement based on loss of adhesion to its substrate, not solubility (Bulluck and Hoppens, 2016). The patent does not disclose the precision and bias for the devised in-house procedure for the testing in accordance with the standard ASTM D-1264; however, the published results likely fall below reproducibility and repeatability of the test method (personal communication from a PFPE manufacturer).

Evidence of PFPEs in the natural environment is limited, but the presence of some PFPEs is a clear indication of some releases. In 2017, the New Jersey, United States, Department of Environmental Protection launched a study in an effort to identify the sources, chemical species, and distribution of both legacy PFASs and newer substitutes (Washington et al., 2020). Soil samples collected around southern New Jersey were subjected to non-target analysis. Ten Cl-PFECAs were tentatively identified, likely from a PFPE product used by Solvay in fluoropolymer production (ADV series; CASRN 329238-24-6) (Washington et al., 2020). The State of New Jersey reported that Solvay uses this PFPE product as replacements to perfluorononanoic acid (PFNA) in its manufacturing of polyvinylidene difluoride (PVDF) products, and that these Cl-PFECAs have been identified in several environmental matrices within Gloucester and Salem Counties (McCabe, 2019). Similarly, McCord et al. (2020) summarize the results of nontargeted analysis on water samples collected from Gloucester and Salem Counties, revealing several Cl-PFECAs and related PFASs. While toxicity studies for these chemicals are limited, the estimated concentrations measured exceeded the state standards for drinking water for PFOA (0.014 µg/L) and PFNA (0.013 µg/L)[31], as well as the interim specific ground water quality criterion of 0.002 µg/L for Cl-PFECAs (NJDEP, 2022). They hypothesize that the compounds detected originated from a regional industrial user. Point-of-entry water treatment systems for PFAS removal reduced the abundance of such compounds by >90%.

Moreover, as previously mentioned, Evich et al. (2022) investigated potential environmental transformations of the Cl-PFECAs found in New Jersey soils. Their study highlights that potential PFPE transformation products are an additional concern with respect to environmental contamination of PFPEs, given that suspected transformation products such as H-PFECAs, epox-PFECAs, and diOH-PFECAs were found in New Jersey soils.

This functionalized PFPE[32] has also been observed in the Bormida di Spigno River, Italy (Lohmann et al., 2020). The analysis carried out on liver sampled from wild boar population in Italy (Moretti et al., 2022; 2023a) suggests that the presence of Cl-PFECAs and related degradation products H-PFECAs in soils is

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[31] For more details, see https://dep.nj.gov/pfas/standards/

[32] From 2023, on behalf of Solvay Polymers, the company Ultrascientific Italia has started to sell certified reference materials of the main Cl-PFECA components of the PFPEs with CASRN 220207-15-8 and CASRN 329238-24-6 products (1-Propene, 1,1,2,3,3,3-hexafluoro-, telomer with chlorotrifluoroethene, oxidized, reduced, Et ester, hydrolyzed, sodium salt), trivially named as ADV 7800 (https://www.ultrasci.it//DocumentiCataloghi/Flyer_PFAS-MFS.pdf). Such Cl-PFECA components, namely e,p = 0,1 (N2), e,p = 1,1 (M3), e,p = 0,2 (N3), e,p = 1,2 (M4), e,p = 0,3 (N4), and e,p = 0,4 (N5), where e and p are represented according to the nomenclature $\{CF_3C(Cl)FCF_2O[CF(CF_3)]_eO[CF_2CF(CF_3)]_pOCF_2COOH\}$ by Washington et al. (2020), are claimed to represent around the 80% of the overall PFAS content, according to the information provided by Solvay to the US NJDEP Authorities (2021). Recent evidences from the analysis of wild boar livers in Italy (Moretti et al., 2023), upon the availability of such reference materials, revealed the presence of other two Cl-PFECAs attributable to the technical mixture, namely e,p = 2,0 and e,p = 2,1. They are not provided as certified materials yet.

not directly from fluoropolymer production plants. This directs attention to the end-life and proper disposal of Cl-PFECAs containing products such as food contact materials films and tapes, where Cl-PFECAs presence could account for up to 0.5% w/w (EFSA, 2010).

More recently, the presence of some Cl-PFECAs has been identified in unhatched eggs of Mediterranean Loggerhead Turtles (Caretta caretta), suggesting biota exposure to PFECAs present in marine polymeric litter from sea turtles mistaking plastic films with jellyfish (Moretti et al., 2023b).

In Italy, the Piedmont region, where a Solvay production plant of Cl-PFECAs is located, announced in September 2022 an ongoing study on Cl-PFECAs in environmental and food matrices, coupled to human biomonitoring in residential and agriculture impacted area[33]. As of July 2023, the preliminary evidence of such activity has not been disclosed.

Furthermore, PFPE production may also lead to the release of monomeric precursors. Chemours reportedly uses PFAS replacement chemicals including HFPO-DA and its ammonium salts in the manufacturing of Krytox™ at Chamber Works (McCabe, 2019). According to the State of New Jersey, HFPO-DA is discharged into New Jersey waters and emitted into the air (McCabe, 2019). Moreover, HFPO-DA has been detected in residential drinking water wells nearby Chamber Works. The extent of environmental releases of PFPE precursors, impurities, and by-products, as well as PFPEs themselves, remains unknown. The points of evidence discussed provide some insight into the environmental presence of PFPEs, but more research is warranted.

## Options for way forward

Historical and current production and use volumes are key parameters that need to be elucidated to better understand the contribution of PFPEs and their impurities to the environment. Specifically, there is a need for more consistent and centralized reporting of PFPE uses in commercial applications, in addition to providing public access to production and use volumes. Having a better understanding of these figures is useful for estimating environmental releases of PFPEs and subsequent exposure to humans.

Transparency from industry is needed regarding the presence of impurities in commercial formulations. Key question include: If other PFASs are present, in what quantities do they occur? Are they of concern for environmental releases and/or human exposure?

With respect to degradation of PFPEs, further studies are needed to better understand how PFPEs degrade at end-of-life, especially in the technical environment (e.g., recycling and incineration). Moreover, further research is warranted with regards to identifying specific degradation products and whether these should be considered chemicals of concern. Given the vast range of PFPE species, degradation mechanisms and products could vary.

Lastly, there is a need for better understanding of which PFPEs are released to the environment, in what quantities, and by what mechanisms. A key question is "What is the fate of these PFPEs?". Substance flow analysis could be a helpful tool in answering this question. Ideally, having an understanding of production volumes and flows of PFPEs to different end-of-life destinations would provide a helpful big picture of PFPE life cycles and would aid in revealing the extent of exposure to humans. Ultimately, this information would help determine which interventions to prioritize. Such substance flow analysis may start with those areas with the highest production/use volumes. Further studies may also be interested in investigating how different organisms are impacted by PFPE releases to ecosystems.

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[33] https://www.regione.piemonte.it/web/temi/sanita/caso-solvay-illustrate-azioni-messe-atto-dalla-regione

# 4 Conclusions

Many data gaps exist; however, it can be concluded that a variety of structurally diverse PFPEs exist on the global market, and their use in various industrial applications and consumer products is extensive. Aspects to improve information on the identity of PFPEs on the global market and aspects regarding their life cycle are highlighted at the ends of Chapters 2 and 3 respectively and the findings here are but a first step.

Concerted action by all stakeholders is needed to address PFPEs efficiently and effectively. This includes allocating time, funding, and research efforts towards addressing the critical knowledge and data gaps identified in this report, especially those most relevant for sound management of PFPEs. Researchers, government officials, and other stakeholders may consider the following actions as possible priorities when addressing critical knowledge and data gaps:

- Develop and/or utilize additional chemical identifiers for PFPEs beyond CASRNs and CAS names, to communicate more comprehensive information with respect to their chemical identities and structural characteristics.
- Collaborate with manufacturers to gain public access to relevant information such as production and use, presence of other PFAS impurities in commercial formulations, degradation during the use phase, and environmental releases from manufacturing sites, where applicable.
- Expand the scope of analysis of this report by including safety data sheets and patents, which were not actively searched in this report due to time and resource constraints.
- Continuously gather new data and synthesize them for a better understanding of PFPEs on the global market and their life cycles.

In addition to addressing critical knowledge and data gaps, parallel action can be taken to promote stewardship programmes and regulatory action on both national and international levels, with the aim of reducing PFPE emissions and exposures.

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