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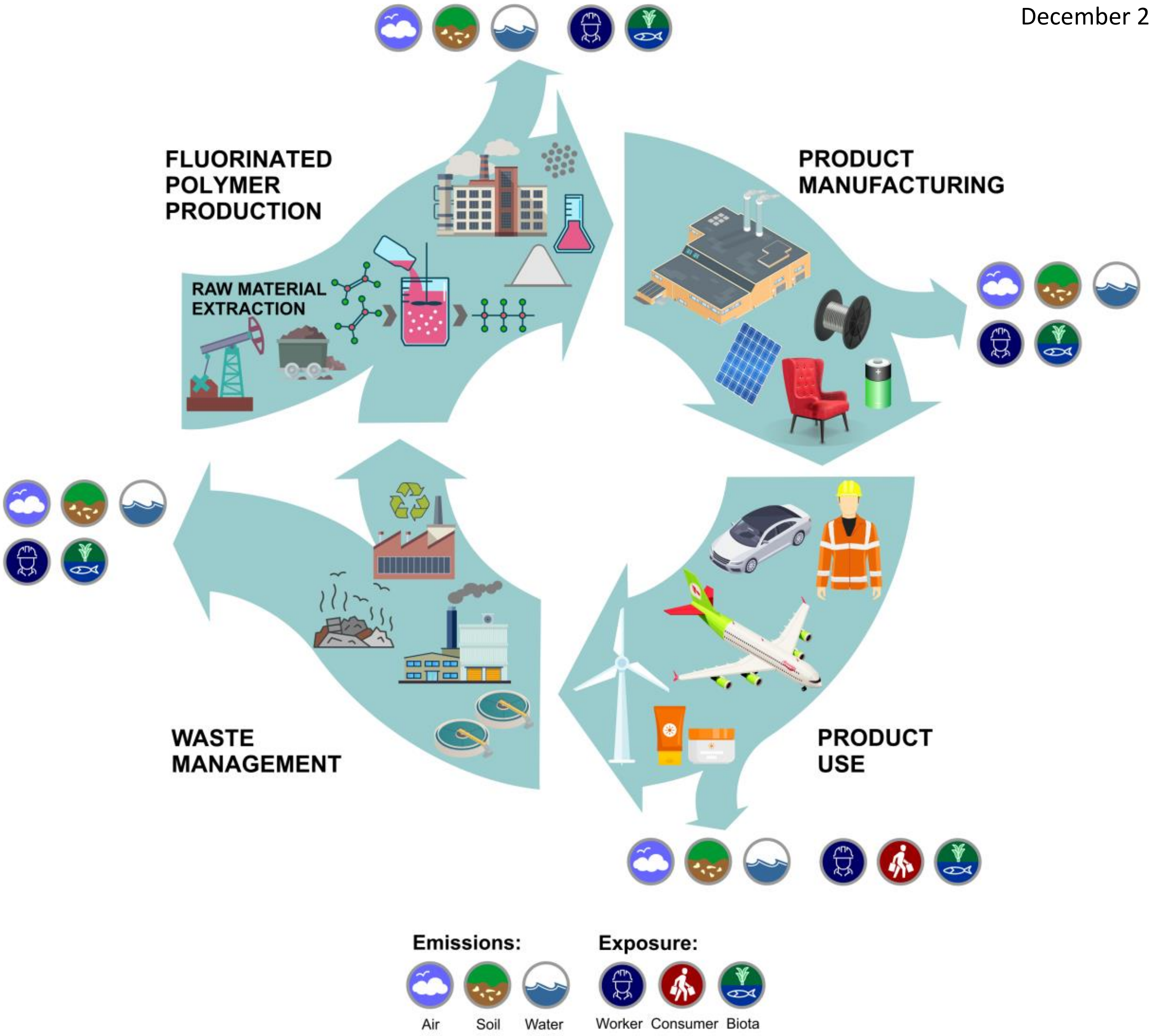
Fluorinated polymers in a low carbon, circular and toxic-free economy

Technical report

December 2021



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Furthermore, Toke Winther from the Danish Environmental Protection Agency and a member of the European Chemicals Agency (ECHA) per- and polyfluorinated alkyl substances (PFAS) working group, followed the work and shared information from previous works on the topic and gave valuable comments to findings. We highly appreciate the valuable comments provided by the reviewers Roland Weber (POPs Environmental Consulting, sections reviewed: 1–6), Jos Bessems (VITO, sections reviewed: 1–3), Barbara Gschrey (Öko-Recherche, section reviewed: 7.3). Bart Ullstein (BEC) provided editorial support.

Executive summary

The aim of this report is to identify potential impacts of fluorinated polymers (FPs) along their lifecycles in a low carbon, circular and toxic-free economy, which could be relevant to consider in future assessments.

Fluorinated polymers are defined as polymers made up of one or several types of monomer blocks (also called repeat units), which contain carbon-fluorine bonds in their backbones and/or side chains. According to the European Chemicals Agency's (ECHA) definition, a polymer has at least three monomers. Fluorinated polymers cover a wide range of chemistries, which may be fully fluorinated (*per*-fluorinated) or partially fluorinated (*poly*-fluorinated) polymers, which can also contain chlorine or bromine. Fluorinated elastomers are a special type of fluorinated polymers which have rubber-like properties.

Fluorinated polymers are used for a variety of purposes in transport, the chemicals industry, power generation, electronics, wire-insulation, coatings, cookware, textiles and cosmetics due to their special properties of being resistant to abrasion, heat and chemical attack, and provide low friction. They are increasingly used in renewable energy applications. In this report the following fluorinated polymers were selected for further analysis: polytetrafluoroethylene (PTFE), which makes up for more than half the market; polyvinylidenefluoride (PVDF), the use of which is the fastest growing among fluorinated polymers worldwide; perfluorinated ethylene propylene (FEP), an example of a copolymer; per- and polyfluorinated polyethers (PFPE), used in coatings for food contact paper, glass and used as machine oils; and fluorinated sidechain acrylate polymers, an example of fluorinated sidechain polymers used as coatings and sizing agents for textiles and food contact paper.

There is a lack of official data on the tonnages produced and consumed in the EU, but according to industry sources about 51 000 tonnes of fluorinated polymers are produced in EU each year (PlasticsEurope, 2018) and 320 000 tonnes globally (AGC, 2020). Even if these amounts are small compared to total amounts of plastics in Europe, about 62 million tonnes of which are produced annually in Europe (PlasticsEurope, 2019), the potential impacts of fluorinated polymers along their lifecycles may be relevant to the success of EU policies and strategies set out in the European Green Deal and the New Circular Action Plan, such as the EU chemicals strategy, the Zero Pollution Ambition for toxic-free environment and the EU plastic strategy.

The main focus of this report is on exploring lifecycle stages and emissions/impacts for which there seem to be significant knowledge gaps. These were found to be on climate-change impacts from greenhouse gases (GHG), pollution from ozone-depleting substances (ODS), both of which affect Earth systems and subsequently human and environmental health, and on circular economy (CE) elements related to recycling processes and rates for GHG and ODS, emissions from feedstocks, by-products and thermal degradation products in the production/manufacturing and end-of-life phases. Impacts from manufacturing products using fluorinated polymers are not assessed and only a few examples are presented. Areas described in less detail include raw material extraction; the use phase; and human health impacts of toxic per- and polyfluoroalkyl substances (PFAS), which have been studied in more detail elsewhere. The report is mainly based on a qualitative analysis supported by some of limited quantitative data available in open literature and patents.

The main observations are as follows:

Lifecycle phase	Key Findings
Raw material extraction	• The fluorine in fluorinated polymers comes from a mineral fluorspar, also called fluorite, the mineral form of calcium fluoride (CaF_2) which is listed as a critical resource on the European Commission's Critical Raw Material list due to high global supply risk. • A future potential resource could be from recycling of fluorosilicic acid (H_2SiF_6) generated as by-product from the fertiliser industry, and from capturing fluoride by adding calcium during incineration of PFAS, thereby turning it into CaF_2.
Production of fluorinated polymers	*Environmental and human health impacts:* Risks of feedstock, synthesis by-products and production aids.

Lifecycle phase	Key Findings
	• Feedstock chemicals of fluorinated polymers can be potent GHG and ODS, which harm Earth systems and thereby people, biota and the environment. An example is chlorodifluoromethane (HCFC-22), which is a major feedstock in PTFE production. Ozone-depleting substances cause health risks by degrading the ozone layer, leading to an increase in ultraviolet B (UVB) radiation and thereby an increase in the rate of skin cancer (melanomas), cataracts and crop loses. Greenhouse gases are risks to health by disrupting the climate, leading to more frequent floods, heat waves, fires and failed harvests. Climate change also destabilises ecosystems and increases the acidity of the oceans, causing death of coral reef ecosystems amongst others. • Feedstock chemicals, monomers and oligomers of fluorinated polymers can harm workers and people during use. Chloroform ($CHCl_3$), for example, is a substance of very high concern (a carcinogenic, mutagenic or toxic for reproduction [CMR] substance); tetrafluoroethylene shows clear signs of being a carcinogen in rats; and fluorinated oligomers are taken up on inhalation, bioaccumulate and form toxic degradation products. • Production aids such as perfluorooctanoic acid (PFOA) and other PFAS used as dispersion agents in the synthesis of fluorinated polymers have caused diseases in workers. They have furthermore contaminated air, soil, surface and drinking water, and food production around production sites with severe consequences for the surrounding communities. The pollution has also spread globally and accumulated in top predators, such as fish, seals, whales and humans. *Emission routes from production to the environment* • Volatile non-ionic and ionic PFAS are used and formed during fluorinated polymer production and manufacturing. Scrubbers, which can capture very volatile non-ionic PFAS, are only known to be in place in a few cases. • Emissions of PFAS from industrial production of fluorinated polymer sites occur through air, wastewater and production wastes. Examples include production aids such as PFOA and GenX[1], released with from fluoropolymer production plants in, for example, the Netherlands, Italy and the United States; and synthesis by-products/impurities/degradation products such as fluorinated ethers in the United States. • Information and data lack on how of production waste is managed in Europe. In the United States, waste disposed of in landfills has caused contamination of the surrounding areas. *Regulatory aspects* • Feedstock chemicals, and to some extent intermediates, are subject to registration under EU's Registration, Evaluation, Authorisation and Restriction of Chemicals regulation (REACH) for annual uses above 1 tonne per substance per application. • Some feedstocks and production aids are classified as substances of very high concern (SVHCs) under REACH and are subject to restriction. • Some aggregated information on emissions of fluorinated gases (F-gases) to air and of perfluorinated carbons (PFCs) to air, water and soil are covered by the European Pollutant Release and Transfer Register (E-PRTR) and have legal reporting obligations. Only few industries producing, using or handling fluorinated polymer wastes are, however, required to report, and the reporting on lifecycle emissions from fluorinated polymers is limited. • The most important hydrofluorocarbons (HFCs) and PFCs as well as some fluorinated ethers are covered by the EU F-gas Regulation and the Kigali Amendment of the Montreal Protocol on ODS, with reporting obligations for their production and uses. The focus lies, however, on gases used in refrigeration, air conditioning and heating and foam-blowing applications. So far, however, reporting is only required for one F-gas by-product from fluoropolymer production, trifluoromethane (HFC-23).
Use phase *(Note: exposure has not been reviewed/described exhaustively in this report)*	Fluorinated polymers are used in a wide range of applications, typically as part of a component or a coating. Exposure of workers, professionals and consumers is highly application specific. Examples of exposure routes include: • inhalation (volatiles/aerosols/dust) during manufacturing, heating or spaying of fluorinated polymers;

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[1] A trademark name for a synthetic, short-chain organofluorine chemical compound, HFPO-DA (hexafluoropropylene oxide-dimer acid)

Lifecycle phase	Key Findings
	• direct human exposure from food-contact materials (PFAS in food-contact materials can migrate into food); • dermal contact – textiles, cosmetics/personal care products, lubricants, oils, waxes, and during occupational use, etc.; • release to the environment: ○ microplastics can be released from fluorinated polymers either directly into the environment due to intentional use in products, or indirectly after physical degradation of macro-sized fluorinated polymers in products or mismanaged waste; ○ release of ionic and non-ionic PFAS from fluorinated polymers from coatings of, for example, textiles, food-contact materials, electronics, medical utensils, building materials, etc. *Regulatory aspects* • Fluorinated polymers are not regulated for most uses and products. • In plastic food-contact materials, monomers, PFAS production aids and processing requirements of the fluoropolymers are authorised for use by the EU, and have specific and total migration-limit values. For other non-harmonised food-contact materials, such as paper and board, fluorinated polymers and other chemicals are not specifically regulated by EU law – there are no authorisation processes or limit values – but the overall framework regulation requires chemicals not to migrate in amounts harmful to human health. • In medical utensils, fluorinated polymers are authorised with some regulation under the EU Medical Devices Regulation. In cosmetic products, fluorinated polymers are regulated under EU Cosmetics Products Regulation.
End-of-life phase	*General:* • Studies on emissions from the end-of-life phase are scarce and hardly exist for real-life conditions. This is the case both for managing wastes and thermal decomposition under controlled conditions (incineration) and uncontrolled conditions, such as the smoldering of electronics to strip metals. • Recovery of fluorinated polymers is made difficult by their widespread use in many applications ranging from liquids through integral parts of wires and electronics to coatings on a variety of materials, such as paper, wood, glass, stone, metal and plastic. • There is very limited information on recycling, though process scrap is recycled to some extent. Some recycling of hydrogen fluoride (HF) may occur in the production phase of fertilisers. • Chemical recycling could potentially depolymerise fluorinated polymers into monomers and subsequently into new polymers. Currently only one plant in Germany has demonstrated this, but has a small capacity. • The possibility of thermally degrading fluorinated polymers is currently being demonstrated for PFAS (PFOA and perfluorooctanesulfonic acid [PFOS]) in cement kilns, by use of calcium as a catalyst and fluoride as a scavenger, by the formation of CaF_2 captured in the cement. • Emissions from municipal wastewater treatment plants occur for perfluorinated acids and other ionic PFAS, as well as non-ionic PFAS such as fluorotelomer alcohol (FTOH), through water, air and sludge. Sources used and degraded PFAS from households and small industries. Very limited data exist on emissions from fluorinated polymers of particularly persistent and mobile (PM) volatile PFAS, such as FTOHs and F-gases; fluorinated polymers in sludge; and for water soluble persistent and mobile PFAS released from the fluorinated polymers. *Regulatory aspects:* • Waste handling and related emissions are poorly documented for products ending up outside Europe. This remains relevant for Europe both because PFAS pollution spreads globally and because of Europeans' responsibility to manage their wastes safely. There are also concerns related to human health about the potential formation of GHG and ODS which can destabilise Earth systems, and toxic PFAS accumulating in food, biota and water systems. • Due to a lack of information on the composition of production wastes, it is generally not possible to assess if they should be classified as hazardous wastes. Similarly, the recovery of materials or the safe disposal of wastes is limited by a lack of clarity about what types of fluorinated polymers and levels of contaminants in products should be treated as hazardous wastes.

Lifecycle phase	Key Findings
	Environmental and human health impacts: Incineration: • Emissions depend on incineration conditions, which can lead to the formation of trifluoroacetic acid (TFA), corrosive HF formed and released at temperatures below 1 100 °C, and other volatile fluorinated gases, including oligomers released at lower temperatures. In non-controlled conditions, fluorinated polymers may degrade thermally to form a variety of volatile and ionic/water-soluble PFAS and small particles. Thermal degradation of PTFE starts at relatively low temperatures of less than 500 °C and forms many fluorinated products such as the highly persistent and mobile TFA. Other fluorinated polymers, including PFPE, start degrading at temperatures of around 230 °C. • Several of the thermally-formed fluorinated substances have an environmental effect in terms of global warming potential (GWP). Landfilling: • In landfill conditions, end-of-life products containing fluorinated polymers, such as textiles, carpets and some furniture, can degrade into PFAS which may then be released in landfill leachate decades after disposal. As a result, even closed landfills may generate leachates that need to be treated. Only limited details of PFAS concentrations in leachate were available in the literature, particularly for Europe, and there was not much information on release mechanism and the fate of released substances. Discharge from wastewater treatment plants: • Little information is available on emissions of volatile PFAS from wastewater treatment plants or on the management of sludge and effluents from wastewater treatment plants.

Overall, impacts along selected fluorinated polymer lifecycles were analysed for this report in the light of EU policies and strategies on the CE, resource efficiency and raw materials, the low-carbon economy and zero-pollution ambitions for a toxic-free environment. Potential impacts that support and conflict with EU strategies were identified below.

Strategy, policy	Potential benefits	Potential risks
Circular economy	High durability, longevity, miniaturisation of products (less waste)	Although fluorspar is on the EU's list of critical raw materials, there is almost no information on recycling or recycling rates. Fluorinated polymers are often integrated in components which make them difficult to recycle.
Low-carbon economy	Use in renewable energy applications, reduced energy need (lighter vehicles, etc.)	Raw materials with greenhouse potential are used in production processes and are likely to form when heated/incinerated at temperatures below that at which they mineralise fully.
Zero Pollution Ambition/ toxic-free environment	Longevity may avoid the need for new products due to wear	Use of chemicals of concern, including PFAS, organochlorines and heavy metals, will in practice lead to emissions and hence to risks during their production, use and at end-of-life phases. The risks may stem from either the substances themselves or their by-products and degradation products, both of which may accumulate and cause long-term, irreversible pollution and impact humans, biota, and the wider environment.

In summary, fluorinated polymers may lead to various severe and irreversible environmental and human-health impacts along their lifecycles and conflict with CE goals due to limited recycling options. Nonetheless several uses of fluorinated polymers may until non-fluorinated alternatives have been identified/developed, be needed in renewable energy solutions, which supports the European aim of becoming a low-carbon economy. Likewise, fluorinated polymers may for now be needed for human health to deliver clean drinking water and in medical devices. Within the overall process of risk governance, there are different options for implementing the concept of essential use. There is a need to unambiguously define criteria or considerations for essential use to enable the application of the concept in decision-making processes.

With forthcoming EU legislative initiatives on PFAS and discussions of reopening the REACH regulation (EC, 2020d), there may be opportunities to better address the costs and risks to human and environmental health of fluorinated polymers along their lifecycles. Governance options include addressing fluorinated polymers separately as polymers of concern as part of the discussion on the reopening of REACH or addressing them through REACH restrictions to phase-out uses which are non-essential to the functioning of society and health, but allow currently essential ones while alternatives to PFAS are being developed.

Knowledge gaps identified in the study include:

- studies/research/monitoring on which substances are emitted from what activities – production, the manufacture of products, incineration/thermal degradation/ineffective capturing of PFAS emitted from wastewater treatment etc.;
- research and demonstrations of potential technologies for recycling fluorinated polymers from production waste and from end-of-life products;
- a broad in-depth analysis of the benefits and risks associated with the use of fluorinated polymers in different applications. This calls for the development of a framework including criteria for the categorisation of different applications as essential or non-essential. This will require the involvement of a wide range of experts and well-informed stakeholders from all aspects of value chains;
- research and development on alternatives so that fluorinated polymers can be replaced by products with fewer negative impacts on the environment and human health. Work should also include information on the benefits and risks related to potential replacements;
- labelling products containing fluorinated polymers – this is especially important for waste management to ensure suitable management of end-of-life products;
- awareness raising among product designers of the importance of material choices. In future, the replacement of fluorinated polymers may create a market value for products with lower environmental footprints. Safe and sustainable by design (SSBD) criteria could ensure that chemicals of concern, as identified by EU's REACH regulation and the European Commission's chemical strategy for sustainability for a toxic-free environment, including PFAS, are avoided in the design of chemicals, materials, processes and products.

1 Introduction

Main authors: Margareta Wahlström and Xenia Trier

1.1 Background and scope

The New Circular Economy Action Plan (EC, 2020a), one of main constituents of the European Green Deal (EC, 2019), includes "*making sustainable products as a norm in Europe*" as a key measure. It is built on the EU's previously published 2015 Circular Economy Action Plan (CEAP) and the 2018 Circular Economy Package, including the EU Strategy on Plastics in a Circular Economy (EC, 2018). The European Green Deal as well as the CEAP have a strong focus on EU Climate Strategies (EC, 2021a) for a Low Carbon Economy.

The European Green Deal mentions the Zero-Pollution Ambition for a toxic-free environment which is a follow-up action to the EU strategy for toxic-free environment mentioned in the 7th Environment Action Plan (7EAP). The Zero-Pollution Ambition (EC, 2021b) particularly addresses the need to rapidly address the risk posed by hazardous chemicals and, more specifically, very persistent chemicals, encourage initiatives that ensure that products are designed to be safe – free from hazardous chemicals – and circular/sustainable by design and support actions for clean material loops. On 14 October 2020, the European Commission published the Chemicals strategy for sustainability towards a toxic-free future (CSS) and set actions for substances of concern, including increased measures to prevent the use of the most harmful chemicals (EC, 2020d).

Member States and the ECHA evaluate chemicals and Agency publishes candidate lists for substances of very high concern (SVHC[2]) for authorisation. The Agency´s 2018 substitution strategy (European Chemicals Agency, 2018) promotes substitution of safer chemicals in the EU. Special attention should be given to the EU persistent organic pollutants (POPs) regulation (No 2019/1021 replacing 850/2004) which requires that wastes containing substances listed in its annexes, such as PFOS and PFOA, and exceeding specific concentration limits need to be destroyed and not re-circulated in new products.

This study on fluorinated polymers in low-carbon, circular and toxic-free economies is linked to the following policies:

- EU policies on plastics closing the loop of product lifecycles by keeping the value of plastics in the economy and minimising waste;
- the climate strategies on GHG promoting action to reduce these with particular focus on fluorinated gases with high global warming effect; and
- the strategy for a toxic-free environment with specific focus on SVHC such as PFAS used in the production of fluorinated polymers. Identification of toxic substances is of great importance so that they can be phased out from society.

Several restrictions and initiatives for PFAS have been included in the REACH and persistent POPs legislation. A timeline for restrictions and initiatives for PFAS in these regulations and legislation is shown in Figure 1.1.

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[2] defined in the REACH regulation as substances that are persistent, bioaccumulative and toxic (PBT), very persistent and very bioaccumulative (vPvB) or have other characteristics of equivalent concern, such as endocrine disrupting, neurotoxic properties or are persistent, mobile and toxic (PMT)

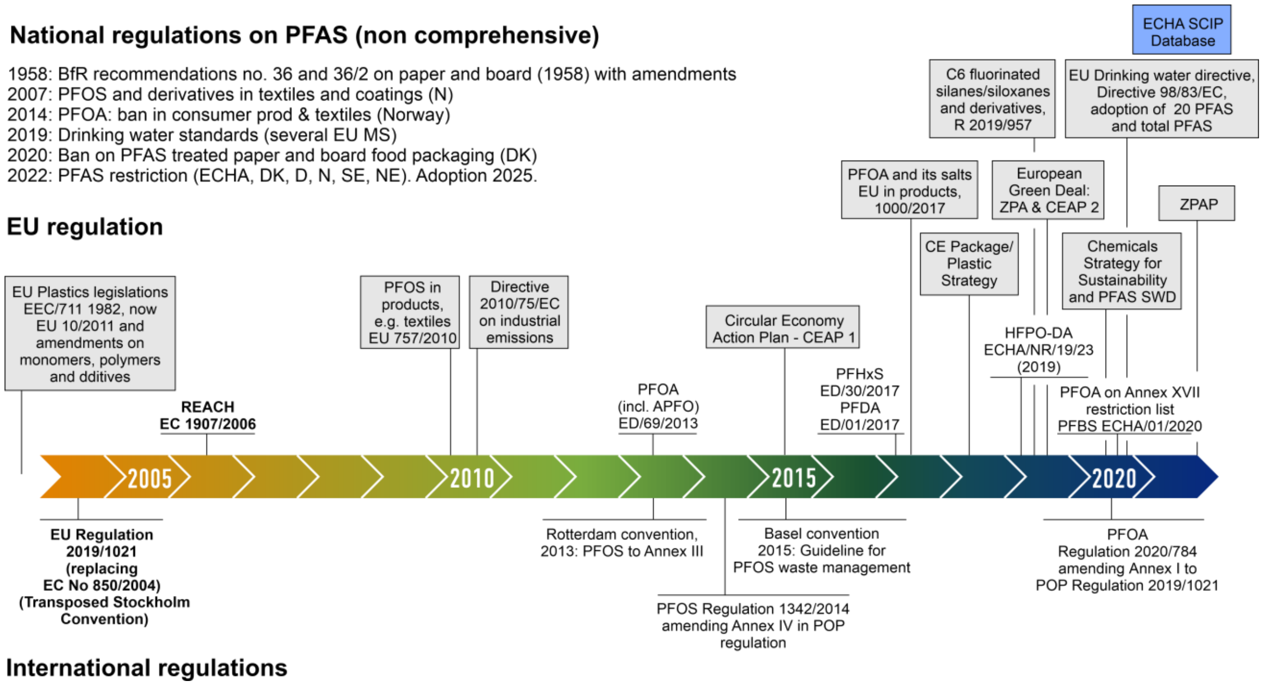

Figure 1.1. Timeline of the restrictions in legislation for specific PFAS – REACH at the top and POPs at the bottom as of May 2020.

Abbreviations: ED: Decision by the Executive Director of ECHA; CEAP: Circular Economy Action Plan; MS: Member States, SWD: Commission Staff Working Document, ZPA: Zero Pollution Ambition Strategy; POP: Persistent organic pollutant; SVHC: Substances of very high concern.

Source: EEA

This report aims to provide an overview of types of lifecycle impacts of fluorinated polymers, from mining through to recovery or final treatment and to frame a lifecycle approach to assess the overall sustainability of fluorinated polymers. The lifecycle for fluorinated polymers is illustrated in Figure 1.2.

The report focusses on two areas of the fluorinated polymer lifecycle that previously have received less attention.

1. Releases of GHG and ODS during the production, manufacture and incineration at the end of life of fluorinated polymers. This includes chemicals that are used, present as impurities, by-products formed or environmentally formed degradation products.
2. The extent to which fluorinated polymers could be integrated into the CE. Along their lifecycles, impacts related to climate change, ozone-depletion and environmental and human health are evaluated. The focus is on fluorinated chemicals which are GHG such as F-gases, ODS and toxic PFAS.

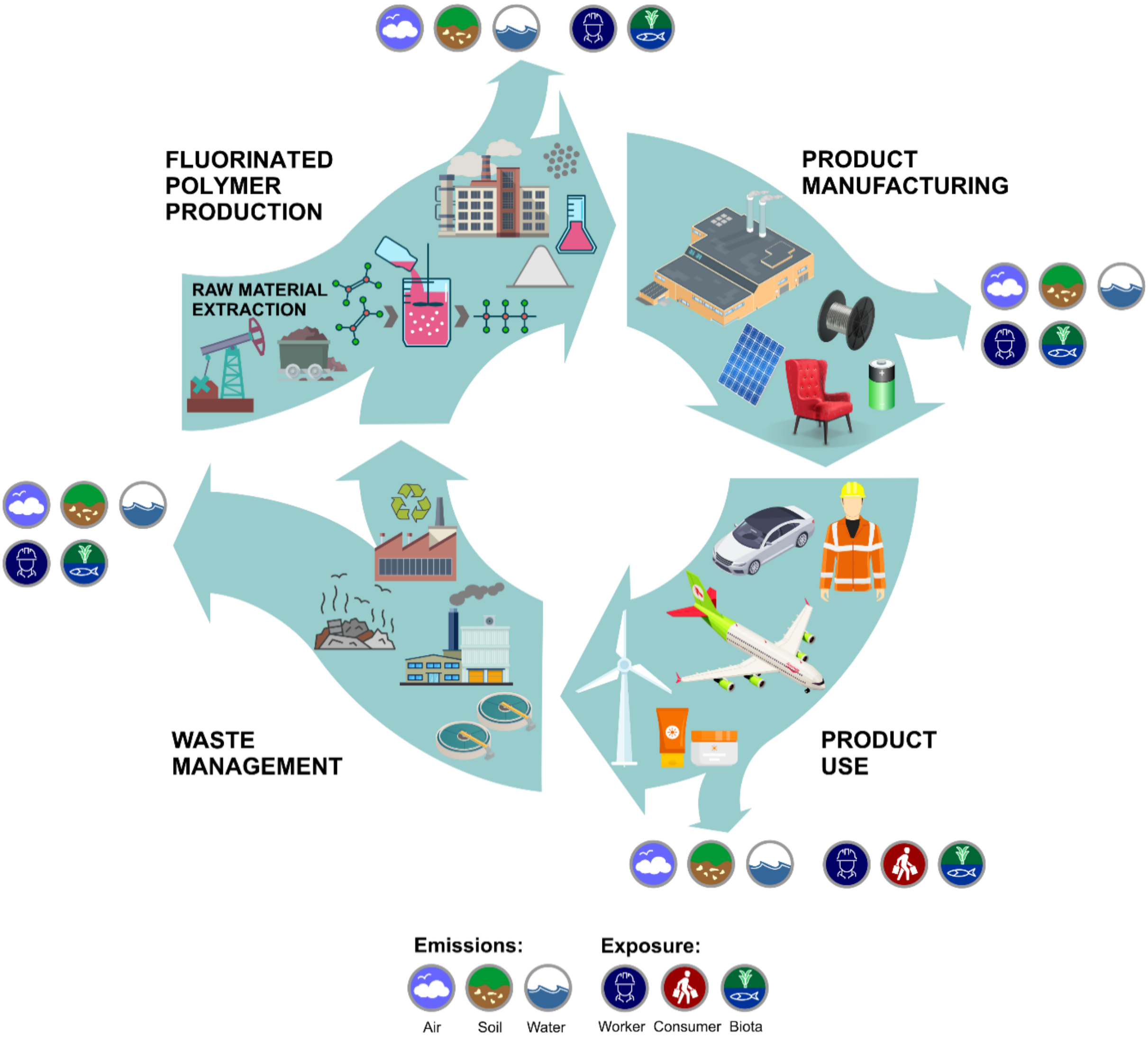

Figure 1.2. The lifecycle of fluorinated polymers from feedstock extraction to end of life.

Source: EEA and ETC/WMGE

1.2 Methodology

For the analysis of lifecycle impacts from fluorinated polymers, the work was divided into the following subtasks.

1. Description of the current status: description of fluorinated polymer flows and current lifecycles (management), including amounts, products, markets. Focus is on Europe. Selection of key flows for further analysis.
2. Value chain analysis: identification and analysis of releases from different lifecycle phases with a special focus on ODS and GWP, and toxic chemicals used in their production.
3. Description of the end-of-life phase: management options for recycling potential and toxic emissions for key streams, generated rejects and impurities of concern.
4. Assessment of impacts in the light of EU policies and strategies.
5. Recommendations for risk governance.
6. Analysis of knowledge gaps.

The work is based on a literature survey of recently published reports and selected peer-reviewed articles, especially those on the release and emissions from the production and end-of-life phases of fluorinated polymers' lifecycles. The main databases used for the literature survey were Scopus and Science Direct. In addition, other, for example grey, literature was referred to where relevant. Market surveys by BCC Research, Frost and Sullivan, Plastic Europe and WOODS on fluorinated polymers were looked into. Patents describing the synthesis of fluorinated monomers and polymers were also used as a source for production pathways, intermediates and by-products. For the production/synthesis of fluorinated polymers and of their thermal degradation/ incineration, primary literature was sought in the domain of material sciences. The impacts of PFAS on human and environmental health has been extensively reported in literature, reviews and reports from EU funded, Nordic or national projects and therefore this study mainly makes references to these.

The study was carried out as joint work with experts from two European Topic Centres (ETCs). The following organizations participated in the work:

- ETC/WMGE Waste and Materials in a Green Economy – VTT, VITO;
- ETC/CME Climate Change Mitigation and Energy – NILU, Öko-Recherche, RIVM.

Furthermore, Toke Winther from the Danish Environmental Protection Agency and a member of the European Chemicals Agency PFAS working group followed the work, shared information from previous works on the topic and provided valuable comments on findings. The draft report was also sent to selected experts for review and feedback on the content and conclusions before publication.

The work made use of the in-house EEA and ETC expertise on reporting and policies on F-gases, ODS and industrial emissions (ETC/CME) and waste management policies, non-toxicity policies and CE (ETC/WMGE). The work also was built on the following EEA/ETC reports:

- 2019 ETC/WMGE report *Plastics in Textiles*, and relevant references on plastics in a CE;
- 2019 EEA web-briefing *Emerging risks of PFAS in Europe*;
- 2021 EEA web-briefing *Safe and Sustainable by Design*;
- EEA reports yearly on the production, import, export and destruction of fluorinated GHG ([3]) and ODS ([4]).

1.3 Structure of report

This report consists of nine chapters (Figure 1.3):

Chapter 2 sets the scene for the study; it defines the fluorinated polymers selected for the study, their main application areas and their key properties. Furthermore, it gives a short summary of the global amounts of fluorinated polymers produced.

Chapter 3 presents information on the origin of fluorspar used for production of fluorinated polymers and information on the environmental impacts of mining.

Chapter 4 describes emissions to air, water and soil during production. It also gives information on the global warming potential and ozone-depleting potential of chemicals used in syntheses and polymerisation.

Chapter 5 gives examples of emissions and exposure routes related to the use of a few consumer products containing fluorinated polymers. Textiles, food-contact materials and cosmetics were chosen as examples.

Chapter 6 focusses on emissions/releases from different end-of-life options for products containing fluorinated polymers. Technologies for recycling options of process scraps are also reviewed.

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[3] https://www.eea.europa.eu/publications/fluorinated-greenhouse-gases-2020

[4] https://www.eea.europa.eu/publications/ozone-depleting-substances-2019

Chapter 7 analyses the benefits and challenges at different stages of the fluorinated polymer lifecycle in light of EU strategies and policies for circular and low carbon economies and non-toxicity. It also includes an example of replacements for fluorinated polymers in one application.

Chapter 8 presents an approach to risk governance.

Chapter 9 summarises knowledge gaps along the fluorinated polymer lifecycle identified in previous chapters.

Appendix A presents data on global warming and ozone-depleting potential of substances linked to fluorinated polymer production.

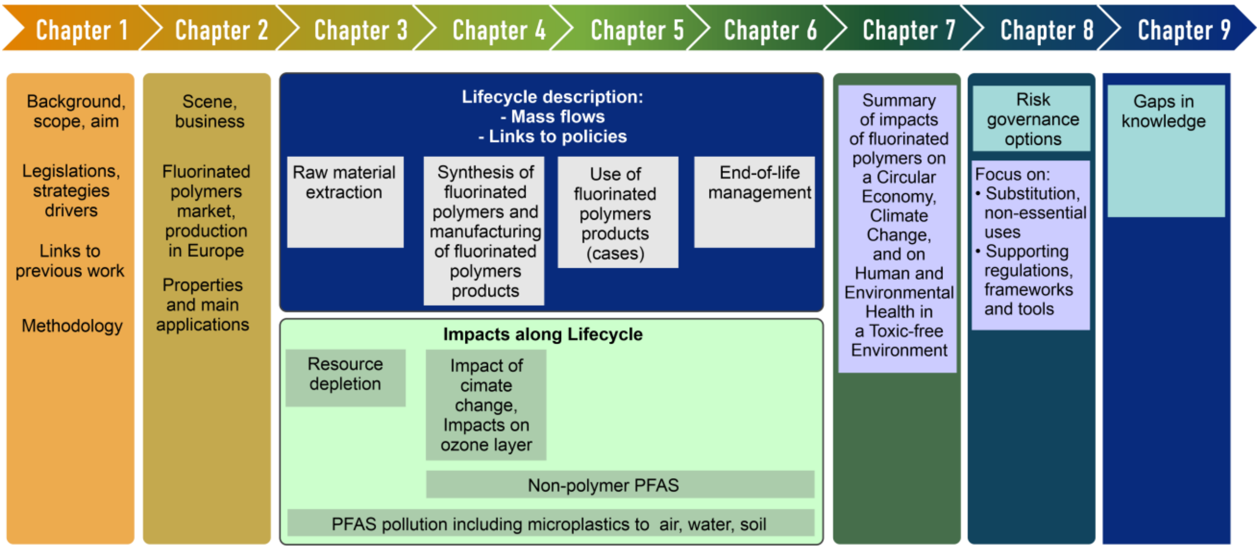

Figure 1.3. Structure of the report.

2 Fluorinated polymers

Main authors: Elina Yli-Rantala, Elina Pohjalainen and Xenia Trier

Key messages

- Fluorinated polymers are defined as:
    - polymers: the ECHA definition: minimum three repeated units or monomers with a fluorinated carbon backbone;
    - fluorinated sidechain polymers;
    - per- and polyfluorinated polyethers.
- Diverse uses in transport, chemicals, laboratories, power generation, cookware, textiles and cosmetics;
    - important in renewable energy applications.
- Solid numbers on EU production/consumption volumes (total/specific uses) are not available in the public domain:
    - global production: 320 000 tonnes (AGC, 2020);
    - European production: 51 000 tonnes (PlasticsEurope, 2019b);
    - European consumption: 52 000 tonnes (PlasticsEurope, 2019b);
    - Major uses: polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) – focus in this report on PTFE, PVDF, perfluorinated ethylene-propylene (FEP), per- and polyfluorinated polyethers (PFPE) and fluorinated sidechain acrylate and urethane polymers.
- Functions include:
    - Oil and water repellent, temperature, chemical and abrasion resistant, low-diffusion coefficient and diffractive index.

2.1 Definitions

Fluoropolymers, by definition, are polymers consisting of carbon-only backbone, to which fluorine atoms are directly attached (Buck et al., 2011). This definition rules out, for instance, fluorosilicones, fluoroacrylate polymers and fluoropolyethers which also containing silicon and oxygen in the polymer backbone, and therefore they are not often referred to as fluoropolymers (Smith Jr. et al., 2014; Russell et al., 2008).

Fluorinated polymers, on the other hand, include both: polymers containing at least one type of monomer unit with fluorine in it *or* which have a hydrocarbon backbone to which fluorinated sidechains are attached.

The term used in this report is ***fluorinated polymer*** which includes many types of fully (per-) or partially (poly-) fluorinated polymers including elastomers (rubbers), which also may contain chlorine (Gardiner, 2015). At times, some fluorinated polymers are referred to as perfluoropolymers to emphasise their fully fluorinated composition compared to partially (poly-) fluorinated compounds (McKeen, 2017). Fluorinated polymers which contain a minimum of one CF_2 – unit in its monomers or attached to its sidechains are per- and polyfluoroalkyl substances (PFAS) (OECD, 2018).

Figure 2.1 shows structures of fluorinated polymers, divided into *fluoropolymers*, where the carbon backbone is fluorinated, and *fluorinated sidechain polymers*, where the fluorinated sidechains are attached to a hydrocarbon backbone. The simplest form of a fluoropolymers is the homopolymer which only has one type of fluoro monomer (also called repeat units) of which there are *n* numbers (shown as an orange circle in the figure). When several types of fluoromonomers are present – shown as orange circles and triangles in the figure – it is called a copolymer (Naka, 2014). At the end of the homopolymer and copolymer there are two end groups, A and B which may be chemically different or the same type, which can be used to control the solubility. Fluorinated sidechain polymers are also shown in the figure and consist of a hydrocarbon backbone (shown as green pentagons and hexagons n the figure), with attached poly- or perfluorinated sidechains shown as orange squares.

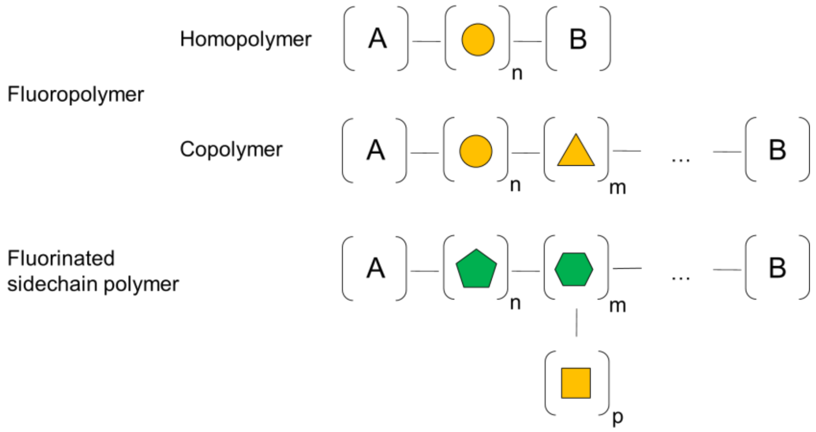

Figure 2.1. Structures of fluorinated polymers consisting of fluoropolymers (homopolymers, copolymers) and fluorinated side-chain polymers.

Symbols ●, ■, ▲ are fluorinated monomer units, A and B describe end groups that help to control solubility of the polymers. Symbols ⬟ and ⬢ are hydrocarbon monomer units, n, m, and p are number of monomer units, also called repeat units.

Source: ETC/WMGE

Polymers are not universally defined in terms of how many repeat units they should contain to qualify as polymers but rather polymers in terms of their material properties. In polymer and material sciences, where polymers, for instance, are described as *"… a substance composed of a molecule of high molecular weight (generally more than ten thousand). This is because polymers having a high molecular weight more than ten thousand show polymer-like properties such as film and fibre forming, and the addition or removal of one or a few of the units has a negligible effect on the properties. On the other hand, a material with regular repeating structure but too low an average molecular weight to achieve their properties is usually called an oligomer. In other words, oligomer is a molecule that consists of a few monomer units"* (Naka, 2014). Depending on the monomers, a polymer with polymer-like properties would typically consist of around 50–100 repeat units. Chain lengths below this limit are called oligomers, in which molecules with two, three or four repeat units are called dimers, trimers and tetramers respectively.

A key point is that what is defined as a polymer varies between regulations. In polymer science a polymer is typically defined as a chain consisting of at least 50 monomers. Chain-lengths from two to 50 are called oligomers. This is also the definition used in the EU food-contact materials legislation, which furthermore states that a polymer should be self-supporting, i.e. not in a liquid form or so thin that the material cannot be, for example, peeled off (EU, 2011). Another point is whether only feedstocks and additives/polymer production aids are (specifically) regulated, or whether the intermediates, transformation by-products, degradation products and/or the final products with all impurities and residuals are also regulated. As a consequence, not all substances which are used and produced throughout fluorinated polymer lifecycles are covered by EU regulations.

In the EU's REACH legislation, a polymer is defined as a molecule which has three or more repeat units, i.e. monomers (ECHA, 2012). In practice this means that a number of detergents and surfactants, which contain homologue series of oligomers, are polymers according to REACH, and hence are exempted from registration. It has been recorded that polyethers have been reclassified as polymers under REACH, whereby they are exempt from registration (Wang et al., 2015b). While polymers are exempt from registration, they are still subject to restrictions. Furthermore, registration is not needed if the manufacturing or import of a substance amounts to less than 1 tonne a year.

In this report the REACH definition of a polymer is used.

Table 2.1 and Figure 2.2 give an overview of some common commercial fluorinated polymers. Since the number of fluorinated polymers is large, only a few examples are described in this report. As a result, some commercially relevant fluorinated polymers/elastomers of fluorinated alkyl silanes and siloxanes (Li et al., 2016b) are not described.

More in depth information on structures, performance and applications of fluorinated polymers is provided, for example, in Ameduri and Sawada's *Fluorinated polymers* Volumes 1 and 2 (2017) – see for example Volume 2, Chapter 1: Industrial Aspects of Fluorinated Oligomers and Polymers (Dams and Hintzer, 2017) and Chapter 4: Fluoroplastics and Fluoroelastomers – Basic Chemistry and High-performance Applications (Ohkura and Morizawa, 2017).

Table 2.1 Examples of common commercial fluorinated polymers and trade names which are or have been in use. Further information is provided below in section 2.3.

Abbreviation	Trade name examples	Full name	Repeat unit
PTFE	Teflon, Zonyl	poly(tetrafluoroethylene)	$(CF_2 - CF_2)_n$
PCTFE	Neoflon, Voltalef, Aclon, Aclar, Hostaflon C2, Fluon, Plaskon, Halon	poly(chlorotrifluoroethylene)	$(CF_2 - CClF)_n$
PVF	Tedlar	poly(vinylfluoride)	$(CH_2 - CHF)_n$
PVDF	Kynar, Solef, Hylar	poly(vinylidene fluoride)	$(CH_2 - CF_2)_n$
FEP	Teflon FEP, Neoflon FEP, Dyneon FEP	poly(tetrafluoroethylene-co-hexafluoropropylene)	$(CF_2 - CF_2)_n \cdots (CF_2 - CFCF_3)_m$
ETFE	FluonETFE, Tefzel, Neoflon	poly(ethylene-co-tetrafluoroethylene)	$(CH_2 - CH_2)_n \cdots (CF_2 - CF_2)_m$
ECTFE	Halar ECTFE	poly(ethylene-co-clorotrifluoroethylene)	$(CH_2 - CH_2)_n \cdots (CClF - CF_2)_m$
PFA	Teflon-PFA, Hostaflon-PFA, Chemfluor	poly(tetrafluoroethylene-co-perfluoropropylvinylether)	$(CF_2 - CF_2)_n \cdots (CF_2 - CFO - C_3F_7)_m$
PFPE	Krytox, Fomblin, Galden, Fluorolink, Demnum	per- and polyfluoropolyethers	various (often copolymers with an ether polymer backbone with F atoms directly attached to carbon backbone)
FKM, FFKM, FEPM	Viton, Aflas, Kalrez, Daiel, Silastic	fluoroelastomers, perfluoroelastomers, tetrafluoroethene-propene rubbers	various

Sources: Améduri, 2018; McKeen, 2017; BCC Research, 2015; Gardiner, 2015

Overviews of production volumes for the various fluorinated polymers are scarce and although several examples exist of industry market reports these studies should be used with caution (Wang et al., 2017, 2020). A few important fluoropolymers constitute the major part of the market: a recent article by Henry et al. (2018), cited by Lohmann et al. (2020) states that PTFE, FEP, ETFE and tetrafluoroethylene-copolymers constitute around 75% of the market, with PVDF, PVF and fluoroelastomers also being important. More information on the fluoropolymer market is presented in Section 2.3.

The fluorinated polymers in this report have been chosen based on the following criteria:

- to illustrate different types of fluorinated polymer;
- how widely they are used;
- their potential to cause impacts along their lifecycles;
- a particular focus has been to investigate fluorinated polymers which may release GHG, contributing to climate change, or ODS along their lifecycles.

Based on these criteria **the fluorinated polymer examples focused on are shown in Figure 2.2 and include**:

- PFTE: a homopolymer, around half of the market;
- PVDF: a homopolymer, the fastest growing fluorinated polymer worldwide;

- FEP: a copolymer, a GHG is used in its synthesis;
- PFPE: polymers according to the REACH definition, typically liquid copolymers, used as industrial machine oils and as coatings for food-contact paper, glass, plastics, etc;
- fluorinated sidechain acrylate and urethane polymers: examples of fluorinated sidechain polymers, used as coatings and sizing agents for textiles and food-contact paper.

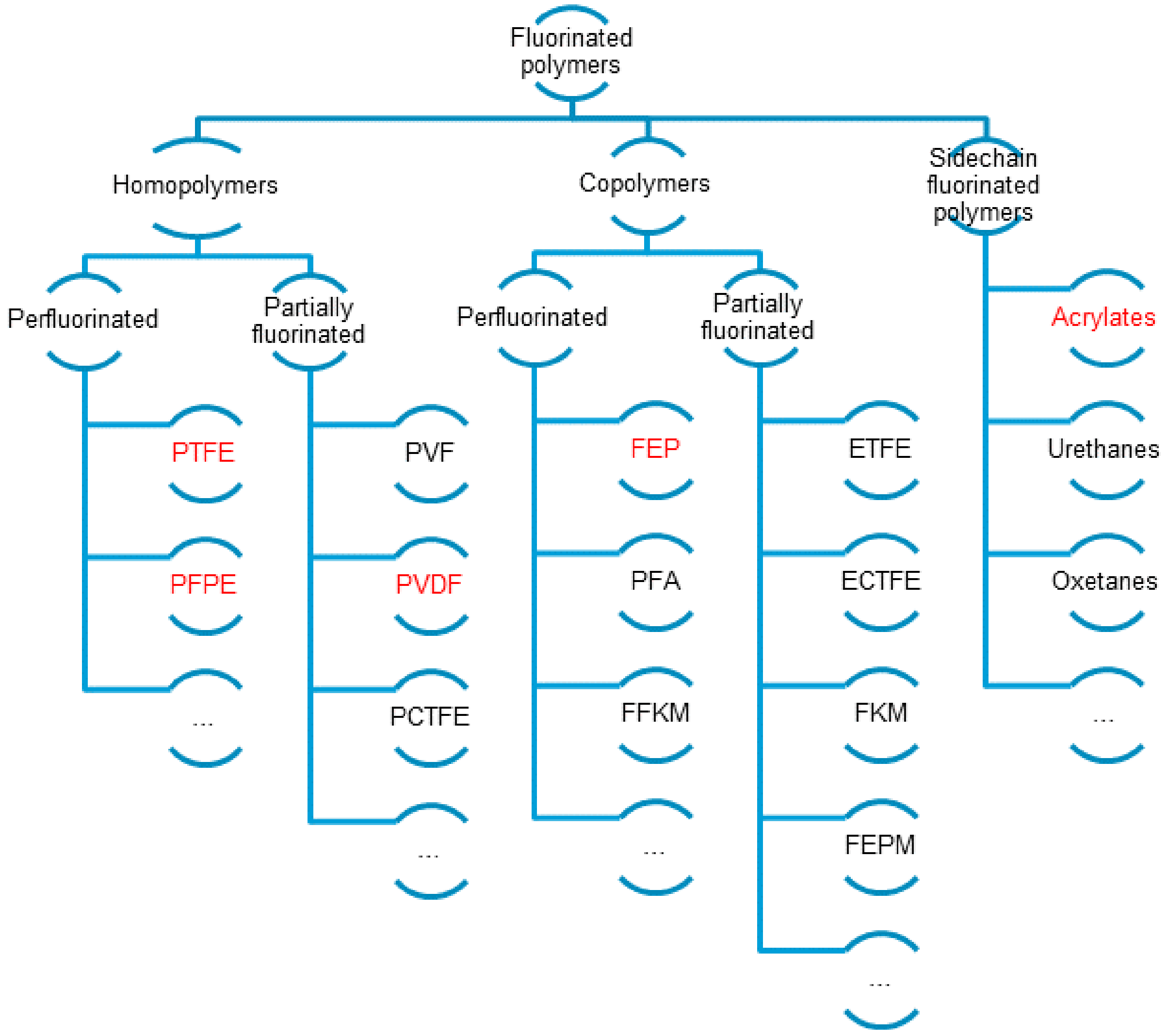

Figure 2.2. Classification of fluorinated polymers based on the number of monomer types.

Note: homopolymer = one type of monomer or copolymer = usually two types of monomer) and degree of fluorination (fully fluorinated = perfluorinated or partially fluorinated = polyfluorinated). The abbreviations in red denote the fluorinated polymers focused on in this report.

Source: ETC/WMGE

2.2 Properties and production process of fluorinated polymers

Fluorinated polymers are widely used in industry, laboratories and consumer products due to their special properties of being resistant to abrasion, heat and chemical attack and providing low friction. The unique properties of fluorinated polymers are a consequence of the strong carbon–fluorine (C-F) bond ([5]), the

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[5] The bond dissociation energy depends on the surrounding molecular environment. For example the bond dissociation energy of the C-F bond in fluoromethane (CH_3F) is approximately 480 kilojoules per mole (KJ/mol), compared to the bond dissociation energy of carbon-hydrogen (C-H) bond in methane (CH_4) that is 440 kJ/mol (Blanksby and Ellison, 2003).

small size of the fluorine atom packing closely around and protecting the carbon chain from attack, and of its un-polarisability (Puts et al., 2019a; Améduri, 2018; Henry et al., 2018; BCC Research, 2015).

Carbon-fluorine bonds containing substances are by definition of concern as they are strong and difficult to break, thereby almost by definition rendering human and environmental persistency issues to fluorinated polymer, even following incineration. Albeit just a little bit less, also carbon-chlorine (C-Cl) and carbon-bromine (C-Br) bonds are strong. This means that any chemical substance containing one or more C-F bonds and/or one or more C-Cl or C-Br bonds is theoretically of concern for persistency in aqueous environments as well as in sediments and soil compartments. Moreover, volatile and semi-volatile fluorocarbons and chlorocarbons are of concern for persistency in the atmosphere and for their potential greenhouse and/or ozone-depleting effect.

Examples of fluorinated polymers uses include membranes and tubing for industrial processes including food production and water cleansing; coatings and lubricants in industrial processes; non-stick coatings on metals on, for example, baking trays, frying pans and kitchen utensils; coatings on glass, stone, wood and plastics on, for example, building materials and windmill wings; lubricants; membranes in outdoor jackets and other textiles; coatings on paper and board; and microplastics in shaving foams and for metal lubrication (Améduri, 2018; Scudo, Alexandra et al., 2017), as illustrated in Figure 2.3. Glüge et al. (2020) provides an overview of some uses of PFAS, including fluorinated polymers. This study did not however include all types of PFAS, because it limited its search to those containing a minimum of $-CF_2-CF_2-$ units. Lohmann et al. (2020) also discuss potential emissions of PFAS along the lifecycle of fluoropolymers, and in relation to some of their uses, but does not address fluorinated sidechain polymers. The recent Organisation for Economic Co-operation and Development (OECD) report on commercial information from vendors (OECD, 2020) also provides information on uses of fluorinated polymers. PTFE and many of the fluorinated polymers are authorised for use in food-contact material (FCM) plastics (EU, 2011), and are also used in so-called non-harmonised FCMs which do not require authorisation by the European Food Safety Authority (EFSA), such as paper and board (OECD, 2020; Trier et al., 2018).

Figure 2.3. Consumer products and industrial applications that may contain fluorinated polymers.

Source: EEA and ETC/WMGE. Illustration by CSCP.

The properties and uses of the fluorinated polymers on which this report focusses are briefly discussed next. Their production is discussed in more detail in Chapter 4 and their applications in Chapter 5.

Polytetrafluoroethylene (PTFE) is the most widely used fluorinated polymer (Henry et al., 2018; Frost and Sullivan, 2016). It is polymerised from the tetrafluoroethylene (TFE) monomer, making it a fully fluorinated counterpart of polyethylene but with a rigid helical chain construction (Teng, 2012). It is the most chemically resistant polymer among thermoplastics and also has excellent heat resistance, electrical insulation properties and one of the lowest coefficients of friction against any solid. Additionally, PTFE is hydrophobic, meaning neither water nor water-containing substances will wet it. These unique properties make PTFE practical in applications for which characteristics such as low friction, excellent thermal resistance, chemical inertness (BCC Research, 2015) and electrical insulation are required. As a result, it is used in numerous transport applications such as seals, gaskets and valves; as coatings on metals including cookware and on plastics, for example on windmill blades (Améduri, 2020; BCC Research, 2015); electronics and batteries, for instance lithium-ion batteries contain 1–2% of PTFE/PVDF (Mossali et al., 2020).

The high weight of fluorine compared to hydrogen and the rigid polymer chain structure results in a relatively high density for a polymeric material, 2.1 grams per cubic metre; a high melting temperature of approximately 320 °C; low permeability to gases and liquids – high barrier properties (Keller and Kouzes, 2017) – and a high melt viscosity. The last property makes it difficult to mould PTFE using traditional polymer processing methods; however, alternative methods have been developed, and today it can be processed into any shapes for almost every application area (Teng, 2012).

PTFE is available as granules, fine powders and water-based dispersions, which are produced by different polymerisation methods (Teng, 2012). Some of these require the use of surfactants, which previously were ammonium salts of PFOA and perfluorononanoic acid (PFNA) (Buck et al., 2012), but which gradually have changed to a variety of other PFAS, such as the fluorinated ethers GenX and ADONA (carboxylate ethers) and F53B (sulfonic fluorinated ether) (Wang et al., 2015b). PTFE may also be filled with other substances, such as glass, graphite, metals, minerals and colorants to obtain specific functions. There is evidence of recycling of PTFE, which may have different properties from its virgin form, but information is limited (Hindustan Nylons, n.d.).

Polyvinylidene fluoride (PVDF) has the second biggest global market share after PTFE (Frost and Sullivan, 2016). It is polymerised from vinylidene difluoride (CH_2–CF_2). This structure provides performance characteristics which do not match those of PTFE, but the key advantage of PVDF is its superior melt-processing characteristics compared: it can be extruded and injection-moulded similarly to common thermoplastics (BCC Research, 2015).

When compared to other melt-processable fluorinated polymers, PVDF has been found to be the strongest and more resistant to abrasion. It provides even better electrical insulation than PTFE, but its heat resistance is not as high (BCC Research, 2015). It is mainly used in industrial metal coatings, membranes, wire insulation, and as a binding material in batteries (Frost and Sullivan, 2016). It is widely used in electronics and batteries; lithium-ion batteries contain 1–2% of PVDF/PTFE (Mossali et al., 2020).

Per- and polyfluorinated polyethers (PFPE) form a class of fluorinated polymers in which the polymer backbone contains carbon and oxygen, and fluorine atoms are directly attached to carbons, i.e. backbone consists of $-CF_2-$, $-CF_2CF_2-$, and possibly $-CF(CF_3)CF_2-$ units separated by oxygen (O) atoms (Bokkers et al., 2019; Buck et al., 2011). The structure of PFPMIE (perfluoropolymethylisopropyl ethers), an example of PFPE, is presented in Figure 2.4. PFPE are low-molecular-weight polymers (500–15,000 daltons (Da)) (Dams and Hintzer, 2017), which means they are typically oils or greases, and therefore their most important application area is in high-performance oils, lubricants for engines and machinery and as electronic liquids (Solvay, 2020). Their unique properties include being resistant to ionising radiation, rendering them applicable to the aerospace and nuclear industries (Gardiner, 2015). They have also been used as coatings of food-contact paper and board produced by Solvay (Trier et al., 2018; Dimzon et al., 2016), and as coatings for, for example, glass. More information on industrial uses is available in *Fluorinated Specialty Chemicals – Fluorinated Copolymers for Paints and Perfluoropolyethers for Coatings* (Hoshino and Morizawa, 2017).

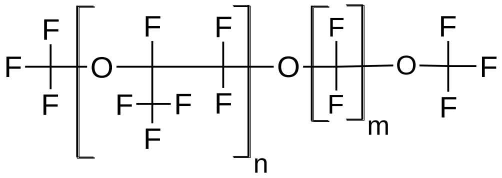

Figure 2.4. The structure of PFPMIE, an example of a PFPE.

Perfluorinated ethylene propylene (FEP) is a copolymer of TFE and hexafluoropropylene (HFP). It has similar mechanical and chemical properties as PTFE combined with the melt-processability of more conventional polymers (BCC Research, 2015). FEP has the third largest market share for fluorinated polymers and is the most widely used fluorinated copolymer. It is used especially in wire and cable insulation in various industries including the automotive, aerospace, chemical processing, oil and gas, and electronics sectors where resistance to chemicals and serviceability over wide temperature ranges is required (Frost and Sullivan, 2016).

Sidechain fluorinated polymers are a class of polymers with nonfluorinated backbones with fluorinated sidechains containing -C_nF_{2n+1} (Buck et al., 2011) or -C_nF_{2n}- moieties. These include fluorinated sidechain acrylate polymers, fluorinated urethane polymers and fluorinated oxetane polymers. Fluorinated sidechain acrylate polymers are used, for example, in water-, stain- and grease-proofing finishes for textile, leather and paper surfaces (Trier et al., 2018) and are further discussed in Chapter 5.

2.3 Market

Fluorinated polymers are widely used in industry and in consumer products. Reported volumes of the global production of fluorinated polymers range between 180 000 tonnes to 340 000 tonnes, depending on the baseline year (2015–2018) and polymers included (Frost and Sullivan, 2016; BCC Research, 2015). One of the most recent information (AGC, 2020) suggests that the global consumption of fluorinated polymers in 2018 amounted to 320 000 tonnes, an increase of 19% over the 2015 global consumption estimated at 270 000 tonnes. Compared to other plastics, they are expensive; the cost of PTFE is roughly10 times that of many other polymers (PlasticsInsight, n.d.) and their production volumes are relatively small – in 2018, global plastics production ([6]) reached almost 360 million tonnes and European production around 62 million tonnes (PlasticsEurope, 2019b).

The largest consumer of fluorinated polymers in 2018 was China, with a share of 37% of global consumption, followed by the United States, 22%, and (western) Europe, 16% (AGC, 2020). In the United States, 78 000 tonnes of fluorinated polymers were consumed in 2018 while production totalled 85 000 tonnes (Wood, 2020). In Europe, 52 000 tonnes were consumed in 2015, slightly more than the 51 000 tonnes produced (PlasticsEurope, 2017). Production and consumption of fluorinated polymers in Europe is discussed in more detail in Section 2.3.1.

Figure 2.5 shows the market shares of different fluorinated polymers – PTFE made up 53%, 171 000 tonnes, of fluorinated polymer consumption, PVDF 16%, 51 000 tonnes, and FEP 10%, 31 000 tonnes.

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[6] Including thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and sealants and polypropylene (PP) fibres. Not included: polyethylene terephthalate (PET) fibres, polyamide (PA) fibres and polyacrylate-fibers.

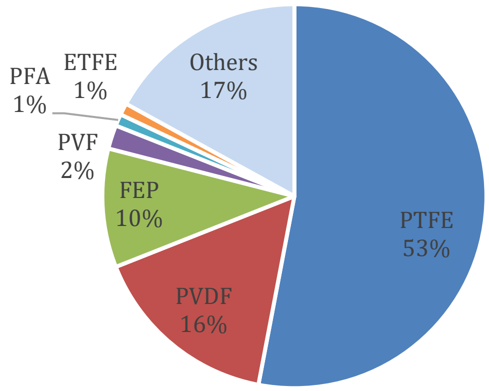

Figure 2.5. Global consumption of fluorinated polymers, 2018, 320 300 tonnes.

Source: AGC (2020).

Major producers of fluorinated polymers include 3M/Dyneon (Germany), AGC Inc (Japan), Arkema (France), Chemours (US), Daikin Industries Ltd. (Japan), Dupont (US), Shandong Dongye Group (China), Shanghai 3F (China), and Solvay (Belgium) (Keller, 2020; Frost and Sullivan, 2016; BCC Research, 2015).

2.3.1 Production and consumption of fluorinated polymers in Europe

In 2015 around 270 000 tonnes of fluorinated polymers were consumed globally, a doubling from the 133 000 tonnes consumed in 2004 (Krämer and Schlipf, 2016). PTFE with 140 000 tonnes, accounted for the majority of fluorinated polymers, followed by PVDF at 41 000 tonnes and FEP with 2,500 tonnes. According to data from PlasticEurope, 51 000 tonnes of fluorinated polymers were produced in Europe, with an additional 21 500 tonnes imported and 20 500 tonnes exported; about 52 000 tonnes were consumed in EU in 2020.

Figure 2.6 shows fluorinated polymer sales in the EU by main sectors in 2015, with transport, chemicals and power being the largest. The cookware sector is the third largest, using 3 500 tonnes per year much of which is likely to enter the waste stream fairly soon given the relatively short life of consumer products. Most of the other sectors using fluorinated polymer also potentially add to the general population's waste stream. If it is assumed that Europe has a similar distribution of downstream applications of fluorinated polymers as the United States, 16% of the fluorinated polymers consumed in Europe are used for the manufacture of a broad range of consumer products. By applying consumption data for the EU mentioned above, an estimated of 8 320 tonnes of fluorinated polymers will be used per year in the production of consumer products that will enter the waste stream end of life.

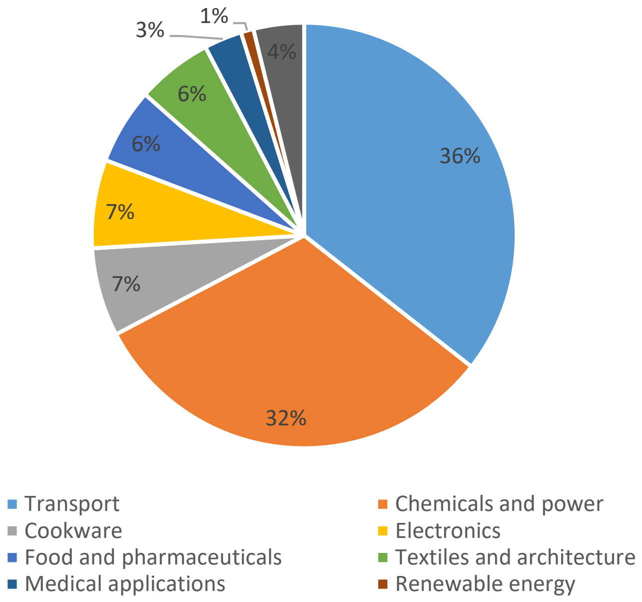

Figure 2.6. Fluorinated polymer sales to key sectors in the EU, 2015, %. Note: percentages may not sum due to rounding.

Source: PlasticsEurope (2018)

While in 2004 western Europe consumed 23 900 tonnes of PTFE, 6 800 tonnes of PVDF and 4 000 tonnes of other fluorinated polymers (Will et al., 2005), by 2016, 32 000 tonnes of PTFE, and 36 000 tonnes of other fluorinated polymers were used (Krämer and Schlipf, 2016). According to recent reports, 4% of PTFE purchased in Europe is used for cooking and baking utensils, resulting in 1 280 tonnes of it potentially entering the waste stream within a few years.

2.4 Production sites of fluorinated polymers

In general, little information is available on where fluorinated polymers are produced in the world or in the EU, though information is likely available in the countries where permits are required. In 2020, many of the existing fluorinated polymer production sites were located in Asia, but a number of production sites exist in Europe.

The EU's European Pollutant Release and Transfer Register (E-PRTR ([7])) requires the European chemical industry, including manufacturers of basic plastic materials such as polymers and synthetic fibres, to report emissions to air, water, and land of 91 pollutants, being single substances or groups of substances. Fluorinated polymer producers, however, do not have to identify themselves as such when they report, so it would only be known that the company belongs to the chemical industry and that it perhaps produces polymers.

It would only therefore be possible to check their emissions if their names and locations were known. Furthermore, it would require their emissions to be above the reporting thresholds for any of the 91 pollutants designated by the E-PRTR, which is generally not the case. Single PFAS are currently not on the pollutant list, and though pollutants such as 'PFCs' in principle could be understood and measured as total PFAS, the description currently only mentions some specific F-gases ([8]). It is therefore generally not

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[7] Regulation (EC) No 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC. It should be noted that the E-PRTR Regulation is going through an Impact Assessment that will result in a revised Regulation. This will likely include new reporting fields, new pollutants and industrial activities.

[8] However, if the definition of PFCs was re-defined to be, for example, 'PFC = per and polyfluorinated carbons' which is the sum of all PFCs, measured as Total PFAS (including relevant F-gases and fluorinated polymers), then the reporting of this pollutant would immediately apply to all facilities producing, using or handling fluorinated polymers.

possible to identify which sites or facilities produce, use or handle fluorinated polymers or their wastes. One exception are fluorinated polymer plants, which emit GHGs that are regulated by the GHG inventory. The one example is the potent GHG trifluoromethane (HFC-23), which is a by-product formed in the manufacture of chlorodifluoromethane (HCFC-22). Since HCFC-22 is used for fluorinated polymer production, residual HFC-23 may be released from the polymer production sites, and must be reported. Also, fugitive emissions from fluorochemical production are reported under the Common Reporting Format (CRF) of the United Nations Framework Convention on Climate Change (UNFCCC). The 2019 Intergovernmental Panel on Climate Change (IPCC) Refinement Report suggests a further breakdown of the reported data into emissions from HCFC-22 (2.F.9a), hydrofluorocarbon (HFC) (2.F.9b), perfluorinated carbon (PFC) (2.F.9c), sulphur hexafluoride (SF_6) (2.F.9d), nitrogen trifluoride (NF_3) (2.F.9e), fluoropolymer (2.F.9f), and other fluorochemical (2.F.9g) production. It is, however, not mandatory for any Parties to the UNFCCC to refer to this new guidance in their emissions reporting. In a report, Goldenman et al. (2019) searched the E-PRTR and only found fluorinated polymer sites registered in relation to chlorofluorocarbon (CFC) emissions, but based on a search for fluoropolymer company names, they estimated that between 12–20 fluorochemical facilities are in operation in Europe.

As an alternative, measurements of PFAS in the air can be used to indicate fluorinated polymer production sites. This can also confirm the correctness of information of known production sites. Figure 2.7 hence shows higher pollution near known fluorinated polymer factories in northern Italy and the Chemours Plant in Dordrecht in the Netherlands.

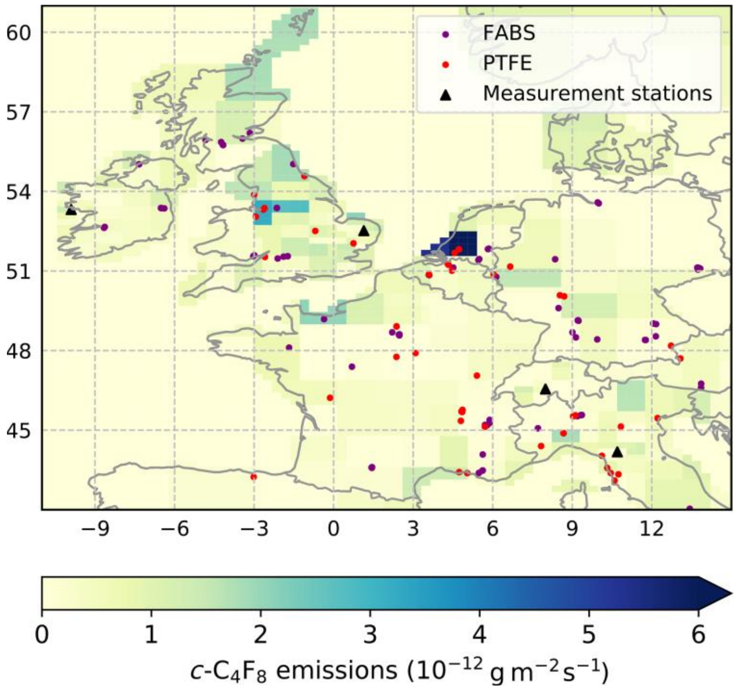

Figure 2.7. Potential industrial emitters of perfluorocyclobutane (c-C_4F_8).

Note: Red dots are PTFE production facilities; purple dots are semiconductor fabrication plants (FABS)
Source: Mühle et al. (2019)

2.5 Knowledge gaps

- Amounts of different types of fluorinated polymers produced.
- Production and manufacturing sites in Europe.
- Amounts of fluorinated polymers in key applications.

3 Raw material extraction

Main authors: Elina Yli-Rantala and Margareta Wahlström

Key messages:

- Fluorspar is a critical resource according to European Commission's Critical Raw Material list due to high global supply risk – only a few countries are responsible for the main fluorspar supply– but also because of its poor substitutability, negligible recycling and economic importance to Europe.
- About 11% of fluorspar consumed in Europe is used for the production of fluoropolymers.
- Similar to any other mining activity, fluorspar mining is associated with impacts on the local environment and landscape. In uncontrolled extraction operations, the lack of measures for preventing the spreading of dust from tailings ponds or spillage during operation may cause elevated fluoride concentrations in soil and water near the mining areas and also cause silicosis, a serious lung disease, in workers as a result of exposure to fine dust.

3.1 Sources and use of fluorspar

Fluorspar is used for production of hydrofluoric acid (HF), which is one of the main chemicals needed in the production of fluorinated polymers. The carbon backbone of fluorinated polymers comes from chlorinated hydrocarbons, as described in more detail in Chapter 4.

Fluorspar is the commercial name for the mineral fluorite calcium fluoride (CaF_2). The mineral fluorspar consists of 51.1% calcium and 48.9% fluorine in its pure form. Commercial fluorspar is graded according to its quality and its specification into acid, metallurgical and ceramic grades (9). HF is produced from acid-grade fluorspar. In principle, metallurgical grade fluorspar can be used for HF manufacturing, for example, in Russia, if the remaining impurities are acceptable (10).

Fluorspar, or fluorite, is the only commercially mined mineral to source fluorine. In the EU, fluorspar is defined as a critical raw material, and in China and the United States as a strategic mineral (CRM Alliance, 2020; European Commission, 2020c; Blengini , G.A. et al, 2017; EC, 2013). The classification of fluorspar as a critical raw material is a combination of several indicators: supply risk, poor substitutability, industrial importance and negligible recycling. The global supply risk is seen as particularly critical due to high concentration of supply – 65% of world mine output is from China and 15% from Mexico (Reichl, 2019).

In 2017, 6 million tonnes of fluorspar were extracted globally, 63% in China and 26% in Mexico, followed by Mongolia and South Africa (Reichl, 2019). China is by far the largest consumer of both acid grade and metallurgical grade fluorspar, and declining domestic supply has led to a search for other sources, particularly the importation of metspar from neighbouring Mongolia (11).

A relatively minor source of fluorine is H_2SiF_6 (fluorosilicic acid), which is a by-product from the production of phosphoric acid from fluorine-containing apatite minerals (CRM Alliance, 2020; Fuge, 2019). An example of such a future source is the Arkema company that is building a hydrofluoric acid facility in North Carolina, United States, where they will use fluorine-containing by-products from phosphate mining as raw materials (McCoy, 2020). According to a Joint Research Centre (JRC) report (European Commission, 2020c) there is, however, very little interest in recycling or closing the loop of fluorspar, because of its disparate use in different applications and the lack of suitable recycling technologies. World known reserves of

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[9] The main grades of fluorspar available are as follows ((EC, 2013; US, 2012; https://www.eurofluor.org/hf-production/):

- crude ore (contains, for example, 25–30% CaF_2)
- metallurgical grade (contains a minimum of 80% CaF_2)
- ceramic grade (contains a minimum of 80–96% CaF_2)
- acid grade (contains a minimum of 97% CaF_2)

[10] Arsenic and phosphate impurities are the most problematic because they are difficult to remove during ore beneficiation and because they have detrimental effects on hydrofluoric acid production.

[11] source: Roskill, *Market Report 2020. Fluorspar Outlook to 2030*, 15th Edition https://roskill.com/market-report/fluorspar/ (accessed 12 April 2021)

fluorspar are estimated at around 310 million tonnes of CaF_2 (European Commission, 2020c). Mexico has the world's largest fluorspar reserves, followed by China and South Africa. The new unexploited resources in South Africa are so extensive and the technology for exploitation are new, simple and feasible, thus even with a number of mine closures around the world, the supply chain is ensured.

The EU production of primary fluorspar over the period 2012–2016 was estimated at 254 000 tonnes per year (CaF_2 content) acid grade fluorspar (Reichl, 2019) compared to the consumption of 755 000 tonnes of both acid grade and metal grade fluorspar. There is no production of metal grade fluorspar in the EU. Fluorspar mines in Europe (European Commission, 2020a; Lauri, L., 2016; Fluorine Forum 2019, 2019) are in:

- Spain: fluorspar production was 130 000 tonnes both in 2016 and 2017 (European Commission, 2020; CRM Alliance, 2020; Fuge, 2019; Dams and Hintzer, 2017; Hintzer and Schwertfeger, 2014);
- Germany: in 2016, a total of 149 000 tonnes of fluorspar were mined from two deposits;
- UK: the Cavendish mine came in operation again in 2013 and produced 65 000 tonnes acid grade fluorspar in 2018;
- mining activity in Bulgaria closed in 2016;
- there are numerous fluorspar deposits in France, Poland and Czechia but mining has not been considered economic.

Figure 3.1 illustrates the use of both acid- and metal-grade fluorspar and the sources of fluorspar used in Europe. Acid-grade fluorspar is used in the chemical sector for the manufacture of hydrofluoric acid, a precursor to the production of most other fluorine-containing chemicals (European Commission, 2020b; CRM Alliance, 2020; Fuge, 2019; Hintzer and Schwertfeger, 2014).

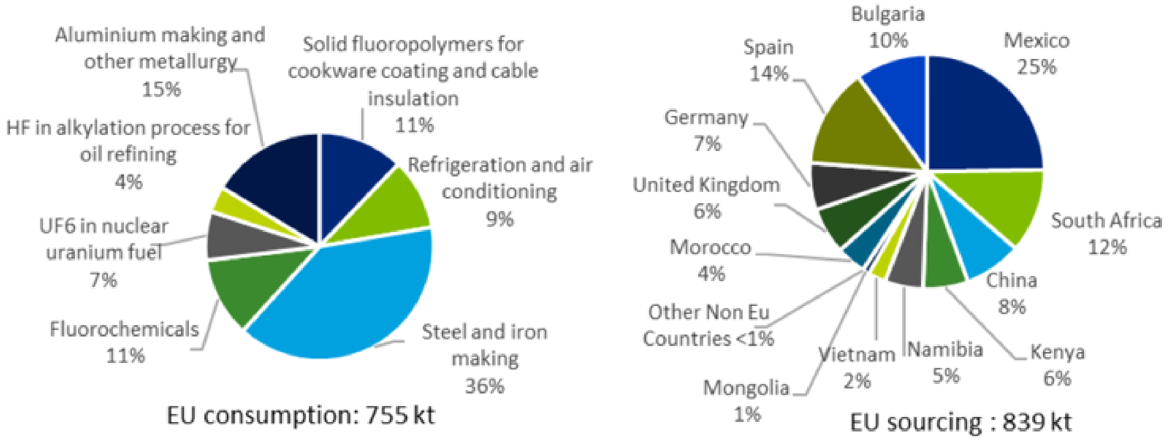

Figure 3.1. End uses and EU sourcing of acid- and metallurgical-grade mined fluorspar.

Note: Solid fluoropolymers are used for cookware coating, cable insulation and membranes: Solid fluoropolymers are used for cookware coating and cable insulation in household electrical appliances, lighting industry, telecommunications, aeronautics, nuclear, military, fuel-cells.
Source: European Commission (2020c)

3.2 Environmental and health impacts from extraction of fluorspar

In mining, huge volumes of rock overburden are removed from earth, treated and finally disposed of. Mining has significant local impact on landscapes, especially in the case of open pit mining (Figure 3.2). Similar to virtually any other mining activity, fluorspar mining is associated with impacts on the local environment and landscape (Villalba et al., 2008).

Mining in the open pit process reduce the functioning and stability of the ecosystem by reducing the biological activity in the vicinity of the mining area as the topsoil is removed and consequently forest or grasslands are destroyed. Additionally, metals and potentially oxidation of sulphides from increased surface ore subjected to air contact often accelerate the release of metal to surface- and groundwater causing local contamination of soil and water. Furthermore, noise, vibration, water pollution and dusts emissions generated during mining inevitably lead to animal migration and potential death. Change in landscape also affects living conditions of communities.

Underground mining influences the hydrogeological conditions at the site, especially with negative impacts on the ground- and surface-water quality due to the increased release of metals and salts from the rock. A special concern both in open pit and underground mining is the risk of acid drainage generation, which can occur when sulphides in the tailings oxide to sulphuric acid and there is a lack of neutralising minerals. (Li et al., 2016a)

Particularly in uncontrolled fluorspar extraction operations, a lack of measures to prevent the spreading of dust from tailings ponds or spillage during operation causes elevated fluoride concentrations in soil and water near the mining areas and also silicosis, a serious lung diseases, in workers from exposure to fine dust. High fluoride concentrations in drinking water cause health problems such as dental fluorosis – in several areas near deposits about half of the children suffer from this – and skeletal fluorosis which is not curable. Elevated fluoride can also lead to considerable intellectual deficits of children. (Grandjean, 2019; Grayson et al., 2016)

As an example of possible environmental impacts, increased levels of fluoride have been found in animal meat and plants around a fluorspar mine in Kenya where the exposure was assumed to result from poorly treated wastewater from the mine (Kibet et al., 2019). Fluorspar mining has also been connected with heavy metal pollution: Forján et al. (2019), for instance, found that the historic and current fluorspar mining on the northern coast of Spain has brought about increased levels of mercury in the area, a result of the inappropriate disposal of processing waste from the mines.

Further information on environmental and health risks related to fluorspar extraction at some mines together with a description of processing of fluorspar ot hydrofluoric acid are included in Annex 1.

Figure 3.2. Okorusu fluorspar mine, Namibia.

Source: Google Maps Globe View (screenshot from 17 June 2021)

4 Production of fluorinated polymers

Main authors: Dorte Herzke and David Behringer
Contributors: Xenia Trier and Margareta Wahlström

Key messages:

- Many halogenated substances with high GWP and ODP are involved in the synthesis of fluorinated polymers with unknown emission volumes. As a result, environmental releases of unknown quantities of harmful chemicals may occur.
- Both neutral (volatile) and ionic PFAS, some of which are substances of very high concern (SVHCs), are used as monomers and processing aids in the production of fluorinated polymers, with unknown emission volumes.
- There are several examples of contamination of communities and the environment around production sites.
- Ionic PFAS emitted to water, soil and air during production cause contamination of livestock feed and human food as well as sources of drinking water.

4.1 Outline of this chapter

This chapter describes examples of the production of some fluorinated polymers and their potential to act as a source for PFAS emissions throughout their lifecycles. The examples chosen are PTFE, PVDF, FEP, PFPE and fluorinated sidechain acrylate and urethane polymers. The manufactured fluorinated polymers are typically further processed into products and by-products as shown in Figure 1.2. The focus of this chapter is the potential emissions of volatile PFAS, some of which are GHGs, ODS and ionic PFAS. Furthermore, the emission potentials to air, soil and water during production are discussed.

The synthesis of PTFE is described in detail as it accounts for half the market. The synthesis of other important fluorinated polymers is also discussed, albeit in less detail. This chapter also includes a common section for all polymers in other key chemicals (feedstock and processing aids) used in the production of fluorinated polymers (Section 4.7). Furthermore, in Section 4.9, the conversion of fluorinated polymers into final products is very briefly covered, but this aspect of the lifecycle was not looked at in detail. Information of PFAS emissions to water, soil and air from production of fluorinated polymers is given in Section 4.8, but waste generated in fluorinated polymer production and PFAS emissions caused by waste treatment are presented further in Chapter 6.

Manufactured fluorinated polymers are further processed in the manufacturing of products which themselves can have human health effects, such as Teflon flu, that occur mainly in fluoropolymer production and manufacturing, but which also can be caused by cooking and baking (Greenberg and Vearrier, 2015).

4.2 A detailed look at the synthesis of important fluorinated polymers

4.2.1 Synthesis of polytetrafluoroethylene

4.2.1.1 Synthesis of tetrafluoroethylene

The polymer polytetrafluoroethylene (PTFE, CAS no. 9002-84-0) consists of a chain of CF_2 molecules (Figure 4.1).

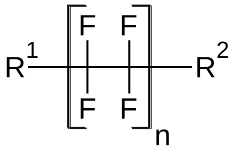

Figure 4.1. PTFE polymers consist of a chain of CF_2-molecules.

Note: R^1 and R^2 denote two end groups of the polymer which may be the same or different
Source: Own illustration

PTFE is synthesised by polymerisation of tetrafluoroethylene (TFE) monomer units. In its preparation process with TFE as feedstock, many environmentally harmful substances are involved. Figure 4.2 shows the major molecules that are involved in the synthesis of TFE that ultimately starts from methane (CH_4).

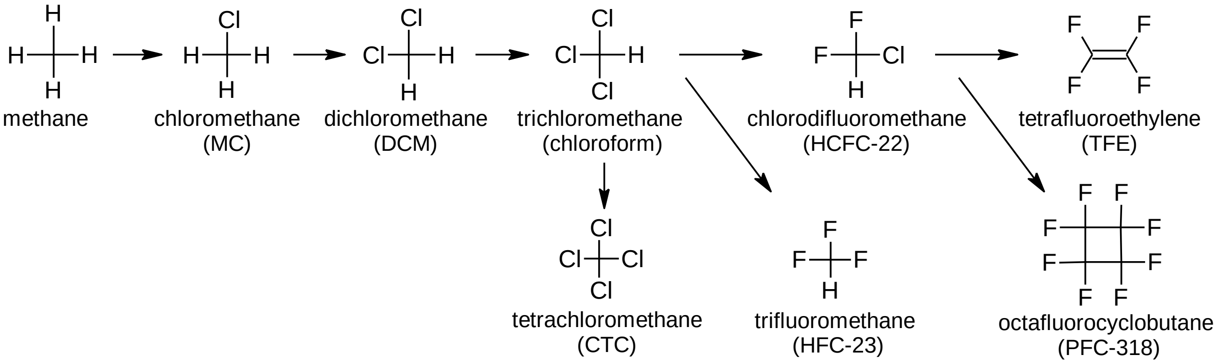

Figure 4.2. Substances involved in the synthesis of TFE, together with some relevant intermediates and by-products.

Source: Own illustration

Methane is chlorinated to produce trichloromethane (chloroform) in a process that leads, through a series of steps, ultimately to tetrachloromethane (carbon tetrachloride, CTC), yielding chloromethane (methyl chloride, MC), dichloromethane (DCM) and trichloromethane (Bohnet, 2002). Table A.1 shows the substances that are involved in the synthesis of trichloromethane, together with their environmental impacts in the form of GWP and ODP.

Trichloromethane is then reacted with hydrogen fluoride (HF) in the presence of a catalyst from the substance class of antimony pentahalides ($SbCl_xF_y$, with x+y=5) ([12]) to produce chlorodifluoromethane (HCFC-22) (Bohnet, 2002). As a highly relevant by-product, the potent GHG trifluoromethane (CHF_3, HFC-23) with a GWP of 12 400 is created in this reaction. Best estimates suggest that 1.5–3%, on average 2%, of the production volume of HCFC-22 is emitted in the process ([13]). Table A.2 gives the substances that are involved in the synthesis of HCFC-22, an ODS and potent GHG with a GWP of 1 760 and a major feedstock for the production of TFE.

Given that around 94 000 tonnes of HCFC-22 were produced in the EU in 2018 ([14]), approximately 1 880 tonnes (2%) of HFC-23 would have been emitted in the process in that year. This corresponds to 23 million tonnes of carbon dioxide equivalent (CO_2-eq). HFC-23 is directly vented to the atmosphere in many cases but can also be partially captured or thermally destroyed. The latter necessitates the use of a caustic scrubber to capture and further process fluorine-containing vent gases ([15]). While in developed countries emissions of HFC-23 decreased strongly after around 1998, remained relatively constant over the past 10 years but increased recently (Stanley et al., 2020), global atmospheric concentrations showed a constant

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[12] https://www.ipcc-nggip.iges.or.jp/public/gp/bgp/3_8_HFC-23_HCFC-22_Production.pdf
[13] Unpublished non-confidential data from the yearly reporting on ozone-depleting substances by the ETC/CME.
[14] Unpublished non-confidential data from the yearly reporting on ozone-depleting substances by the ETC/CME.
[15] https://cdm.unfccc.int/public_inputs/inputam0001/Comment_AM0001_Honeywell_061004.pdf

increase over the last decades ([16]). Since the recent uptake in emissions in developed countries is due to Russia and the US (Stanley et al. 2020), and the corresponding HCFC-22 production quantities have been relatively constant in the last decade, it can be concluded that in Europe measures are routinely in place to abate some of the emissions of HFC-23 from manufacturing facilities. Very roughly, it can be approximated that around 240 gigagrams[17] of HCFC-22 were produced annually in the last decade in developed countries, with around 1.6 Gg of by-produced HFC-23 (Figure 1 in Stanley et al. 2020). Given a 2% rate of by-produced HFC-23, around 4.8 Gg are expected to be emitted to the atmosphere each year, roughly three times what is being reported. Assuming proper reporting, facilities in Europe should abate around two-thirds of by-produced HFC-23, with one-third being vented to the atmosphere.

TFE is commercially synthesised from HCFC-22 by pyrolysis at 750–950 °C (Puts et al., 2019; Siegemund et al., 2000) but HFC-23 can be used instead of HCFC-22.

By-products of both routes include, apart from HF and HCl, perfluoro- and chlorofluorocarbon products, such as hexafluoropropylene (HFP, $CF_3CF=CF_2$) (Puts et al., 2019) that degrades entirely in the atmosphere to the highly persistent trifluoroacetic acid (Mashino et al., 2000a), the strong GHG octafluorocyclobutane (PFC-318) (Mühle et al., 2019), which has a GWP of 9 540 and the acutely toxic perfluoroisobutylene (PFIB) used as a warfare agent (Puts et al., 2019a). Table A.3 gives an overview of substances involved in the synthesis of TFE.

TFE used for polymerisation is usually 99.99% pure and contaminants include HCl, CF_4 (GWP 6 630), HFP, trifluoroethane ($C_2F_3H_3$, GWP 328 or 4 800, depending on the isomer: 1,1,2-trifluoroethane (HFC-143) or 1,1,1-trifluoroethane (HFC-143a)), difluoroethane ($C_2F_2H_4$, GWP 16 or 138, depending on the isomer: 1,2-difluoroethane (HFC-152) or 1,1-difluoroethane (HFC-152a)), and hexafluoroethane (PFC-116, C_2F_6, GWP 11 100) (Puts et al., 2019).

Box 4.1

Global warming potential and ozone-depleting potential

Some gases have the potential to contribute to global warming or harm the protective ozone layer. So-called GHGs absorb infrared radiation in specific frequency ranges, thus trapping heat within the troposphere, the lowest layer of the atmosphere. The most abundant GHG is CO_2, which serves as a reference for calculating the GWP of other gases on a per kg basis. Typically, the GWP is calculated over a time horizon of 100 years. Based on the 5th IPCC Assessment Report, CH_4, for example, has a GWP of 28, meaning that 1 kg of CH_4 that is released into the atmosphere will lead to an increase in temperature that is equal to the emission of 28 kg of CO_2. The higher the GWP, the stronger the GHG in terms of its contribution to global warming. Generally, more stable molecules can exert their effect for a longer time, and therefore halogenated gases, mostly containing chlorine, fluorine or bromine, usually have high GWPs.

It should be noted that the 6th IPCC Assessment Report, on average, lists higher GWPs for CFCs, HCFCs and HFCs than the 5th Assessment Report. Also, GWPs are only calculated for the specific substance in question without regard for any other GHG that may be produced in the process of manufacturing or destroying the specific substance along their lifecycles.

Apart from increasing global temperature, and due to their long atmospheric lifetimes, halogenated gases, mostly containing chlorine or bromine, can reach the stratosphere, the upper part of the atmosphere. Here, they can react with ice crystals in polar stratospheric clouds, releasing chlorine and bromine radicals that, energised by sunlight, can break down ozone (O_3) into oxygen, (O_2), destroying the protective ozone layer and leading to a seasonal ozone hole, mainly over the southern hemisphere. Analogously to the GWP, the magnitude of ozone-depletion of a gas is expressed as ODP and calculated based on the effect of the reference molecule trichlorofluoromethane (CFC-11), which has an ODP of 1. For example, HCFC-22, a potent GHG with a GWP of 1 760, has an ODP of 0.55, that is, 1 kg of HCFC-22 has the same effect on the ozone layer as 0.55 kg of CFC-11.

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[16] http://agage2.eas.gatech.edu/data_archive/data_figures/monthly/pdf/HFC-23_mm.pdf

[17] Gigagram (109 grams)

4.2.1.2 Polymerisation of polytetrafluoroethylene

PTFE can be polymerised from TFE by different methods. The most frequently employed method in large-scale industrial facilities is conventional radical polymerisation (Puts et al., 2019). The PTFE polymer is grown by successively adding TFE monomer blocks to the polymer chain. In industrial processes, dispersion or emulsion polymerisation in an aqueous medium are most frequently employed, which necessitates adding different substances to the reaction mix. For example, less than 0.6 mol % of perfluoromethyl vinyl ether (PMVE) is frequently added to impart specific mechanical properties (Puts et al., 2019). Many other substances are added in the polymerisation process that will be briefly introduced.

4.2.1.2.1 Initiators

To initiate the polymerisation reaction, certain chemicals are added to generate free radicals. Many different initiators can be used, which will influence the mechanical properties and the stability of the polymer towards degradation. Degradation typically occurs at the residual radical sites or end-groups in the PTFE, and through radical reactions which may be initiated upon heating, oxidative or other kinds of stress (Puts et al., 2019). From the group of inorganic initiators, persulfates, and especially ammonium persulfate, are the preferred choice. Most commonly, however, organic peroxides are added as initiators. Also, fluorinated initiators, mainly from the group of oligo (hexafluoropropylene oxide) peroxides and bis(pentafluoropropionyl) peroxide, are employed by industry. A selection of initiators is presented in Table A.4.

4.2.1.2.2 Solvents/carriers

Polymerisation of TFE needs an electron source that can be the solvent or better, carrier, the choice of which is, among other aspects, linked to the used initiator (Puts et al., 2019). Preferred solvents are water, PFCs, as well as CFCs, HCFCs and HFCs. Table A.5 gives an overview of possible halogenated solvents/carriers.

4.2.1.2.3 Dispersants

Dispersing agents are needed in emulsion polymerisation to produce fine PTFE powder (Puts et al., 2019). Historically, perfluorinated monocarboxylic acid, including their salts, have been the most frequently employed dispersants, for example perfluorooctanoic acid (PFOA). Table A.6 gives an overview of some dispersants (surfactants).

Perfluorooctanoic acid (PFOA), or its salt ammonium pentadecafluorooctanoate (APFO), have been the dispersant of choice for the polymerisation of TFEs since the 1950s. Replacements need to contain fluorinated moieties in order to be compatible with TFE in the polymerisation step. Commercialised fluorinated alternatives are, for example, per- and polyfluorinated polyethers (PFPEs), including ADONA and GenX (see Table A.6). Many other suspected perfluoroether carboxylic acids (PFECA) are in use, causing harmful emissions to the environment.

4.2.1.2.4 Chain transfer agents

Chain transfer agents (CTAs) cause problems in the reaction since they terminate the polymer chain but they are sometimes needed because without them macroradicals can be trapped in the polymer matrix, resulting in lower thermal stability (Puts et al., 2019). Further, they prevent the product from sticking to the walls. For this purpose, substances such as H_2, hydrocarbons, certain HFCs (listed in Table A.7), such as HFC-23, or citric acid are added as chain transfer agents.

4.3 Polyvinylidene fluoride

Polyvinylidene fluoride (PVDF) (Figure 4.3) is the fastest growing fluorinated polymer worldwide and is used as insulating material in electrical and electronic applications and as a coating in the construction industry.

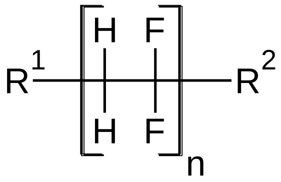


Figure 4.3. PVDF.

Note: R^1 and R^2 denote two end groups of the polymer which may be the same or different
Source: Own illustration

PVDF is synthesised by polymerisation of vinylidene fluoride (VDF). Three main methods for synthesising VDF are described by (Siegemund et al., 2000):

1. Dechlorination of 1,2-dichloro-1,1-difluoroethane (HCFC-132b), an ODS and a potent GHG with a GWP 320, at 500 °C in the presence of a metal catalyst, for example nickel (Ni) or zinc (Zn);
2. Dehydrochlorination of 1-chloro-1,1-difluoroethane (HCFC-142b), an ODS and a very potent GHG with a GWP 1 980, at 700–900 °C; and, less often mentioned,
3. Dehydrofluorination of 1,1,1-trifluoroethane (HFC-143a), a very potent GHG with a GWP of 4 800, at 1 100–1 300 °C.

The route using 1,2-dichloro-1,1-difluoroethane (HCFC-132b) is shown in Figure 4.4. 1,2-dichloro-1,1-difluoroethane itself is synthesised by fluorination of trichloroethylene (TCE, Tri) (Domininghaus, 1998). Today, most TCE is synthesised from 1,2-dichloroethane (DCE, $ClCH_2$-CH_2Cl, CAS no. 107-06-2), a process that also yields tetrachloroethylene (perchloroethylene, PCE, CCl_2=CCl_2, CAS no. 127-18-4) (Weissermel and Arpe, 1988). 1,2-dichloroethane itself is synthesised from ethylene (H_2C=CH_2, CAS no. 74-85-1) (Weissermel and Arpe, 1988).

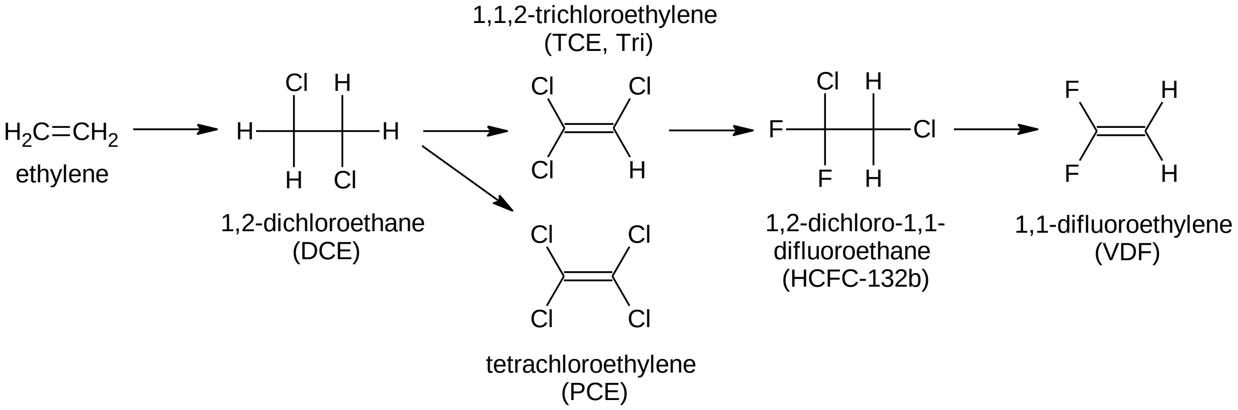


Figure 4.4. Substances involved in the synthesis of VDF.

Source: Own illustration

Relevant substances involved in the synthesis of VDF and PVDF, together with their GWPs and ODPs are listed in Table A.8.

VDF is also marketed as a copolymer with HFP, which is synthesised by pyrolysis of HCFC-22, in which TFE and perfluorocyclobutane (PFC-318) are by-produced (Halliwell, 1967).

Applying similar assumptions as for PTFE and APFO-technologies, perfluorinated carboxylic acids (PFCA) emissions caused during the production of PVDF can be estimated, resulting in global emissions of 17.1 tonnes per year, of which 3.3 tonnes per year are from Europe.

4.4 Per- and polyfluorinated polyethers

Per- and polyfluorinated polyethers (PFPEs), also called perfluoroalkylether (PFAE) or perfluoropolyalkylether (PFPAE), are a diverse group of liquid to pasty fluorinated polymers. Apart from their use as lubricants, they are also contained as emollients in skin-care products and other cosmetics. Most frequently, the subgroup of perfluoropolymethylisopropyl ethers (PFPMIEs) are mentioned as representatives of the PFPE group (Figure 4.5). PFPMIEs are sold under brand names such as Galden or Fluorinert for low molecular mass perfluoroethers, and Krytox or Fomblin for high molecular mass ones (Siegemund et al., 2000). Low molecular mass PFPMIEs are prepared by the electrochemical fluorination of aliphatic (not aromatic) ethers, alcohols or carboxylic acids, such as isomers of $C_6F_{12}O$, C_7F_4O or $C_8F_{16}O$, or by fluorination of partially fluorinated or nonfluorinated ethers (Siegemund et al., 2000). High molecular mass PFPMIEs, on the other hand, are synthesised from hexafluoropropylene oxide (HFPO, 2,2,3-trifluoro-3-(trifluoromethyl)oxirane, CAS no. 428-59-1) or from perfluorinated olefins, such as TFE or HFP. The latter is also the feedstock for hexafluoropropylene oxide (HFPO) (Oppenheimer et al., 2007).

The PFPMIE demnum ($F-(CF_2CF_2CF_2O)_n-CF_2CF_3$) can be synthesised from tetrafluorooxetane (2,2,3,3-tetrafluorooxetane, $C_3H_2F_4O$, CAS no. 765-63-9) (Howell et al., 2004).

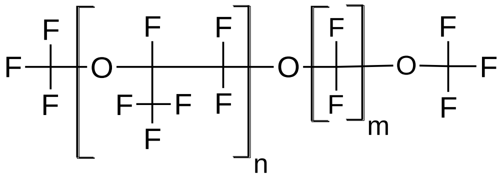


Figure 4.5. Structure of PFPMIE with the repeating monomer units n and m.

Source: Own illustration

Appendix 8.A in the Intergovernmental Panel on Climate Change's *Climate Change 2013: The Physical Science Basis* (IPCC 2013) lists one PFPMIE with the formula $CF_3OCF(CF_3)CF_2OCF_2OCF_3$ (Figure 4.5 with n = 1 and m = 1) with a GWP of 8 070. Based on the atmospheric lifetime and radiative forcing of $CF_3OCF(CF_3)CF_2OCF_2OCF_3$, Young et al. (2006) derived a GWP of 1.95 times that of trichlorofluoromethane (CFC-11, CCl_3F), which would amount to 9 535, given a GWP for CFC-11 of 4 890.

4.5 Perfluorinated ethylene-propylene copolymers

Perfluorinated ethylene-propylene (FEP) is a copolymer of TFE and HFP. It retains most of the desirable characteristics of (PTFE) but with a melt viscosity low enough for conventional melt processing. The introduction of HFP lowers the melting point of PTFE from 327 °C to about 260 °C. As a thermoplastic, it can be processed by extrusion and compression, injection and blow moulding. Films can be heat bonded and sealed, vacuum formed, and laminated to various substrates. Aqueous and nonaqueous dispersion polymerisations are the most convenient routes of producing these copolymers. The polymerisation conditions are similar to those of TFE homopolymer dispersion polymerisation (Gangal and Brothers, 2010). Dispersion is used as a coating for glass fabric, chemical barriers and wire insulating tapes; as adhesive coatings for bonding seals and bearings of PTFE to metallic and non-metallic components; and as antifriction or antistick coatings for metals. The fusion of FEP to provide a continuous film depends on a time-temperature relationship; 1 minute at 400 °C or 40 minutes at 290 °C is sufficient to achieve good fusion (Gangal and Brothers, 2010).

4.6 Fluorinated sidechain polymers

Sidechain fluorinated polymers consist of a carbon chain backbone not containing any fluorine, with attached polyfluorinated and perfluorinated side chains (Figure 4.6). Some examples are fluorinated acrylates, urethanes and oxetanes. During the lifetime of these fluorinated polymers, unreacted side chains can be released – mostly telomeric PFAS as, for example, fluorotelomer alcohols (FTOHs)– or these sidechains can degrade and release ionic PFAS (Figure 4.7). Perfluorinated carboxylic acids are the most common breakdown product (Dinglasan-Panlilio and Mabury, 2006). In 2006, polymers made up approximately 80% of the reported production in the fluorotelomer market (Dinglasan-Panlilio and Mabury, 2006). In the same paper, unbound alcohols from the monomer phase of the process were found as residuals from the methacrylate monomer, indicating either incomplete synthesis or poor purification at the monomer step of the manufacturing process. Due to the high volatility of the telomeric PFAS used as sidechains, this group of fluorinated polymers can act as a substantial contribution to the atmospheric burden of volatile PFAS and subsequently as an environmental pollutant with ionic PFAS as a final degradation product.

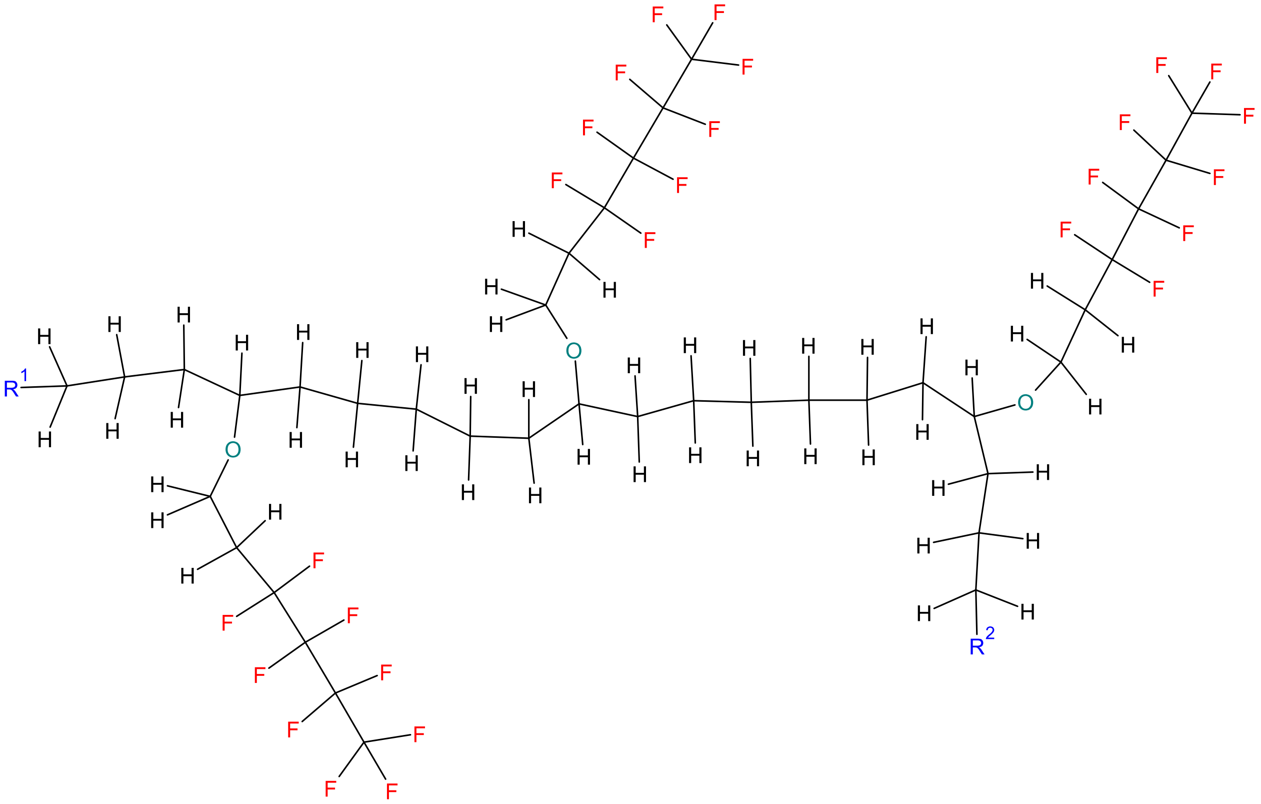


Figure 4.6. Molecular structure of sidechain fluorinated polymers.

Note: R^1 and R^2 denote two end groups of the polymer which may be the same or different
Source: Own illustration

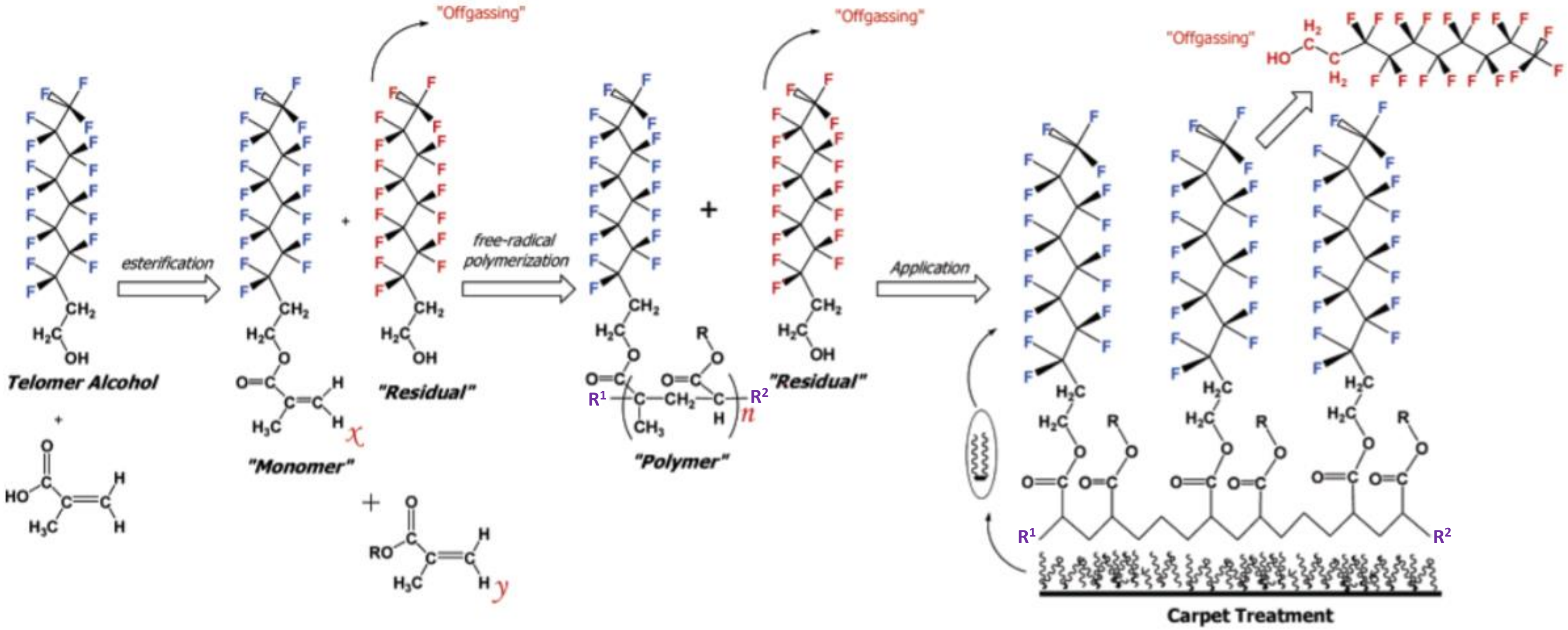


Figure 4.7. Stylized schematic of postulated steps leading to the production of telomer-based polymers using 8:2 FTOH as an example.

Note: The potential source of unreacted telomer alcohols is depicted from the reaction producing the monomer and leading to its point of release to the environment from polymeric materials if left unpurified. Polymeric materials produced will have a mixture of varying chain lengths of perfluorinated and hydrocarbon chains as well as varying carbon backbones depending on reactants used.

R^1 and R^2 denote two end groups of the polymer which may be the same or different

Source: Modified from Dinglasan-Panlilio and Mabury,(2006). Copyright 2006 American Chemical Society.

4.7 Feedstock and processing aids used in the production of fluorinated polymers and the by-products generated

4.7.1 Fluorinated chemicals in the synthesis of fluorinated polymers

Different chemicals are used as feedstock to make fluorinated homo- or co-polymers; typically, all are fluorinated and chlorinated organics. For the fluorinated sidechain polymers, hydrocarbon chemicals are used to make the hydrocarbon backbone, for instance an acrylic polymer, to which fluorinated sidechains are attached. The fluorinated sidechains may be linked to the polymer backbone through heteroatoms such as oxygen, sulphur or amino groups, in the form of esters, thioesters, ethers, amines, imine, etc., which will make the fluorinated sidechains more or less amenable to degradation. Fluorotelomer alcohols have been used as sidechains. The chemicals used to produce these fluorinated sidechains are described elsewhere. Information on GWP and ODP values of substances linked to fluorinated polymer production are provided in Annex 2.

4.7.2 Fluorinated production aids involved in the synthesis of fluorinated polymers

In the majority of cases, fluorinated polymer production requires not only fluorine-containing feedstock chemicals but also fluorinated production aids for polymers, as defined by the Plastics regulation for food-contact materials EU 10/2011, such as dispersion aids and polymerisation initiators. Production of such fluorinated production aids can also lead to emissions of a large number of poly- and perfluorinated by-products, both highly volatile and water soluble (Hopkins et al., 2018).

Secondly, the fluorinated polymers, such as PTFE, are themselves processed at high temperatures of 340–400 °C, using up to 0.5% w/w of perfluoro- and polyfluoro-emulsifiers and dispersing agents including ADONA, GenX and other PFOA replacements (Table A 6) (Gomis et al., 2015). In general, the use of salts of PFECA substances with 4−9 per- or polyfluorinated carbons and 1−3 ether bonds – Chemours products GenX (CAS no. 62037−80−3), ADONA (CAS no. 958445−44−8) and products from Asahi (CAS no. 908020−52−0) and Solvay (CAS no. 329238−24−6) are mostly reported (Song et al., 2018). Their molecular structures often contain perfluorinated alkyl chains no longer than four fluorinated carbons. Fluorinated sidechains or ether linkages interrupt the carbon chains and fluorine is replaced with chlorine atoms at the end of the perfluoroether chain. Though heteroatoms can increase degradability in some cases, ether and thioether links tend to be very stable towards degradation and therefore do not substantially decrease the persistency (Krafft and Riess, 2015). The bioaccumulation of the fluorinated emulsifier may also correspond to the long chain PFAS according to modelling. The inclusion of Cl will mean that the PFAS evade restrictions such as being precursors of specific chemicals such as PFOS, where one F has been replaced by Cl (Washington et al., 2020). Their fluorinated degradation products may however still be persistent. As one consequence of the modified molecular design, higher emissions to the atmosphere can be expected, because the volatility of the replacement chemicals, perfluoro triether carboxylic acids (PFTECAs), is higher than that of PFOA, and as seen by their higher air-water partition coefficient (K_{AW}) values (Crookes and Fisk, 2018; Gomis et al., 2015), PFTECAs show lower partitioning into water, i.e., they are less mobile. Calculation of long-range transport potentials (LRTP) by Gomis et al. (2015) estimated a similar overall persistence (P_{ov}) of the PFOA replacements of 1 038 days (GenX, PFTECA), and conclude that even though PFECAs and polyfluoroalkyl ether sulfonic acids (PFESAs) which are alternatives to PFOA and PFOS, respectively, contain some structural differences, their physicochemical properties are not significantly changed compared to those of their predecessors.

Further, several additional production aid candidates have been reported in wastewater or river water downstream of plants manufacturing fluorinated polymers including monochlorine-substituted perfluoroalkyl carboxylic acids (Cl-PFCAs), monohydrogen-substituted PFCAs (H-PFCAs), hydrogen-substituted PFCAs (x H-PFCAs), monoether PFECA substances, and polyether PFECA substances as well as polyether sulfonic acids (Gebbink et al., 2017; Newton et al., 2017; Sun et al., 2016; Liu et al., 2015; Shi et al., 2015; Strynar et al., 2015). Other compounds are suspected to be by-products emitted from fluoromonomer and Nafion production. For example, the C3 Perfluoro(2-methyl-3-oxahexanoyl) fluoride (also called a HFPO dimer, acid fluoride) is a useful HFPO intermediate typically used in the synthesis of fluoromonomers, fluorinated polymers and to add fluorine functionality to a variety of organic precursors (Hopkins et al., 2018).

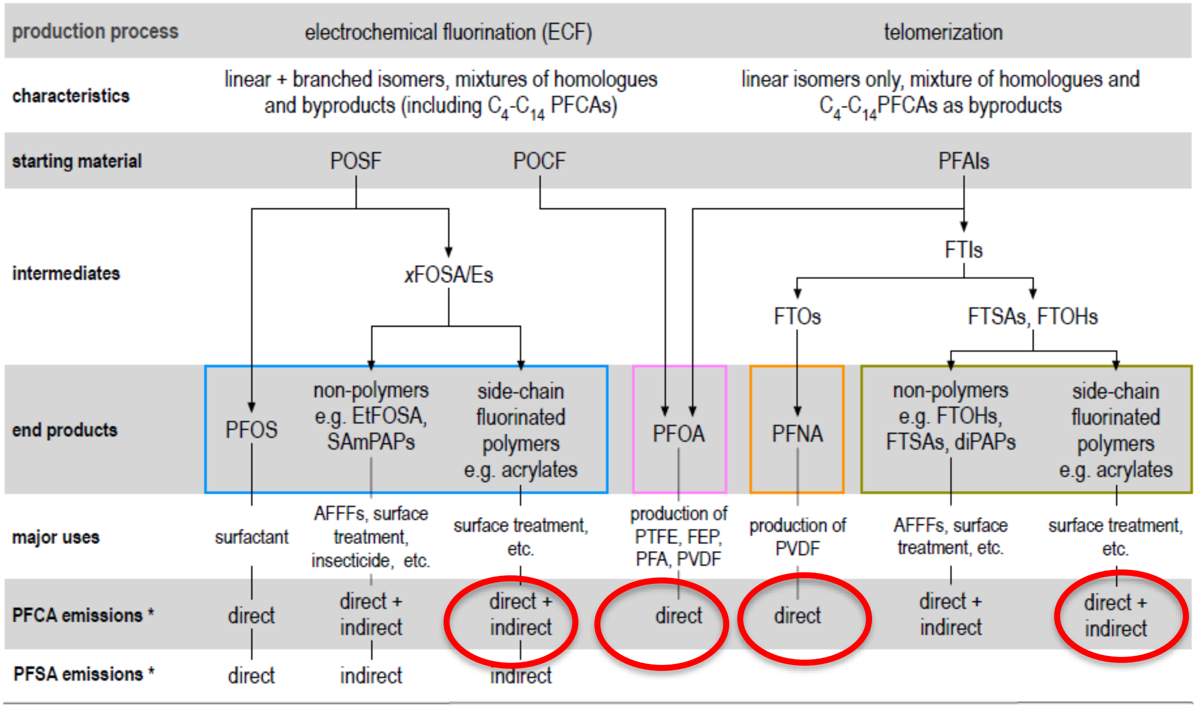
4.8 Emissions by fluorinated polymer production

As described in Chapter 4.7, transformation and degradation products may be formed from the polymerisation aids used in the fluorinated polymer production. Emitted PFAS may be neutral or ionic. In addition to the examples given below, there are several pollution cases reported around the globe, including the discovery of new pollutants around the well-known site of the 3M factory in Belgium.

No information on the emission of neutral, small-sized PFAS molecules was available aside that mentioned above on their potential formation during the production process and what is reported by Mühle et al. (2019). These authors report that several facilities in Belgium, France, Italy, the Netherlands and the United Kingdom, which likely produce PTFE, are co-located with identified perfluorocyclobutane (c-C_4F_8) emission hot spots (0.026 ± 0.013 Gg per year). Potentially, both GHG and ODS can also be formed and subsequently emitted if no suitable and efficient removal measures are applied.

For emissions of ionic PFAS, however, model estimates are available in the literature. To estimate the magnitude of ongoing ionic PFAS emissions during PTFE production, PFCA emission estimates from the lifecycle of PFOA-based products published by Wang et al., (2014) were used.

The available modelled emission data covering the complete lifecycle of PFOA-based products, enable the extraction of the emission estimates for PFCAs during the production of a number of fluorinated polymers (PFOA-based PTFE, FEP and PFA) (Figure 4.8).



* direct = PFCAs/PFSAs are emitted as ingredients and/or byproducts (impurities); indirect = PFCAs/PFSAs are emitted as degradation products of precursors

☐ commercial POSF-based derivatives ☐ commercial PFOA ☐ commercial PFNA ☐ commercial fluorotelomer-based derivatives

PFCA = perfluoroalkyl carboxylic acid; PFSA = perfluoroalkane sulfonic acid; POSF = perfluorooctane sulfonyl fluoride; POCF = perfluorooctane carbonyl fluoride; xFOSA/Es = (N-methyl/etheyl) perfluorooctane sulfonamide / sulfonamidoethanol; SAmPAPs = EtFOSE-based diphosphate; PFAI = perfluoroalkyl iodide; FTI = fluorotelomer iodide; FTO = fluorotelomer olefins; FTSA = fluorotelomer sulfonic acid; FTOH = fluorotelomer alcohol; PFOS = perfluorooctane sulfonic acid; PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; diPAP = fluorotelomer diphosphate; AFFF = aqueous film-forming foam; PTFE = polytetrafluoroethylene; FEP = perfluorinated ethylene-propylene copolymers; PFA = perfluoroalkoxyl polymers; PVDF = polyvinylidene fluoride

Figure 4.8. Illustration of used data for emission estimation of ionic PFAS production aids during fluorinated polymer production.

Note: PFCA emissions can be explained by four processes marked with red circles: direct and indirect formation during the production of sidechain fluorinated polymers, direct emissions during the production of PTFE and other fluorinated polymers
Sources: OECD (2018); modified from Wang et al. (2014)

Wang et al. (2014) expected that after 2015 there would be no fluorinated polymer production using APFO technology in western Europe. To cover the worst-case scenario for ionic PFAS emissions, 2015 data for the 'higher' scenario in Wang et al. (2014) were used to estimate possible emissions of PFCA substitutes caused by the ongoing global PTFE production. Unsurprisingly, the global PFAS emissions caused by fluorinated polymer production of PTFE, FEP and PFA constitute 609 t/year, about 97% of the estimated total emissions of 627 t/year estimated for all fluorinated polymers. Since European fluorinated polymer production represents about 20% of the global total, the resulting PFAS emissions (of PFOA and PFNA substitutes) can be estimated to be about 120 t/year, when assuming similar usage and emissions by the substituted PFAS on the basis of the similarities between PFOA and replacement chemicals, and assumed limited changes in emissions control during fluorinated polymer manufacture. A different composition of the emissions is, however, expected with fewer PFCAs containing a perfluorinated chain length of eight carbon atoms (C8) and a longer and rather broader variety of branched, ether-linked or chlorine containing replacement PFAS. Due to the broad variety of the composition of emissions, a differing environmental distribution of emitted PFAS to the aquatic phase, the atmosphere and/or the terrestrial sphere is also expected. However, besides GenX, no emission volumes of PFOA replacements are available, either in the shape of measured field data or modelled emission data.

On the other hand, Adona and GenX, which have a similar polarity but a smaller molecular size than PFOA, display slightly more hydrophilic behaviour. Conversely, larger molecules, such as PFTECAs, have a higher air-water partition coefficient (K_{AW}) than PFOA, supporting increased atmospheric distribution.

Adding even more complexity to PFAS used as fluorinated polymer production aids is the manufacture of the chemicals themselves. Hopkins et al. (2018) also report that atmospheric emissions of the GenX precursor, a tricarbon (C_3) dimer acid fluoride (CAS no. 2062-98-8), possibly causes elevated aquatic levels of hexafluoropropylene oxide–dimer acid (HFPO-DA/GenX) in lakes and rivers (Hopkins et al., 2018).

A recent study reported that only 50% of the fluorinated polymer processing aid GenX is captured from the production waste streams of the Chemours plant in Dordrecht, the Netherlands (Gebbink and van Leeuwen, 2020). Emissions of PFOA, PFNA and synthesis by-products from other fluorinated polymer production sites have been thoroughly documented in China and the United States over the years, and probably in Europe as well in the past (Fang et al., 2020; Panikkar et al., 2019; Chen et al., 2018; Jin et al., 2015; Shi et al., 2015; Strynar et al., 2015). The emissions have been shown to lead to widespread environmental contamination of air, soil, water and food (Guillette et al., 2020; Pellizzaro et al., 2018; Valsecchi et al., 2015), but whether these emissions are still ongoing in the EU is unclear. However, the emissions of c-C_4F_8 linked with TFE/HFP/PTFE/FEP production facilities show the potential of other emissions of both neutral and ionic PFAS from such facilities (Mühle, et al., 2019).

Due to the high volatility of most of the neutral PFAS, the atmosphere is expected to act as the target sink for the majority of these compounds. Telomeric PFAS as FTOHs, will eventually degrade to form the environmentally stable PFCAs while neutral sulphonamides might degrade to PFSAs, further distributing into the terrestrial and aquatic global spheres and adding to the overall global ionic PFAS burden as indirect sources. On top of this, direct emissions of ionic PFAS are also still happening as outlined above, possibly more so than through indirect sources, causing a complex mix of final degradation products including

Box 4.2 Impact on soil and water – case example of emissions

In several studies from the Netherlands (Gebbink and van Leeuwen, 2020; Brandsma et al., 2019), France (Bach, 2017), China (Song et al., 2018; Shi et al., 2015b), the United States (Hopkins et al., 2018), and Japan (Shiwaku et al., 2016) water samples and in some cases in soil, grass and leaf samples were collected at different distances from fluoropolymer manufacturing plants for measurement of PFAS or fluorinated substances. Vegetables used for human consumption and grown close to PFAS production facilities in China contained high concentrations of short chained PFCAs, proving an efficient uptake of water soluble PFAS in plants (Zhang et al., 2017). In most cases, the highest PFAS concentrations were detected near the manufacturing plants supporting the hypothesis that plants are primary sources for PFAS emitted in the surroundings.

Emissions to the environment from a Dutch Chemours manufacturing plant have been in analysed (Gebbink and van Leeuwen, 2020; Gebbink et al., 2017) based on information in public databases. Key figures from the articles include the following.

- In a Dutch manufacturing plant producing PTFE, and FEP, PFOA was used until 2012 as a polymerisation aid. Since 2013, it has been substituted by GenX, an ammonium salt of 2,3,3,3-tetrafluoro-2-(heptafluoroporoxy)propanoic acid.
- In 2012, emissions of PFOA to the air were estimated to 134 kg, considerably less than in 1995 when emissions peaked at 6 800 kg. The cumulative amount emitted to air was calculated to be around 36 tonnes based on years for which data were available. Emissions to water, however, have not been reported.
- It has been estimated, based on mass balance calculation, that 55% of the GenX used was incinerated and 40% recycled. The emissions to water and air were approximately 4% and 1% respectively. Based on GenX usage of 50 tonnes in 2017, approximately 2 000 kg and 500 kg were emitted to water and air, respectively.
- Wastewater directed to a treatment plant contained, on average, 0.15 micrograms per litre (µg/l) PFOA and 2.3 µg/l GenX (2017). Due to the higher water solubility of GenX than PFOA, the removal of GenX is less efficient in the municipal water treatment plant.
- Generally, the detected concentrations of PFOA and GenX in surface and groundwater samples were low, with concentrations decreasing further from the plant.
- GenX and PFOA have been detected in leaves and grass within 3 kilometres northeast of the plant with concentrations decreasing with distance. It was advised not to consume vegetables grown within a radius of 1 kilometre of the plant (Brandsmaa, 2019).
- The tolerable daily intake for PFOA and GenX was only exceeded in the maximum exposure scenario based on year-round consumption of local vegetables and exposure to drinking water and air.

PFCAs and PFSAs, intermediates and precursor compounds polluting the environment. Surface and drinking water, soil and agricultural produce have been reported to exhibit major contamination with PFAS in the vicinity of manufacturing sites in China, Europe and the United States (Box 4.2).

According to Li et al. (2017), 99% of C_4 to C_7 PFCAs and to a slightly lower extent C_8 to C_{12} PFCAs will distribute to the hydrosphere, while C_{13} and longer chained PFCAs will increasingly be adsorbed by sediments and soil (Li et al., 2017).

In general, a broad contamination of the surrounding environment, spreading in both the terrestrial and the aquatic spheres, has been documented for a range of fluorinated polymer production sites and is to be expected for all fluorinated polymer manufacturing and fabrication sites. Harmful impacts on wildlife and human health are to be expected, especially in terms of food and drinking-water safety.

4.9 Manufacturing/conversion of fluorinated polymers into final products

In addition to production sites, the manufacturing of fluorinated polymers, for example by conversion into final products, sintering or their application may also cause environmental contamination by, for example, PFAS. Information provided by companies to the United States Food and Drug Administration shows that some types of fluorinated sidechain acrylate polymers may only be 88–91% retained when applied to food-contact paper and board (EDF, 2018; Neltner and Maffini, 2018). Some is released to water and some retained in sludge which should be landfilled or incinerated – in the United States 80% is landfilled and 20% incinerated. No such assessment is available in Europe, even though there are known occurrences of accidental releases in, for example, Germany and Italy (Goldenman et al., 2019; Ministerium für Umwelt, Klima und Energiewirtschaft Baden-Württemberg, 2018).

As an additional step, fluorinated polymers can also be applied as coatings to other surfaces, such as cooking utensils, by baking on and/or sintering at high temperatures of up to 420 °C for up to 10 minutes. Many materials and articles made using these coatings are intended for repeated use in contact with all types of foodstuffs. The conditions of use include short-time contact at temperatures up to around 100 °C for food processing equipment and food contact articles. Contact conditions for high temperature application coatings include 230 °C for 1–2 hours and may even reach 250 °C for a short time (EFSA, 2010). Emissions during the coating of products with fluorinated polymers can be cleaned by a two-stage air pollution control device used to collect the submicron particulate matter released during the sintering of the PTFE. The fibre-bed diffusion filters are designed to collect both solid and liquid particulates.

During the manufacturing and conversion, PFAS processing aids, impurities and degradation products may be released. For instance, processing aids, such as PFTECA (CAS no. 329238-24-6), are volatile and completely evaporate at 190 °C. PFTECA is soluble in water and in organic solvents but is expected to be stable to heat and not to react with food constituents. Considering the type of application, such as non-stick coatings on cookware, these coatings are processed at very high temperatures, above 300 °C. Under such conditions, any residues of the volatile substance and other migratable impurities will be removed efficiently (EFSA, 2010). To avoid atmospheric and other emissions, however, closed systems are required for the manufacturing of fluorinated polymers.

4.10 Knowledge gaps

- Identity and usage of fluorine-containing fluorinated polymer production aids.
- Emission data of fluorine-containing fluorinated polymer production aids (PFOA and PFNA alternatives) and other emitted PFAS.
- Emission data of PFAS emissions during production of fluorine-containing fluorinated polymer production aids.
- Physical-chemical properties of PFOA and PFNA alternatives including bioaccumulation potential and persistency.
- Identity, usage and physical-chemical properties of poly- and perfluorinated sidechains used in fluorinated polymers.

5 Use phase: uses and potential emissions from pollutants

Main author: Elina Pohjalainen
Contributors: Dorte Herzke (Microplastics) and Elina Yli-Rantala (Degradation to micropowders)

Key messages

- Fluorinated polymers are used in a diverse range of applications due to their unique properties such as the ability to repel water/dirt and chemical stability. The transport, chemical and power sectors are the largest users of fluorinated polymers.
- Typically, fluorinated polymers are only a part of component or in coatings. Thus, exposure is highly application specific. Impacts of their use phase are not deeply analysed in this report
- The use phase of fluorinated polymers may lead to PFAS entering the environment:
  - degradation of materials in use: for example, the wearing and tearing of durable, water-repellent (DWR) textiles due to ultraviolet (UV) radiation, high temperatures and humidity;
  - overheating of PTFE kitchenware; etc.
- Direct human exposure during use phase:
  - dietary intake as a result of leaching of substances from food-contact materials into food;
  - inhalation as a result of indoor dust impacted by carpets, furniture, textiles and other surface treated materials, heating or spaying products containing fluorinated polymers;
  - dermal contact from textiles and cosmetics/personal care products;
  - medical utensils such as implants or ophthalmic uses.
- Microplastics:
  - released either directly into the environment due to intentional use in products, or indirectly after the physical degradation of macro-sized fluorinated polymers in products or mismanaged waste;
  - microplastics end up in wastewater treatment plants and are not recovered. For example, fibres including fluorinated polymers are released from textiles during washing, cosmetics and personal care products when they are washed off during/after use, etc.

5.1 General remarks on the use of fluorinated polymers in different applications

The use of fluorinated polymers is widespread. The main industrial sectors using fluorinated polymers and their market shares are briefly discussed in Sections 2.2 and 2.3. The transport, chemical and power sectors are the largest users of fluorinated polymers, accounting for approximately two-thirds of their sales in Europe. In the automotive industry, for example, fluorinated polymers make up approximately 350 grams per car and are used in items such as seals, gaskets and transmission components, as well as cables and hoses (Améduri, 2020). Consumer products such as kitchenware, electronics and textiles are the next largest users of fluorinated polymers. An interesting application of fluorinated polymers is in the renewable energy sector where they are used in photovoltaic panels, fuel cells and batteries, all increasingly important applications in the transition to a low carbon economy. Different applications for various fluorinated polymers are described in, for example, Puts et al. (2019), Améduri, (2018; 2020), Dams and Hintzer (2017) and Gardiner (2015).

Potential impacts of fluorinated polymers from the use phase are not the main focus in this report and impacts from all potential uses are not thoroughly reviewed. Instead in the following sections, three example cases of fluorinated polymer use are briefly presented, with an emphasis on PFAS releases to the environment as well as human exposure during use phase. The use and pollution from (PTFE) microplastics is also discussed in Sections 5.3 and 5.4. More information on risks to human health and environment from PFAS can be found in, for example, a recent EEA briefing (EEA, 2019). Different pathways of human exposure to PFAS and their health effects are reviewed, for example, in Sunderland et al. (2019). In general, direct human exposure to specific PFAS due to the use of products that contain them can be quickly phased out by shifts in product compositions, whereas much longer timescales must be expected for the amelioration of their accumulation in groundwater and the wider environment.

5.2 Fluorinated polymers in consumer products

5.2.1 Textiles – outdoor clothing

Fluorinated polymers and sidechain fluorinated polymers are used in the textile industry because of their ability to create water-, oil- and dirt-repellent surfaces (Kotthoff et al., 2015). An example of this type of application is outdoor clothing made of multiple layers and different types of polymers. These fabrics typically include a membrane made of extended PTFE, which is included in Gore-Tex and similar products. This multiporous layer has high permeability for water vapour but low permeability for water molecules (Ebnesajjad, 2017). In addition, sidechain fluorinated polymers are used as finishes in the outer layer of fabrics to create water, oil and stain resistance. These finishes, also called DWR treatment, are typically composed of fluoroalkyl acrylates and (meth)acrylates (Knepper et al., 2014).

Outdoor clothing and other DWR treated textiles are a potential source of PFAS into the environment (Holmquist et al., 2016; Knepper et al., 2014). Different routes for environmental contamination of (fluorinated) DWR substances are presented in Figure 5.1. High levels of volatile FTOHs, which are emitted to the air, have been detected in outdoor clothing (Knepper et al., 2014; Herzke et al., 2012). Another route for PFAS to enter the environment is through washing, for example, the release of fibres coated with fluorotelomer-based polymers have been measured during washing (Schellenberger et al., 2019b; Knepper et al., 2014). The loss of PFAS from textiles can also occur in the use phase due to wearing and tearing. Ultraviolet radiation, high temperatures and humidity have been detected increasing perfluoroalkyl acid (PFAA) concentrations in textiles due to degradation of DWR polymers such as FTOHs (van der Veen et al., 2020; Gremmel et al., 2016).

The ability of outdoor clothing to repel water typically diminishes after continuous use and repeated washing cycles. Water repellency can be partly regained by using impregnating agents, but these are another potential source of human exposure to PFAS through the inhalation of sprays and their release to the environment. Fluorosilanes and FTOH substances have been detected in impregnating agents for textiles and footwear (Knepper et al., 2014; Noergaard, 2010). Several incidents have been reported in Europe where short-term exposure to impregnating agents containing, in most cases, fluorinated polymers have been associated with respiratory illness and other health problems (ECHA, 2017).

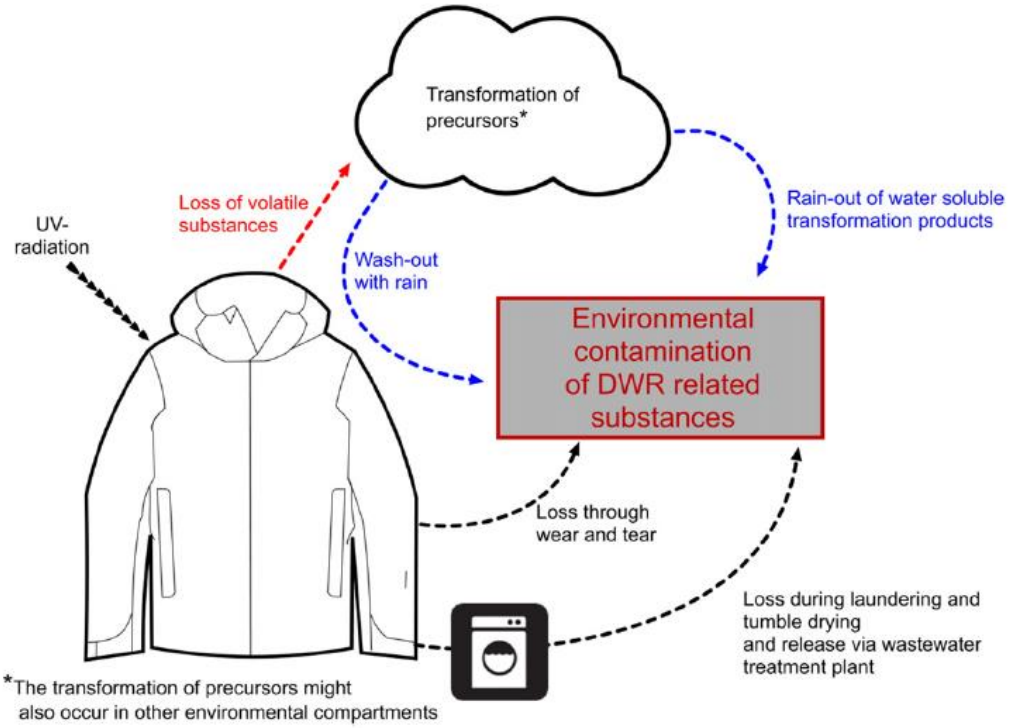


Figure 5.1. Possible mechanisms for loss of chemicals from DWR treated textiles during the use phase.

Source: Holmquist et al. (2016)

In recent years, there has been a trend for reducing the use of long-chain sidechain fluorinated polymers in textile finishes and other consumer products (18). Substitution alternatives include short-chain sidechain fluorinated polymers or even completely fluorine-free finishes. Concerns have been raised, however, due to persistence and lack of data on the health effects for short-chain PFAS (Cousins et al., 2019; OECD, 2013). Non-fluorinated DWR finishes might be a possibility for consumer products such as outdoor apparel as similar water-repellent properties can be achieved with non-fluorinated finishes (Hill et al., 2017). Non-fluorinated alternatives, however, do not perform as well as fluorinated ones in repelling oil (Schellenberger et al., 2019a; Holmquist et al., 2016) and might not be sufficient for use in, for example, occupational protective clothing (Cousins et al., 2019).

5.2.2 Food-contact materials

Food-contact materials (FCM) (19) cover a wide range of materials that may come into contact with food during its production, processing, storage, preparation and serving. Examples include food-production equipment and machinery, packaging and kitchen utensils such as non-stick forms and pans. Many of these use fluorinated polymers due to their ability to resist grease and water (Goldenman et al., 2019). Food-contact materials are regulated in the EU by the framework regulation 1935/2004 on materials and articles intended to come into contact with food (EU, 2004). The principle underlying this regulation is that “any material or article intended to come into contact directly or indirectly with food must be sufficiently inert to preclude substances from being transferred to food in quantities large enough to endanger human health or to bring about an unacceptable change in the composition of the food or a deterioration in its organoleptic properties” (20).

Non-stick PTFE coatings are used various kitchenware, for example, in frying pans and other utensils (Cousins et al., 2019), due to their high chemical and thermal stability as well as oil/water repelling properties. PTFE polymer coatings are considered to be of less concern than fluorinated substances in paper and cardboard packaging (21) due to the negligible release of PFAS during use (Bokkers et al., 2019). If, however, they overheat, PFCAs can be emitted from heated PTFE kitchenware surfaces. There have been incidents of Teflon flu, or polymer fume fever, a medical condition arising from inhaling of PTFE and its thermal degradation products during use (Greenberg and Vearrier, 2015). These cases have been largely the result of overheating PTFE-coated cooking equipment and the condition appears to be reversible but long-term health impacts have not been assessed. No information has been published regarding the specific compounds that lead to the flu-like symptoms. There seems to be no risk to human health at normal application temperatures related to PFCA emissions from PTFE coated kitchenware based on current tolerable daily intake (TDIs) according to some studies (Schlummer et al., 2015), whereas some earlier studies suggest that perfluoroalkyl carboxylates, originating from PFAS residues of the manufacturing process, might be released from non-stick frying pans even at normal cooking temperatures (Sinclair et al., 2007).

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[18] For example, Polartec has announced the elimination of PFAS in its DWR treatments https://www.polartec.com/news/polartec-announces-full-use-of-non-pfas-dwr-treatments

[19] https://ec.europa.eu/food/safety/chemical_safety/food_contact_materials_en

[20] Recently the EFSA Panel on Contaminants in the Food Chain published a draft scientific opinion on the risks to human health related to the presence of perfluoroalkyl substances in food (EFSA Panel on Contaminants in the Food Chain, 2020). The draft opinion assesses four PFAS, namely PFOA, PFNA, perfluorohexane sulfonic acid (PFHxS), and PFOS, and recommends a tolerable weekly intake (TWI) of 8 nanograms per kilogram (ng/kg) of body weight per week for the sum of PFOA, PFNA, PFHxS and PFOS.

[21] Various PFAS are used in paper and cardboard packaging materials, for example, plates, popcorn bags, pizza boxes, fast-food containers and baking papers (Bokkers et al., 2019). Nowadays, typically short-chain fluorotelomer based polymers are used in paper and cardboard food-packaging materials (Cousins et al., 2019). PFAS, that are not allowed in food-contact materials, have also been detected, possibly from impurities present in the substances used to treat paper and cardboard (Bokkers et al., 2019). PFAS in food-contact materials are a possible source for direct human exposure as PFAS can leach into food resulting in increased dietary exposure. Microwave popcorn consumption, for example, has been associated with increased PFAS serum concentrations, suggesting a leaching from the fluorinated coating of the food packaging (Susmann et al., 2019).

5.2.3 Cosmetics and personal care products

Fluorinated substances are used in various cosmetics and personal care products, such as hair products, foundations and powders in which they act as emulsifiers, antistatics, stabilisers, surfactants, film formers, viscosity regulators and solvents, amongst others, and their properties enable the production of water- and oil-repellent and weather resistant products (Brinch et al., 2018; Schultes et al., 2018). As a result, PFAS are found in cosmetic products as both ingredients and unintentional degradation products and impurities from the production of precursors used in some cosmetic products. Cosmetics products including polyfluoroalkyl phosphates (PAPs), for example, have been reported to contain high levels of PFCAs either as impurities or degradation products of PAPs (Fujii et al., 2013). Foundations and powders have particularly been shown to include perfluorinated carboxylic acids – perfluoroheptanoic acid and perfluorohexanoic acids –and polyfluoroalkyl phosphate esters (Schultes et al., 2018).

A recent risk assessment of cosmetic products on the Danish market showed that a wide variety of fluoroalkyl substances and other fluorinated compounds are used in cosmetics, and PTFE was most often found in different product types, followed by $C_{9\text{-}15}$ fluoroalcohol phosphates (Brinch et al., 2018). According to the Cosmetic Ingredient Review, for example, PTFE is used in concentrations of up to 13% in such leave-on products as mascara, up to 3% in face powders and at concentrations of up to 2.4% in such rinse-off products as hair bleaches in the United States (Johnson, 2018b). Brinch et al. (2018) measured PFAS concentrations in cosmetics products that contained certain fluorinated substances in the ingredients list and carried out a risk assessment. Although PFAS were found in almost all products in varying concentrations, it was concluded that measured PFCA concentrations did not pose a risk to consumers, although risk could not be completely ruled out if several products were used simultaneously (Brinch et al., 2018).

Direct human exposure to PFAS from cosmetics occurs through skin contact; studies suggest that, for example, PFOA penetrates human skin (Franko et al., 2012). Several studies reviewed in Sunderland et al. (2019) suggest, however, that the contribution of dermal contact to PFAS exposure is negligible when compared to dietary intake, household dust or drinking water contamination. In addition to direct human exposure, environmental contamination from cosmetics can occur through wastewater treatment plants, but the magnitude of such contamination is unknown (Goldenman et al., 2019). Pollution from fluorinated microplastics is briefly discussed in Section 5.4. Due to the risks of PFAS to health and the environment, several cosmetics brands have announced the phase out of PFAS in their products (Chemsec, 2018, 2019).

5.3 Polytetrafluoroethylene micropowders/microplastics

A large proportion of clean and unfilled PTFE scrap, which mainly originates from machining operations, is degraded thermally or by high-energy irradiation in order to radically reduce the molar mass of the material and finally create micropowder which is also a microplastic, typically with a particle sized 2–20 µm (Dams and Hintzer, 2017; Lakshmanan and Chakraborty, 2015). The degradation aims to reduce the length of the molecular chain to approximately 1% of the original (Pro-K, 2018)**.** Such micropowders can be used over a wide range of temperatures from -190 to 250 °C to provide non-stick properties, improved lubricity, wear resistance and reinforcement, and are thus mainly used as additives in coatings, lubricants, oils, printing inks and plastics (Dams and Hintzer, 2017; Lakshmanan and Chakraborty, 2015; Hintzer and Schwertfeger, 2014)**.** These are mainly dispersive uses of PTFE microplastics resulting in their release indoors and to the wider environment over time.

The thermal degradation of PTFE occurs at about 500 °C in ovens, kneaders or extruders in commercially established processes. The resulting low-molecular-weight PTFE materials are then milled to micropowders (Hintzer and Schwertfeger, 2014). The degradation by irradiation can be performed by electron beams, X-rays or gamma radiation. Degradation by irradiation is considered such a mature technique by the United States Food and Drug Administration that the generated micropowders may be used as additives in plastics that may come into repeated contact with food (Pro-K, 2018).

According to Lakshmanan and Chakraborty (2015), however, the use of electron beams induces the generation of gases such as hydrogen fluoride vapour which should be ventilated from processing areas. There is also evidence that other, long-chain PFAS are generated in the process (ECHA, 2015). The generation of hydrogen fluoride is much less notable in irradiation with gamma rays as the irradiation rate is several orders of magnitude less than that of electron beams. According to Makuuchi and Cheng (2011), however, the majority of irradiation is done using electron beams – Hintzer and Schwertfeger (2014) state that the degradation of PTFE by electron beam irradiation is “commercially widely used” by continuous processes.

Although micropowders were first developed as a means of disposing of the PTFE scrap, they are also produced from virgin materials (Ebnesajjad and Morgan, 2019; Lakshmanan and Chakraborty, 2015). The use of secondary PTFE feedstocks for the generation of micropowder is much more accepted by the cost-driven ink market than by other areas, as PTFE scrap is the cheapest source of micropowders. In addition, PTFE scrap often contains hydrocarbon contaminants, possibly causing colour defects, which can be less of a problem in coloured inks (Ebnesajjad and Morgan, 2019)**.**

In 2010, the market for irradiated micropowder was assumed to be approximately 7,000–10,000 tonnes per year, of which the largest share was consumed in the United States. Recycling by irradiation to micropowders has been shown to be a profitable means of adding value to PTFE scrap. About 60–70% of the total volume of the world’s PTFE micropowders was processed by companies providing toll irradiation services in the early 2010s, whereas the rest was processed by PTFE manufacturers themselves (Makuuchi and Cheng, 2011).

5.4 Microplastic pollutants from the use of fluorinated polymers

As for common polymers, micro-sized fluorinated polymers can be released either directly into the environment due to intentional use in products, or indirectly after physical degradation of macro-sized fluorinated polymers in products or mismanaged waste. One major intentional use application is in cosmetic products, both for leave-on and rinse-off products, as described in Section 5.2.3. It can be expected that a large part of fluorinated polymer-containing cosmetics will be removed from the face during daily cleaning routines, with a considerable share being washed down the drain, thereby entering wastewater effluent along with other microplastic particles. Most of today's wastewater treatment plants (WWTPs) are unable to remove large parts of the microplastic content from wastewater and, as a result, they are emitted to receiving aqueous bodies. PTFE microplastics use in coatings, lubricants, oils, printing inks and plastics, another potential source of fluorinated microplastic pollutants to the environment, is described in Section 5.3.

Little is known about the environmental processes that lead to the accelerated sinking and sedimentation of microplastics in aqueous environments. It is not understood, for example, whether or not biofouling occurs with fluorinated polymers, as it does with other microplastic types, due to the special chemical-physical properties of fluorinated polymer surfaces. It can, however, be assumed that the chemical inertness and general persistency of fluorinated polymers to environmental degradation and weathering will result in their even slower removal from the environment compared with other common microplastic particles.

6 End-of-life phase: Waste management and potential emissions of pollutants

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Key messages:

- Recycling:
  - A very low percentage of fluorinated polymers is recycled due to their use in a wide range of applications and their low share in end-of-life products.
  - Recycling activities are mainly concentrated on production scrap because large amounts of waste are generated during the production of fluorinated polymers. The majority of fluorinated polymers from end uses end up in landfill or are incinerated. The barriers to recycling are mostly technical.
- Thermal treatment:
  - Fluorinated polymers start degrading at relatively low temperatures (> 200 °C) and up to approximately 1 100 °C after which mineralisation to HF occurs. Which degradation products are formed depends on a number of physical and chemical conditions? Examples include volatile and ionic/water-soluble compounds such as TFA; volatile fluorinated gases some of which are GHG; oligomers; and nano- and micro-particles. Emissions of PFAS are likely to occur from uncontrolled thermal treatment below 1 100 °C that does not capture the volatile PFAS.
  - Low temperature heating is used in some processes to strip fluorinated polymers, for instance to regenerate metal baking surfaces before recoating them with fluoropolymers, or to strip fluoropolymers from lithium-ion batteries to recover metals. Studies, however, do not mention or indicate that volatiles including PFAS are captured.
  - Most EU waste incineration occurs at relatively high temperatures, 850–1,150 °C, through which HF is mostly formed and captured by scrubbers. It is not known if, and to what extent, volatile PFAS are captured.
  - There is no data on PFAS emissions from the thermal degradation (smouldering) of electronic and other wastes containing fluorinated polymers, shipped beyond the EU for recycling.
  - Plastic pyrolysis, chemical recycling, at temperature below 600 °C has been promoted in recent years in the United States and Europe and small-scale plastic pyrolysis of mixed polymer inputs is carried out mixed polymer input such countries as India and Pakistan. It is not known if, and to what extent, volatiles are captured.
- Landfilling:
  - Consumer products containing PFAS have previously been landfilled and it is likely that landfilling still occurs in some EU Member States.
  - Landfill sites may be a source of the very persistent PFAS leaching from impurities in fluorinated polymers and from the degradation of fluorinated sidechain polymers. In addition, fluorinated non-ionic gasses such as FTOHs may be formed and emitted to the atmosphere. Emissions may occur a long time after closure of landfills.
  - Landfill leachates are often treated in wastewater treatment plants which are not designed to remove persistent chemicals such as PFAS chemicals. Cost efficient methods are needed to reduce PFAS in landfill leachates.
  - There is also lack of harmonised protocols for sampling and analysing leachates.
  - To improve the estimation of long-term impacts, there is a need to better understand key factors influencing the degradation of fluorinated polymers and the leaching mechanisms of PFAS in landfills.
- Discharge of PFAS from fluorinated polymers treated in wastewater treatment plants:
  - There is little information on the influx of fluorinated polymers and emissions of ionic and volatile to air from wastewater treatment plants;

- There is little information on the presence, levels and contributions of fluorinated polymers to PFAS in municipal sludge, and how much from households as opposed light industry. This information is needed to assess the contribution of PFAS from fluorinated polymers to agricultural and other soils, treated with wastewater treatment plant sludge. Management of urban wastewater treatment plant sludge differs among EU Member States.

6.1 General consideration of waste management

In Chapter 6, circularity aspects in waste management of fluorinated polymers containing waste is analysed, especially assessing the possibilities to turn the waste management towards circularity. Waste management currently tends to rely on a linear economic model of take, make, use and dispose of. In a CE, the circularity is ensured in all phases of the lifecycle by maintaining the value of the material and products in the loop for as long as possible and reducing the escape of resources, thus minimising impacts during different lifecycle stages. Waste landfilling and incineration are avoided as long as possible. Nonetheless, legislative requirements of waste management need to be followed.

As previously discussed, fluorinated polymers are used in a wide range of applications, especially in the transport, energy and chemistry sectors, as well as in construction and consumer products (Améduri, 2020; 2018). From a waste management perspective, fluorinated polymers are typically incorporated in products such as in membranes, O-rings, mantling/covers, coatings, and electric insulators to provide them with specific properties. As a result, it is often not either possible or manageable to separate the thin layers containing fluorinated polymers. Moreover, when products enter the waste stage depends on their lifespans which can vary from just a few months to decades for some products such as cars, photovoltaic panels, medical implants, buildings, and electronic equipment.

Waste from **consumer products**, such as textiles, carpets and furniture containing fluorinated polymers, end up in the municipal waste stream. Textiles, which make up around 4% of all municipal solid waste (Taylor et al., 2014), are important in this context as they may include fabrics that have been treated with or contain membranes of fluorinated polymers, primarily to enhance stain resistance and provide waterproofing. Carpets are also frequently treated with fluorinated polymers to improve their stain resistance.

Within the EU, the vast majority of waste generated by consumers is collected and disposed of centrally through a range of recycling and other options. The management of municipal waste differs between Member States but, on average, 48% was recycled, 29% incinerated and 23% landfilled in 2018 (Eurostat, 2020). Impacts of incineration and landfilling, particularly of municipal waste, are discussed further in Sections 6.4 and 6.5.

Open waste or backyard burning is a relatively rare in Europe (Cogut, 2016). This type of combustion typically occurs with low oxygen availability in a barrel at relatively low temperatures compared to regulated municipal incineration sites. In less developed countries and in the rural areas of the United States, for instance, a significant percentage of the total waste generated is incinerated at low temperatures – Cogut (2016) estimates that 41% of global waste is burned this way. There is a high risk of the release of toxic emissions (dioxins and POPs) in open burning of plastics and electronic waste. Electronic waste has in the past been imported in large quantities from developed countries by developing ones, especially Africa, often for the recovery of valuable metals.

In the **transport sector**, applications containing fluorinated polymers typically have long lifespans in contrast to the electronics sector where the lifespans vary depending on the application. Waste arising from the automotive and electronic sectors typically end up in metal shredding plants and are often treated jointly for the recovery of metals with a high monetary value. In the shredding plants, reusable/recyclable plastic fractions – bumpers, fuel tanks and some plastics from electronics – are removed prior to shredding. Potentially coated metals and those with tightly attached components are sent for metal recovery in high temperature smelters.

It is estimated that a typical car contains around 350 grams of fluorinated polymers (Améduri, 2018). This corresponds to 4,200 tonnes of fluorinated polymers ending as waste from vehicles in Europe each year, given that around 12 million vehicles a year are deregistered and sent to waste. Within a few years, the amount of fluorinated polymers in cars is forecast to increase to 1–2 kilograms (Améduri, 2020), considerably increasing the amount of affected waste. In the shredding of vehicles, the plastic fraction, excluding bumpers, fuel tanks and batteries, ends up in the light fraction of the shredder waste, which consists of a mixture of plastics, rubber, wood and other non-metal residuals – typically around 30% is plastics (Zevenhoven and Saeed, 2002). According data from 20 European countries (Eurostat, 2020), about 0.86 million tonnes of shredder waste were treated in 2017 of which 34% was landfilled, 33% incinerated with energy recovery and 33% recycled.

In **renewable energy production**, fluorinated polymers provide desired functionality to applications. Wastes from photovoltaic panels are an emerging and growing waste stream after a lifespan of 25–30 years (Deng et al., 2019). Backsheets, containing fluorinated polymers, can be peeled off from modules at elevated temperatures or can be mechanically separated before the solar cells are recycled, but the residue after the recovery of such valuable metals as aluminium, copper, silver and steel, is for cost reasons typically sent for incineration or landfilled. Section 7.6 presents a comparison of environmental impacts from waste management of backsheets with fluorine-free and fluorinated polymers. Other energy related devices in which fluorinated polymers play an important role, including fuel cells, rechargeable batteries and other applications for energy capture, are now entering the waste stream after 10–20 years. The applications often contain valuable metals, critical raw materials such as cobalt in lithium-ion batteries and platinum in fuel cells, that are recovered by pyrometallurgical or hydrometallurgical processes. It is not clear to what extent these wastes are exported beyond Europe for metal recovery.

Fluorinated polymers are used in numerous **electronic applications** due to their dielectric properties and chemical stability. The share of the fluorinated polymer is, however, typically rather low relative to the total weight of the application. In addition, not only the small share of fluorinated polymers, but also the poor separability of the polymers limits their recyclability. For example, in **lithium-ion batteries** PVDF, which is used as a binder in the electrode layer, makes up just 1–2 wt% of the total (Mossali et al., 2020). The major driver for recycling of spent lithium-ion batteries is the economic value of metals, cobalt and nickel, in the cathode layer, whereas feasibility of recycling of polymers is rather low. As mentioned earlier, various industrial processes for metal recovery exist combining, for example, pyrometallurgical and hydrometallurgical approaches, however details of the processes or pre-treatment methods used by the recycling industry are not widely available. While the formation of harmful decomposition products of the binder and electrolyte, which also contains containing fluoride, is well documented during thermal runaway of the battery cells, gas emissions from recycling processes have received less attention. A recently published study describes the decomposition of PVDF binders starting from 386 °C with a maximum peak for fluoride-containing gases at 522 °C (Chen et al., 2019). Attention is thus needed on the end-of-life management of the applications to deal with toxic emissions that may be formed in the thermal treatment in certain conditions.

The risks for uncontrolled emissions at **commercial bakeries** have been raised up by Lohmann et al. (Lohmann et al., 2020). In bakeries, fluoropolymer coatings are regularly removed from baking forms after 12−24 months of use either by burning or blasting, with unknown emissions of PFAS and fluoropolymer particles to air, water, and soil, and then the forms are recoated. In the thermal treatment, the old coating is burned off at 450 °C over 4−5 hours, followed by blasting by grit or water at 1 500 bar.

Fluorinated polymer products are also used in **buildings** in, for example, facades and coatings to improve wetting properties, and paint or surface treatment applications such as coatings, lacquers, and stains (Janousek et al., 2019). Fluorinated polymers may also be used in adhesives for timbers due to their ultraviolet transparency and beneficial weight-to-surface ratio. Fluorinated polymers can also replace glass in solar panels, greenhouses, or buildings' sunroofs because they have good dirt and water repelling properties. Due to the long lifespans of buildings, the wastes are generated decades after construction and it is likely that these types of waste are yet to be removed from buildings. Today, a major concern is the release of PFAS to the environment near construction sites due to the weathering of products in contact with rainwater. Products from the renovation or demolition of buildings are typically disposed of in landfills for mineral wastes. As stony construction waste and metals can largely be recovered to use in new applications, they must be free of pollutants. Coated surfaces are therefore problematic for recovery, especially in high-grade recycling. Fabrics are treated as municipal waste and incinerated or landfilled depending on the country. Releases from construction waste containing PFAS have only been addressed in a few articles.

Box 6.1 Focus on hazardous waste and waste containing POPs

Waste is classified as hazardous or non-hazardous. Hazardous waste is a waste that, due to its (intrinsic) chemical or other properties poses a risk to the environment and/or human health. The classification is primarily based on the European List of Waste (LoW) (2014/955/EU) or based on a waste's hazardous properties. In the LoW, wastes are primarily categorised as hazardous, non-hazardous, or potentially hazardous/non-hazardous according to their origin or source – for example, electronic wastes are classed as hazardous whereas textile waste from households are deemed to be non-hazardous. In some cases, a particular type of waste on the list can be either hazardous or non-hazardous depending on its specific properties and in these cases the waste status has to be assessed based on its hazardous properties. The European Commission's Regulations No 1357/2014 and 2017/997 define the hazardous properties for hazardous waste classification referring to assessment methods developed in the European Commission's Classification, Labelling and Packaging Regulation (CLP). For example, the hazardous classification limits for the content of PFOS and PFOA in waste are given in Table 6.1.

The waste classification has several implications. There are numerous EU regulations, including the Waste Shipment Regulation (Regulation EC No 1013/2006 and Regulation EU No 660/2014), the Landfill Directive (1999/33/EC), the waste acceptance criteria at landfill (Council Decision 2003/33/EC), the Industrial Emissions Directive (2010/75/EU) and the Environmental Impact Assessment Directive (85/337/EEC), setting special requirements for waste defined as hazardous. The Waste Shipment Regulation (WSR) (No. 1013/2006), for example, requires permits for the export or import of hazardous waste both within EU and between the EU and OECD countries outside the EU and bans exports to OECD countries.

The Stockholm Convention on Persistent Organic Pollutants, adopted by the EU Regulation (EU) 2019/1021 on Persistent Organic Pollutants, which is a revision of Regulation (EC) No 850/2004, requires wastes containing substances listed in Annex IV to the Regulation and exceeding certain concentration limits to be destroyed and not circulated in new products. Products containing POPs may, however, continue to be used. Both PFOS and PFOA are examples of the POPs (Table 6.1). The list of these pollutants is continually updated by the addition of new substances. Limits for POPs and hazardous waste classifications differ meaning that wastes containing POPs may be classified as hazardous or non-hazardous depending on whether the hazardous waste limit has been exceeded. Textiles containing POPs, for example, are classified as non-hazardous, and following collection may be sent for recycling if not removed by skilled personnel at waste collection centres.

Table 6.1. Examples of PFOS and PFOA limit values above which the waste is considered as hazardous or as POP waste if either or both are exceeded.

Chemical	Limit for hazardous waste, mg/kg (Commission Regulations No 1357/2014, 2017/997)	Limit for POP waste, mg/kg (Regulation (EU) No 2019/1021)
PFOS	3 000	50 (Annex IV) (i)
PFOA	3 000	No limits presented in Annex IV (ii)

i) Potentially to be revised according to European Commission Staff working paper COMMISSION STAFF WORKING DOCUMENT Poly- and perfluoroalkyl substances (PFAS) 2020 (https://ec.europa.eu/environment/pdf/chemicals/2020/10/SWD_PFAS.pdf).

ii) Annex I of POP regulation: prohibition (with specific exemptions) on manufacturing, placing on the market and use if limits exceeding: 0.025 mg/kg for PFOA and any of its salts, 1 mg/kg for each PFOA-related compound and a combination of PFOA-related compounds, 20 mg/kg for PFOA-related compounds in substances as a transported isolated intermediate for the manufacture of fluorochemicals with a carbon chain of no more than 6 atoms and 1 mg/kg for PFOA and its salts in PTFE micropowders produced by specific techniques, as well as mixtures and articles for industrial and professional uses containing PTFE powder.

6.2 Recycling

Across the world, 60% of fluorinated polymers in products is currently landfilled, and 12% are incinerated (Dams and Hintzer, 2017; Geyer et al., 2017; Hintzer and Schwertfeger, 2014). Of the remaining 28% only a minor part is recycled.

Contrary to most other plastics, there is a notable economic incentive in recycling fluoroplastics due to their high value and stability (Ebnesajjad and Khaladkar, 2005). Recycling activities are, however, mainly concentrated on scrap from production and manufacturing, which generate large amounts of fluorinated polymer wastes (Schlipf and Schwalm, 2014). This is especially the case for the manufacturing of semi-finished parts and end-use articles made of PTFE, the processing steps, such as moulding, sintering, machining and cutting, which usually produce 10–30% waste and in some cases more than 50% (Dams and Hintzer, 2017). If 10–30% waste is assumed for all uses of PTFE and its annual global production is taken as the 2015 figure of 140 000 tonnes (Chapter 2), global PTFE process waste would be in the range 14 000–42 000 tonnes. For Europe, with a production capacity of 52 000 tonnes of fluorinated polymers per year, mostly consisting of PTFE, process wastes would be 5 200–15 600 tonnes annually.

The barriers for recycling of fluorinated polymers in products are mostly technical: a major part of the end-use of fluorinated polymers is scattered over a variety of uses in often complex products. In these, the amount of fluorinated polymers is often low compared to other materials, and dedicated recovery is therefore not put in place for the variety of products. It may also be difficult to collect some products for recycling, such as wire and cable insulation, printed circuit boards in electronics, seals and hoses from the transport sector, coatings of metal surfaces in various areas, medical applications such as ligament replacements, coated fabrics and films for buildings and windmill wings, additives in inks and lubricants, and tubing and valves in the chemical and semiconductor industry (Améduri, 2020). Given that the global recycling rate of all plastics is approximately 9% (Geyer et al., 2017), it can safely be assumed that the recycling rate of end-of-life fluorinated polymers is substantially lower.

This study did not find examples of full-scale recycling of fluorinated polymers themselves. However, from one type of fluoropolymer production, a synthesis by-product is captured and sold for use as a refrigerant (United Nations Environment Programme, 2018). Studies conducted in laboratories or small-scale kilns do, however, indicate that wastes containing PFAS, when mixed together with calcium, will form CaF_2, which is incorporated into cement and as such is recycled (Section 6.5). Whether the levels captured are high enough to make fluorine extraction worthwhile depends on many factors such as the efficiency and cost of the extraction compared to virgin materials, and also how critical the supply of fluorine becomes, which is not assessed in this report.

6.2.1 Mechanical recycling

Most melt-processable fluoroplastics, such as PVDF, can be recycled in a similar way to other commodity thermoplastics, that is, by re-melting through extrusion (Drobny, Jiri G., 2017; Ebnesajjad and Khaladkar, 2005). There are companies carrying out PVDF recycling in the United States ([22,23,24]) and Europe ([25,26,27]), and at least one of the major fluoroplastic producers has, in 2013, released a range of PVDF products based on recycled PVDF scrap. The scrap originates from their own production process, as well as from post-moulding processes at their customers' sites (Solvay, 2013).

PTFE scrap, such as shavings and machine cuttings, is recycled by different methods from conventional thermoplastics because it does not melt when heated, but only softens at temperatures above 327 °C and therefore, re-melting by extrusion cannot be used. Instead, PTFE scrap can be ground into fine powder

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[22] https://www.polycleantech.com/pvdf/

[23] https://powerplasticrecycling.com/pvdf-plastic/

[24] http://www.prsei.com/recycling/material/30-pvdf

[25] https://www.mcam.com/en/recycling-solutions/

[26] https://repolymer.de/?lang=en

[27] https://www.m-chemical.co.jp/en/news/2020/1208424_7667.html

and sintered under pressure in compression moulding, or used in ram extrusion (Drobny and Jiri, 2017; Lakshmanan and Chakraborty, 2015). Before grinding, the scrap is usually shredded and heated to remove any volatile contaminants. After grinding, the powder is treated with acids, such as a mixture of nitric and perchloric acids, to dissolve inorganics, after which it is washed (Ebnesajjad and Morgan, 2019; Lakshmanan and Chakraborty, 2015).

The recycled PTFE powder cannot be used for the same applications as virgin PTFE since it cannot be moulded in a similar fashion. Furthermore, it is off-white, which also decreases its value. Recycled PTFE has, however, certain advantages over its virgin equivalent, such as better wear resistance (Lakshmanan and Chakraborty, 2015). The use of micropowder PFTE is also discussed in Section 5.3 and microplastic pollutants from the use of fluorinated polymers in Section 5.4.

In industrial terms, in its recycled form PTFE is known as reprocessed or repro PTFE, or mechanical grade PTFE. Most commonly, the recycled powder is mixed with virgin PTFE and used in cost-driven applications in which high purity is not required, such as in non-critical chemical, electrical and mechanical applications. It is not the choice for pharmaceutical, food-contact materials, cosmetics or medical applications (Lakshmanan and Chakraborty, 2015).

The recycling route described above only exists for unfilled, or virgin, PTFE. In contrast, there is a lack of large-scale recycling technologies for PTFE compounds. This primarily results from the presence of a large variety of different fillers, such as glass fibre, graphite, carbon, metal compounds, ceramics and pigments in variable concentrations (Dams and Hintzer, 2017).

Whereas recycling of production scrap takes place, recycling of fluorinated polymers from industrial or commercial applications is challenging. A pilot-scale study (Rubino et al., 2021) has been conducted in Italy focussing on mechanical recycling of the backsheet polymer (PVF based film – Tedlar) from photovoltaic panels and also the thermal recovery of valuable metals. It was demonstrated that the polymer can be effectively separated from the milled coarse fraction of end-of-life photovoltaic modules (>3 mm) using a cyclohexane solvent treatment and subsequent filtration operation for recovery of the Tedlar fraction. For an optimised process, it was estimated that 4.3 kg of polymer of high purity can be recovered from 100 kg of input material of milled photovoltaic panels. The applicability of the recovered polymer was not part of the study. The authors also emphasise that the recovery process prevents the release of toxic components from the fluoropolymer backsheet in thermal metal recovery.

6.2.2 Pyrolysis

Depolymerisation by pyrolysis, also referred to as high-temperature conversion (HTC), is effectively the only recycling method applicable to end-of-life fluoroplastic components. In this, fluoroplastics are decomposed into their monomers at temperatures above 600 °C in the absence of oxygen (Dams and Hintzer, 2017; Schlipf and Schwalm, 2014). In 2015, the chemical company Dyneon commissioned a pilot pyrolysis plant that claimed to be the first fluorinated polymer up-cycling facility in the world. Up-cycling refers to recycling in which the material quality is improved rather than downgraded. The plant was constructed in Germany and it has a capacity of treating 500 tonnes of fluorinated polymer waste per year (PlastEurope, 2015). Suitable materials for Dyneon's pyrolysis process include the perfluorinated polymers PTFE, PFA and FEP, even with mineral fillers, and it is claimed to produce the monomers TFE and HFP with a recovery rate of 90–95% (Dams and Hintzer, 2017; Schlipf and Schwalm, 2014). It is claimed that each tonne of TFE produced by the HTC process saves 5 tonnes of Cl, 10 tonnes of hydrochloric acid, 1.6 tonnes of CaF_2, 2 tonnes of sulphuric acid and 10 tonnes of CO_2 emissions (Dams and Hintzer, 2017).

In addition, pyrolysis of mixed plastics to produce fuel has occurred in recent decades in the United States and Asian countries using carpets and auto-shredder residue as feedstocks (OCEAN RECOVERY ALLIANCE, 2015; 4R Sustainability, Inc, 2011), which may contain fluorinated polymers. Furthermore, plastic pyrolysis plants are operated in developing countries with mixed plastic inputs for fuel production (Banu et al., 2020; Beston, 2020). These pyrolysis plants are normally operated at temperatures below 650 °C in which the thermal degradation of fluorinated polymers result in toxic emissions including toxic nano- and microparticles (Boucher et al., 2000; Seidel et al., 1991; Waritz, 1975) and such PFAS as PFOA (Ochi et al., 2008). There is no published study that assesses pilot and full-scale pyrolysis processes for PFAS and other toxic degradation products from fluorinated polymer degradation.

6.3 Emissions of PFAS to water, soil and air from wastewater treatment plants

Emissions of PFAS from wastewater treatment plants have been studied to some extent, mostly the releases of PFAAs into water and less for releases to air and its content in sludge. In this chapter the overall processes are described but not in great detail. Also, a broad range of ionic PFAS are detectable in wastewater treatment plant effluents, but a direct link to fluorinated polymer production and use might be overshadowed by the plethora of alternative PFAS emission sources.

Wastewater treatment plants are classified by regulation as urban and industrial facilities and are referred to as urban and industrial wastewater treatment plants respectively. In both, influent water is treated and the effluent wastewater is let into surface or marine waters.

During the treatment process, PFAS processing agents, impurities and degradation products, as well as the fluorinated polymers themselves, may be released to air, water or be precipitated into the plant's sludge. The partially or non-degraded fluorinated polymers may be present in solution or dispersion or be in the form of nano- or microplastics.

The PFAS degradation products will distribute into different media depending on their physical-chemical characteristics:

- Air: volatile degradation products, such as FTOHs, FTSs and potentially other small PFAS volatiles such as fluoroform (CHF_3). It has been shown that FTOHs have air residual times of more than 20 days, which makes them long range transboundary air pollutants. Indeed, emissions of FTOHs have been shown to be a source of the PFAAs in the Arctic (D'eon and Mabury, 2011). Neutral (nonionic) and ionic PFAS may be emitted to air, both in the gas-phase and through aerosols. A number of volatile per- and polyfluorinated compounds have been detected in the air above the influent of selected wastewater treatment plants (Coggan et al., 2019). Atmospheric emissions dominate FTOHs emissions from wastewater treatment plants but emissions to the aquatic environment have been shown to be significant during seasons with less wind in a study conducted near Beijing (Chen et al., 2020).
- Water: short-chain and water soluble PFAAs, such as PFCAs and PFTCAs which are the intermediate transformation products from 6:2 FTOH sidechain polymers, such as 5:3 fluorotelomer carboxylic acid (5:3 FTCA) (Coggan et al., 2019). Additionally, PFPEs used in fluoropolymers such as GenX, F-53B and Adona will partition to the water phase. Several of these are or form persistent and mobile chemicals.
- Sludge: nano- and microplastic fluoropolymers, fluorinated sidechain polymers in dispersion or adhering to particulate matter such as dust or textile and paper fibres, and long-chain PFAS (PFAAs and other PFAS) that have low or no water solubility will end up in the sludge. All neutral (nonionic) PFAS that are not volatile will partition to the sludge.

6.3.1 Urban wastewater treatment plants

PFAS from fluorinated polymers in urban wastewater treatment plants come from both households and from light industry. Which contributes the most varies depending on the number and type of smaller industry in the catchment area using these chemicals. A study conducted in Sweden in 2014–2015 suggests that levels of total organofluorine and unidentified PFAS in wastewater treatment plant sludge are more related to types of industry rather than the number of households connected to the plants in that area (Yeung et al., n.d.). A review summarising the occurrence of PFAS in water and wastewater environments shows very large differences in various PFAS concentrations in wastewater influents/effluents which was explained by the origin of wastewater from either domestic, or PFAS non-intensive or intensive industrial wastewater (Phong Vo et al., 2020). Wastewater treatment plants downstream of the aqueous firefighting foam (AFFF) industry and firefighting training grounds, for example, receive high PFAS concentrations. A monitoring study conducted in Italy in 2010–2013 investigating the occurrence of PFAA in the aqueous environment and drinking water concluded that wastewater treatment plants receiving industrial wastes discharged up to 50 times the PFAA loads of plants receiving municipal wastes (Castiglioni et al., 2015).

While there are studies investigating release of PFAS from fluorinated sidechain polymers in textiles, there do not seem to be studies specifically looking at how much fluorinated polymers contribute to PFAS levels compared to fluorinated non-polymers. Examples of household sources are the release of PFAS from fluorinated sidechain polymers from washing textiles, dust and fibres on coated furniture, floor and surface polishes and spreading agents in detergents and excretion after human ingestion. Another possible source is recycled toilet paper, since recycled paper for food contact has been shown to contain PFAS from sizing and coatings, although there do not seem to be studies of toilet paper as a potential source of these chemicals. All types of fluorinated polymers used by light industry could be emitted (Glüge et al., 2020). Examples of sources include textile, glass, wood and steel coating manufacturers; commercial printers; and paint and electronics manufacturers as well as the use of detergents and food companies. Another source could be run-off from urban areas and roads into the water sewage system. Other sources could be the result of abrasion of buildings, products and vehicles as well as from industrial uses and leaks, which could contain both fluorinated polymers and fluoropolymer nano- and microplastics.

Urban wastewater treatment plants are classified as having primary, secondary and tertiary water-treatment processes. The primary process is a simple sedimentation of particulate matter from the water; secondary treatment involves sedimentation and filtration typically through sand or soil; while tertiary treatment involves sedimentation, filtration and biological degradation. All processes can also involve aeration of the water. None of these traditional wastewater treatments – coagulation, flocculation, sedimentation, micro/ultrafiltration, oxidation (chlorination, ozonation and advanced oxidation processes [AOPs]) and UV irradiation – however, are designed to degrade persistent chemicals, meaning that, typically, urban wastewater treatment plants do not remove PFAS from water or sludge (CMD Smith, 2020). Full-scale conventional treatment, including coagulation followed by physical separation processes, and chemical oxidation, aeration and disinfection, has, for example, been reported ineffective at removing PFAS such as PFSAs and PFCAs (Appleman et al., 2014).

Activated carbon adsorption, ion exchange and high pressure membrane processes (nanofiltration and reverse osmosis) may be more effective treatment technologies for PFAS removal from water (CMD Smith, 2020; Franke, 2020). These techniques have been shown effective for the removal of various PFAS in drinking water production (Franke et al., 2021), however their implementation on wastewater effluents is challenged due to the high total organic carbon content (CMD Smith, 2020). Advanced oxidation and reduction processes are also much researched for PFAS removal from water, but mostly at a laboratory scale and their full potential is yet to be evaluated (Ahmed, 2020).

As the removal of PFAS from the wastewater effluents and sewage sludge is poor, wastewater treatment plants are significant point sources for PFAS emissions to the environment. Studies from all over the world exist, in which PFAS levels are measured in wastewater effluents and sludge. In a recent study conducted in Denmark, Faroe Islands, Finland, Greenland, Iceland, Norway, and Sweden, for example, 99 conventional and emerging PFAS were screened in various environmental samples including wastewater treatment plant effluents and sludge. Effluent samples contained a mix of PFAS classes including PFCAs, PFSAs, ultrashort PFAS (mainly perfluoropropionic acid [PFPrA]) and PFCA precursors in a concentration range 34–113 ng/l (Kärrman et al., 2019). Sludge samples, on the other hand, were dominated by PFCA precursors, on average accounting for 75% of all identified PFAS, and mainly contributed by different isomers of polyfluoroalkyl phosphoric acid diesters (diPAPs). The study highlighted the low level of identified PFAS when compared to the total extractable organic fluorine (EOF) in wastewater treatment plant effluents and sludge. Another example is an Australian study which analysed 21 different PFAS in aqueous and solid samples from nineteen treatment plants (Coggan et al., 2019). The mean concentration of 21 PFAS measured in aqueous samples was 110 nanograms[28] per litre (ng/l), which results in a rough estimate of 339 kg of PFAS discharged per year from Australian wastewater treatment plants in effluents. As in many previous studies, concentrations of some compounds (perfluoropentanoic acid [PFPeA], perfluorohexanoic acid [PFHxA], perfluoroheptanoic acid [PFHpA], PFOA, PFNA, and perfluorodecanoic acid [PFDA]) increased significantly between influent and final effluent due to the degradation of precursors to stable PFAAs.

Table 6.2 presents an overview on findings of selected European monitoring studies for PFAS in wastewater treatment plant effluents/sludges conducted in 2008–2018.

Table 6.2. Main findings of selected PFAS monitoring studies related to releases from wastewater treatment plants in Europe.

Location	Main findings in the studies	Reference
Nordic countries (Denmark, Faroe Islands, Finland, Greenland, Iceland, Norway and Sweden), 2016–2017	99 PFAS were screened in various environmental samples and compared to the total extractable organic fluorine (EOF) content. Detected average total PFAS concentration were 34–113 ng/l in effluents and 36.8–142 ng/g in sludge samples. The target analysis of PFAS could explain 9 % of the measured EOF for plant sludge and 11% for plant effluents,	(Kärrman et al., 2019)
Belgium (Wallonia and the Brussels Capital Region), 2015–2018	Environmental monitoring study in Wallonia and the Brussels Capital Region on a multitude of hazardous substances, including several PFAS. For surface water measurements from wastewater treatment plants, PFHxS and PFOA were detected in all samples; PFHpA and PFOS were found in 95 % of all samples; and PFSHxs was found in 60% of them. The sum of these PFAS on average did not exceed 50 ng/l in the samples, with the exception of samples from Louvain-la-Neuve treatment plant.	(Frippiat et al., 2018)
Norway, 2017–2018	Organic pollutants including 22 PFAS were analysed in sludge samples from 18 treatment plants. PFAS were detected in all samples, the average value 40 µg/kg TS, while the mean was 25.2 µg/kg TS. Treatment plants receiving wastewater from airports had higher values of PFAS than others.	(Blytt and Stang, 2018)
Sweden, 2012–2015	Samples from three treatment plants were analysed for PFAS and precursor compounds. 41 PFAS compounds analysed: The ΣPFAS concentrations were in the range 29.8–77.0 ng/l in the effluent water. Precursor compounds made a significant contribution to the total amount of PFAS.	(Eriksson et al., n.d.)
Sweden, 2018–2019	The presence of PFAS and their potential degradation/reduction in sludge in different treatments was studied. Decreasing trends for concentrations could be observed in composted sludge over the storage time while the non-composted showed variable time trends for different substance classes. For PFAS, the sum concentrations of target analytes increased by almost an order of magnitude during 12 months of storage in the non-composted sludge. Furthermore, the results from Total Oxidizable Precursors (TOP) and EOF analyses furthermore suggested that the sludge from both treatment experiments contained a significant fraction PFAS that could not be quantified by the targeted analysis.	(Giovanoulis et al., 2020)
Germany, 2008–2013	4 981 sludge samples from 1 165 different treatment plants were analysed between 2008 and 2013 for 11 PFAA compounds. Contamination of analysed PFAAs in sewage sludge clearly decreased due to phase out of long chain PFAAs, but the decrease of total flux of PFAS was not verified. Very high PFAA concentrations in sewage sludge were detected related to firefighting foams containing PFAAs or emissions from industries using PFAAs.	(Ulrich et al., 2016)

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[28] nanogram (10^{-9} grams)

Sewage sludge from wastewater treatment plants may be applied to agricultural fields, incinerated, or sent to landfills for disposal (Stoiber et al., 2020). In the majority of European countries, sludge is used as a fertiliser on soil, indeed in some Member States more than 80% of urban wastewater treatment plant sludge ends up on the land. Currently there are no EU criteria for organic contaminants in fertilisers or in soil, and hence no limit values for PFAS or legal obligation to monitor for them in urban wastewater treatment plant sludge. EU Member States may have set their own criteria, in Denmark, for instance the amount of 12 PFAS in soil is limited to 400 µg/kg dry matter soil (DK EPA, 2015). In Europe and the United States urban wastewater treatment plant sludge has caused contamination of soil, water and crops. In Europe this has been documented in the EU research project PERFOOD (2008–2012) ([29]), and in later research and national publications from, amongst others the Netherlands and Sweden. The EU also funded the NonHazCities ([30]) regional study on PFAS emissions from cities to the Baltic Sea which demonstrated that these chemicals are released from households to urban wastewater treatment plants.

Once PFAS containing sludge is applied on soil, these compounds may bioaccumulate in plants. The plant uptake depends on various factors, but particularly shorter chain PFAS seem to accumulate in leaves and fruit, whereas higher chain PFAS tend to be more concentrated in roots (Costello and Lee, 2020; Ghisi et al., 2019). Perfluorobutanoic acid (PFBA) and PFPeA have been detected in lettuce and tomatoes grown in soil to which biosolids had been applied (Blaine et al., 2013). It is difficult to treat wastewater sludge and remove PFAS due to its complex nature. Information on treatment of PFAS contaminated soils is scarce, whereas numerous reviews on PFAS removal from aqueous environments are available. Currently available methods for remediation of PFAS contaminated soils seem to be expensive, impractical for *in situ* treatment, use high pressure and temperatures, and/or result in toxic waste (Shahsavari et al., 2021). A variety of remediation technologies have been introduced at a laboratory scale such as chemical oxidation, ball milling, and electron beams, however, additional research is needed to make them feasible, cost-effective and applicable in the field.

6.3.2 Industrial wastewater treatment plants

Detection of volatile PFAS in air above industrial effluent wastewaters show that they are emitted in the production/manufacturing processes (Dams and Hintzer, 2017). This is also confirmed, for example, by the Food Contact Substance Notifications which reported that United States Food and Drug Administration has approved fluorinated acrylic polymers for use in coating food-contact paper and board (EDF, 2018) and noted that 88% was retained on the paper with 4% going to wastewater and 8% to sludge. Compared to their urban equivalents, industrial wastewater treatment plants typically have more developed treatments for the removal chemicals from water, with the sludge going for incineration or landfilling. There are, however, several instances in both Europe and the United States of widespread pollution from treatment plants, the most well known of which concern fluoropolymer facilities in the United States such as DuPont (now Chemours) and 3M manufacturing sites. Here PFOA used as a dispersion agent (polymer production aid) in PTFE was emitted to lakes, rivers, soil and groundwater through wastewater treatment plants, landfills and emissions to the air. The contamination led to widespread pollution of the surrounding communities and livestock as well as the wider environment resulting in court cases that were settled by payments totalling more than US$ 700 million. Both in the United States and Europe sludge mixed into biosolids as soil improvers have been spread on farmland and has thereby contaminated the environment, crops, drinking water, people and livestock. The best-documented case concerned the German district of Rastatt where papermill sludge contaminated with PFAS was mixed into a soil improver – the exact type of chemical and whether a polymeric or non-polymeric PFAS was used remains uncertain. Contamination from a paper factory was also recently discovery in Tyrifjord, Norway (Langberg et al., 2021). In both cases the presence of PFOS indicates that non-polymeric surfactants might have been used, but the exact PFAS type and its source remains unknown.

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[29] PERFOOD: https://ibed.fnwi.uva.nl/perfood/index.html

[30] NonHazCity: https://thinkbefore.eu/en/

In summary, studies are scarce on both the fraction of PFAS from fluorinated polymers that are released to air, water and sludge and the extent to which they have and are contaminating soil, water and crops through the application of urban wastewater treatment plant sludge.

The EU Chemical Strategy for Sustainability and its European Commission's supporting PFAS Staff Working Document call for the inclusion of PFAS in the recast of the Fertiliser Directive. This may provide an option to determine the amounts of both specific and total PFAS in wastewater treatment plant sludge from both urban and industrial sources. The recommended inclusion of these chemicals in the revision of the European Pollutant Release and Transfer Register may also provide more information and better control of PFAS emitted from industrial and urban wastewater treatment plants. Given the diversity of these chemicals, effective control may require limit values and monitoring of all PFAS as well as specific ones. The comprehensive screening of PFAS is challenging due to the large number of different PFAS. One method proposed to investigate unknown PFAS is to measure the total EOF in addition to targeted PFAS in a sample (Kärrman et al., 2019).

6.4 Landfilling of wastes from fluorinated polymer production and end-of-life products

6.4.1 Management of waste from fluorinated polymer production and products

In the production of fluorinated polymers, wastes containing PFAS are generated but very little information is available in scientific literature about their management. A Dutch study (Gebbink and van Leeuwen, 2020) mentions that at the Chemour plant in Dordrecht, the Netherlands, 50% of GenX ends up in the waste streams and is sent to a nearby incineration plant. In Europe, waste containing PFAS are classified as hazardous if their PFAS content exceeds a substance specific limit value (Box 6.1). According to Council Decision 2003/33/EC, hazardous wastes may only be disposed of at hazardous waste landfills if the waste acceptance criteria are met; for example, low organic content measured as loss of ignition not exceeding 10% at 550 °C. Since the landfill legislation came into force, organic hazardous process residues are incinerated rather than disposed of in landfills.

In the past, wastes from organofluorine industries were disposed of in landfills resulting in associated releases (Oliaei et al. 2013). These old landfill sites need particular assessment. In Switzerland, for example, landfills in which the pharmaceutical and pesticide industries disposed of their waste for decades have been excavated and, according to an internet source ([31]), the materials removed sent for further treatment and destruction.

6.4.2 Emissions of PFAS from the landfilling of end-of-life products

Since 2016, most European countries have introduced restrictions on landfilling waste which have generally been implemented in Member States as bans on landfilling specific waste streams such as plastic, textiles and carpet wastes, and these wastes are increasingly incinerated. Furthermore, the revised Waste Framework Directive has set a target for reducing the amount of municipal waste sent to landfills of 10% of total waste by 2035. According to Eurostat data, in the member and cooperating countries of the European Environment Agency in 2006, 44% of municipal waste was disposed of in landfills, but by 2017 this had fallen to 23%. Nonetheless, in 18 of the 38 countries, corresponding to 33% of the European population, landfill rates were more than 50% in 2017 (Figure 6.1).

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[31] https://en.wikipedia.org/wiki/Bonfol; accessed May 28, 2021

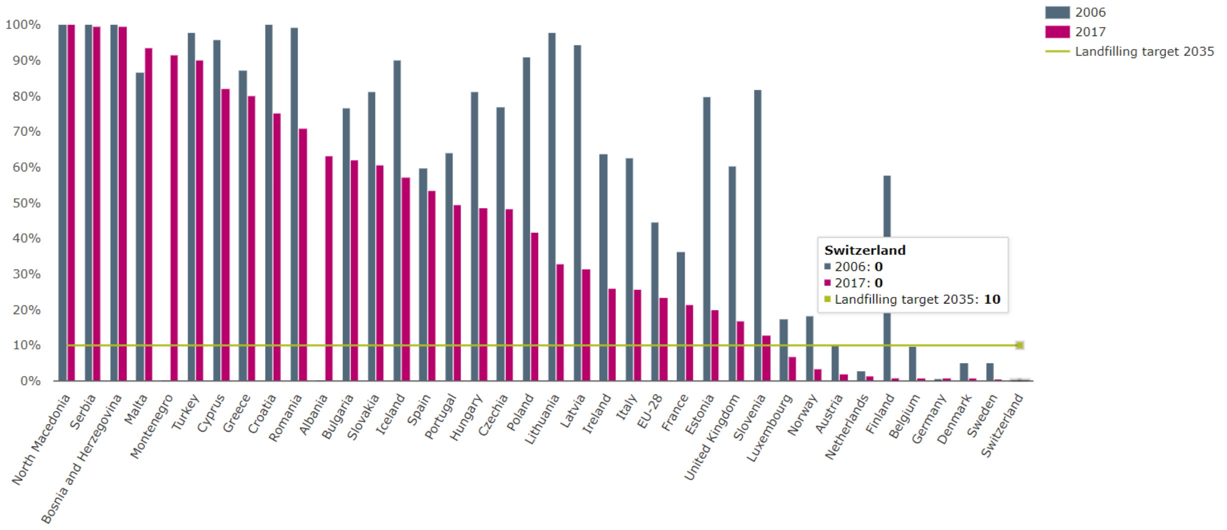

Figure 6.1. Landfill rates in member and cooperating countries of the European Environment Agency, 2006 and 2017, %.

Source: EEA (https://www.eea.europa.eu/data-and-maps/daviz/municipal-waste-landfill-rates-in#tab-chart_1)

In landfill conditions, waste containing PFAS will decompose and release them (Lang et al., 2017; 2016a). Many of these substances occur in soluble form; anionic PFOA, for example, is highly soluble, and are therefore likely to be released into the percolating water in the landfill as leachate. As discussed in Chapter 4, neutral, volatile PFAS, such as FTOH, can be released by sidechain fluorinated polymers as breakdown products. As only a few articles on release behaviour of PFAS from specific waste types in landfill conditions are available, there is still lack of information on the release mechanism and factors influencing their behaviour and potential transformation in landfill conditions. One study showed that in an anaerobic landfill reactor a contact time of more than 100 days was needed before PFAS are released in measurable concentrations from carpet and clothing (Lang et al., 2016b). The results indicate that carpet and clothing are likely sources of PFAS in landfill leachate in the United States (Knutsen et al., 2019; Lang et al. 2017; 2016).

Leachates and sediments from a Norwegian landfill were analysed for PFAS (Eggen et al., 2010). Results indicated a potential for dissolved organic carbon (DOC) to facilitate transport of fluorinated compounds. PFCA substances up to perfluorodecanoic acid (PFDcA) have been detected in the water phase, while PFDcA, perfluoroundecanic (PFUnA), perfluorododecanic (PFDoA) and perfluorotridecanic acids (PFTrA) where detected in sludge; this has also been reported elsewhere including in a Danish study by Bossi et al. (2008). Leachate, particularly from organic waste at municipal landfills, contains high concentrations of DOC due to the degradation of organic matter.

In the Norwegian study (Eggen et al., 2010), particular concern was raised about the high concentrations of PFAS, up to 6 231 ng/l, in the leachate from landfills. Furthermore, several PFAS, such as long-chained PFCAs not detected in either water or particle phases in leachates, were in some cases found in relatively high concentrations in sediments taken from treatment systems of landfill leachates. A potential explanation is that they were formed during the transformation of perfluorinated precursors. Precursors are compounds, both known and unknown, which have the potential to form perfluorinated compounds (PFCAs and PFSAs) (Houtz and Sedlak, 2012) at degradation.

In an Australian study (Gallen et al., 2017), some general trends in leachate characteristics were observed: higher concentrations were found in operating landfills for municipal waste compared to closed ones. Landfills that also accepted construction and demolition waste generated higher concentrations of PFHxA and PFHpA than purely municipal waste landfills. Both PFHxA and PFHpA are minor impurities in commercial PFOS and PFOA formulations, and potentially precursor chemicals released in landfill conditions or PFOA alternatives. Also elevated DOC content and increased acidity in leachate were linked to higher leachate concentrations.

The released PFAS are transported in water to the bottom of the landfill from where leachates are collected and typically sent to wastewater treatment plants prior to their discharge into surface water bodies. Part of the leachate may however escape to groundwater without undergoing treatment, especially from old, unlined landfills. Articles on leachate composition from landfills still in operation are available in the literature, although PFAS compounds are also released from closed landfills, even if the amount of leachate is reduced.

The discharge of PFAS to the environment can be roughly estimated based on total leachate volumes and average concentration in the leachate. Table 6.3 summarises PFAS discharges reported in some recent studies, with further calculations showing discharges per person and per year. Contrary to expectation, the release reported from landfills in Spain, which has a high landfill rate, was significantly lower than in Norway and Sweden. The specific substances and the number of substances measured should, however, be taken into account in the comparison of the data – the sum results from German study, for example, cannot be directly compared to results from other countries. Furthermore, there might be differences in analytical procedures – for example, threshold values for analysis or filtration of samples prior to analysis that might reduce the concentration. Furthermore, PFAS precursors and their degradation products should be included in the analytical programme in order to avoid their underestimation and comparisons ideally made on substance basis. According to a Norwegian study (Knutsen et al., 2019), 3.5% of PFOA is estimated to be released from municipal landfills.

A total yearly release of PFAS from municipal landfills in Europe can be roughly calculated assuming that all countries' annual releases per person are of the same magnitude as Spain, which has higher landfill rates than most European countries. This would suggest total annual releases of 430 kg of PFAS from municipal landfills in 37 European countries (calculated based on population in the countries included in Fig. 6.1[32]). If, however, all countries have releases similar to Sweden's, then Europe's total annual releases from landfills would increase significantly to 3.7 tonnes.

It needs to be stressed that this does not include releases from landfills in which the organofluorine industry (Oliaei et al., 2013) or such users of PFAS as the plating or paper industries dispose of their waste. The release from such landfills are likely higher (Oliaei et al., 2013).

Table 6.3 Discharge to the environment of PFAS by landfill leachate reported in some studies.

Note: the table also includes information on landfill rates per country

Country (source)	Landfill rate (year)	Estimated discharge per year	Calculated annual discharge per person (mg)	Comment
Germany (Busch et al., 2010)	< 1 % (2006, 2017)	Around 90 kg/year for 55 PFAS (calculated amount in treated leachate from about 1 700 landfills)	1 000	Samples of treated and untreated leachate from 22 landfill sites in Germany were analysed for 43 PFAS. PFBA and perfluorobutane sulfonate (PFBS) were the dominating substances in leachate.
Norway (Knutsen et al., 2019)	18 % (2006) 3 % (2017)	Sum of 28 PFAS was estimated to be 17 ±29 kg year / (median 6.3 kg/year)	3.2	Four short- and 24 long-chain PFAS compounds were investigated from 10 Norwegian landfills, including a remote landfill as reference. Short-chain PFAS dominated in leachates from six of 10 landfills at concentrations of 68–6 800 ng/l (mean

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[32] base for calculation: year 2017. Data retrieved from Eurostat news release from 2018 on "First population estimate". https://ec.europa.eu/eurostat/documents/2995521/9063738/3-10072018-BP-EN.pdf/ccdfc838-d909-4fd8-b3f9-db0d65ea457f

Country (source)	Landfill rate (year)	Estimated discharge per year	Calculated annual discharge per person (mg)	Comment
				980 ±1 800 ng/l, median 360 ng/l). In sediments, long-chain PFAS such as PFOS and PFOS-precursors were the main substances at concentration of 8.5–1 200 µg/kg (mean: 47 ± 36 µg/kg; median 41 µg/kg).
Spain (Fuertes et al., 2017)	60 % (2006) 54 % (2017)	Sum of 16 PFAS contained in landfill leachates was estimated as 1209 g/year. The landfill served 1.8 million people	0.7	Occurrence of PFAS in leachates from four municipal waste landfills.
Sweden (Hansson et al., forthcoming)	5 % (2006) <1 % (2017)	Discharge from landfills to wastewater plants was approximately 60 kg/year, sum of 26 PFAS	6	To some extent, discharge directly to surface waters and forest land (about 4 kg/year each, sum of 26 PFAS)
China (Yan et al., 2015)	No information	Discharge of the total concentrations of PFAAs to groundwater from landfill leachate was estimated to be 3 110 kg/year	2	Raw and treated landfill leachate samples were collected from five municipal landfill sites in China. The total concentrations of PFAAs were in the range of 7 280–292 000 ng/l in raw leachate and 98.4–282,000 ng/l in treated leachate. The dominant compounds measured were PFOA (mean contribution 28.8 and 36.8% in raw and treated leachate, respectively) and PFBS (26.1% and 40.8% in raw and treated leachate, respectively).
Australia (Gallen et al., 2017)	No information	National estimate 31 kg of PFHxA per year	1	Leachates from 27 landfills were analysed for nine PFAS.
United States (Lang et al., 2017)	Primarily municipal waste landfill	Estimated PFAS from landfill leachate to wastewater treatment: 563–638 kg for 2013	Around 2	95 leachate samples collected from 18 landfills were analysed for 70.

Landfills, even after closure, generate leachates that needs to be treated. Therefore, information about the environmental fate and toxicology of emerging compounds is needed for the installation of adequate treatment technologies for the sustainable and efficient removal of these compounds.

Table 6.4 summarises technologies reviewed for removal of PFAS from landfill leachates. Besides efficiency, the treatment costs, such as costly regeneration and energy costs, and challenges with handling of the high volume of wastewater sludge need attention. Furthermore, the efficiency of the methods is substance specific and degradation of PFAS to other substances.

Table 6.4. Examples of cleaning treatment systems for removal of PFAS from landfill leachate.

Method	Specification	Mechanism	Advantage	Disadvantage
Physical separation	Adsorption, active carbon	Electrostatic attraction, hydrophobic interaction	Easy to scale up	Contaminants are not degraded, costly regeneration
	Resin	Ion-exchange reactions	Fast and selective removal	High material cost, costly regeneration
	Membrane filtration, nanofiltration	Size exclusion, electrostatic interaction	High removal rate, easy to scale up	High operation cost, further disposal of the concentrate
Oxidation	OH^-	Electron transfer, decarboxylate, CF_2 elimination	Easy activation of the radical precursor	Not effective
	SO_4^{2-}	Electron transfer, decarboxylate, CF_2 elimination	Easy activation of the radical precursor	Slow degradation, partial mineralization
	H^+	Decarboxylate, unimolecular decomposition	Energy-effective	Easily scavenged
Reduction	e^-, CO_2^{2-}	Electron transfer, unimolecular decomposition	Faster degradation	High chemical dosage, easily scavenged
Thermolysis	Incineration, sonolysis	Thermal dissociation	Complete mineralisation	High energy demand, unscalable
Biological	Biodegradation	Degradation of chemicals	Commonly used method	Not effective; Persistency of PFAS for degradation, possible degradation of precursors of PFAS

Source: Wei et al. (2019); Busch et al. (2010)

The need for further information on emissions of semi-volatile PFAS compounds from landfills has been brought up in Canada (Hamid et al., 2018). In Europe, municipal landfills are generally covered by sealing layers after closure and therefore emissions to air from these semi-volatile PFAS compounds are assumed not to be significant in closed European landfills.

Landfill sites, at least in those studied in Ireland (Harrad et al., 2020), had similar atmospheric concentrations of PFOA and related compounds both up- and downwind suggesting these landfill sites are not a significant source of these compounds to the atmosphere. This corroborates information obtained in Germany where only the volatile non-ionic per- and polyfluorinated compounds were found to be enriched in the atmosphere near landfills (Weinberg et al., 2011). General German domestic waste contains 0.01–0.035% fluorine (Aleksandrov et al., 2019). In samples collected at Chinese landfill sites, however, Wang et al. (2020) were able to detect concentrations of ionic per- and polyfluorinated compounds in the picogram ([33]) per cubic metre range.

In their study of emissions from landfill sites in Germany (Weinberg et al., 2019), a wide range of volatile and semi-volatile compounds were detected at the sites and also at lower concentrations at the reference sites. The enhancement above ambient concentrations was between 1.5 and 3 times. The greatest enrichment at the landfill sites was derived from the fluorotelomer alcohols.

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[33] Picogram: 1 trillionth of a gram (10^{-12})

Recent laboratory studies (Hamid et al., 2020) have shown the potential for fluorotelomer alcohols and sulfonates to produce PFOA and other carboxylic acids in landfill aqueous leachates albeit with a long half-life of greater than a year. It is possible that this slow process may be responsible for some future emissions from landfills, although the long half-life coupled with the low incidence of the precursors in landfill waste make these emissions hard to detect in ambient air.

6.5 Emissions of PFAS to air from the incineration of fluorinated polymers

The Industrial Emissions Directive (2010/75/EU) requires that waste incineration plants must be designed to ensure the flue gases reach a temperature of at least 850 °C for 2 seconds to ensure the complete breakdown of toxic organic substances. If hazardous waste with a content of more than 1% of halogenated organic substances ([34]) is incinerated or co-incinerated, the temperature should be at least 1 100 °C with a minimum residence time of 2 seconds in order to mineralise all organic compounds. Lemieux et al., (2000), however, showed that peak temperatures in backyard open burning systems reached only 250–620 °C.

This the following section on incineration therefore describes the thermal degradation at temperature ranges of 250–1400 °C.

6.5.1 Thermal degradation of fluorinated polymers, demonstrated theoretically or in laboratories

As with pyrolysis, incineration or combustion is the decomposition of chemicals at high temperatures. The difference lies in the presence of oxygen that is part of the reaction in incineration but not in pyrolysis. Depending on the temperature, incineration can result in very different end products. Ellis et al. (2001) differentiate incineration from thermolysis because of the presence of a fuel source in incineration that ensures complete combustion of the material being incinerated. Thermolysis, with no fuel source, can run at lower temperatures, but enables the emission of different fluorocarbons in the process. It must be noted, however, that the definition of the term thermolysis in Ellis et al. (2001) is not definitive; other sources define it as thermal decomposition without the presence of any oxygen, even less than in pyrolysis (35,36) For the purpose of this report, incineration means thermal decomposition of chemicals in the presence of oxygen, irrespective of the temperature range.

The thermal decomposition of wastes is a multistage process and may additionally use a post-combustion fuel to raise the flue gas temperature above critical thresholds to ensure complete degradation of recalcitrant compounds including halogenated materials. The flue gas is likely to be washed and filtered before release to the environment. The 2017 European Pollutant Release and Transfer Register lists 171 facilities that annually discharged more than 5.0 tonnes the reporting threshold of inorganic fluorine compounds as HF. The top 10 discharge facilities are a mixture of aluminium smelters, thermal power stations and ceramics producers. There are no waste and wastewater management facilities that report HF discharges.

Studies on the behaviour of PTFE during thermal degradation showed that the process involved random chain cleavage, depolymerisation and disproportionation (Garcia et al., 2007). Slow decomposition occurs at 260 °C (Simon and Kaminsky, 1998) although there is a notable threshold at 400 °C above which the rate increases significantly. Decomposition is essentially complete by 650 °C. At 800 °C, the half-life of PTFE is 0.1 seconds and so 1 second at this temperature is equivalent to 10 half-lives. Yamada et al., (2005), for example, showed that there were no detectable emissions of PFOA during the combustion of fabrics or paper treated with fluorotelomer-based acrylic polymers in municipal incinerators as the temperature were likely to have been high enough to ensure complete conversion to HF. In a pilot test of PTFE and

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[34] expressed as chlorine (requiring recalculations for fluorine)

[35] https://www.suezwaterhandbook.com/processes-and-technologies/dewatered-sludge-treatment/thermal-processes-used-to-destroy-the-organic-matter-contained-sludge/pyrolysis-and-thermolysis-applied-to-sludge (last accessed: 17.07.2020)

[36] http://www.dgengineering.de/Thermolysis-Pyrolysis-Knowledge.html (last accessed: 17.07.2020)

wood co-incineration, however, the HF mass balance for fluorine recovery was only 56% at 870 °C with a 4 second residence time, and 78% at 1 020 °C with 2.7 seconds residence time (Aleksandrov et al., 2019). In Australia, companies licensed to incinerate soil and water contaminated with PFAS, operate at temperature of 1 050–1 100 °C (Seow, *pers comm*, 2020).

The degradation stages at high temperatures are likely to be (Garcia et al., 2007):

PTFE $\rightarrow$ $C_3F_6 + C_2F_4$ (in an inert atmosphere such as nitrogen);
PTFE $\rightarrow$ $C_2F_4 + CF_4$ (with some oxygen present);
$2\ C_2F_6 + O_2 \rightarrow 3\ CF_4 + CO_2$ (when oxygen present in excess).

At a lower combustion temperature of 750 °C, more hexafluoroethane (PFC-116, C_2F_6) is formed.

Tetrafluoromethane (PFC-14, CF_4) is a potent greenhouse gas with a GWP of 6 630, while the unsaturated hexafluoropropene (HFP, C_3F_6) and tetrafluoroethane (TFE, C_2F_4) decompose rapidly in the atmosphere. HFP, however, degrades completely to the highly persistent and highly mobile trifluoroacetic acid (TFA) (Mashino et al., 2000).

According to Simon and Kaminsky (1998), the main thermal degradation products of PTFE are TFE (the monomer) and difluorocarbene radicals ($:CF_2$) although secondary reactions may lead to hexafluoropropene (HFP, $CF_3CF{=}CF_2$) and perfluorocyclobutane ($c\text{-}C_4F_8$).

Alternatively, Koch (2002) suggests:

PTFE $\rightarrow COF_2 + C_2F_4$
$C_2F_4 \rightarrow :CF_2$
$COF_2 + H_2O \rightarrow CO_2 + HF$
$:CF_2 + HF \rightarrow CHF_3$

Among HFCs, fluoroform (trifluoromethane, CHF_3, HFC-23) is the most potent greenhouse gas with a GWP of 12 400.

Ellis et al. (2001) summarised the combustion of PTFE after conducting experiments in an oven up to 500 °C. They also identified difluorocarbene molecules as part of the major thermal degradation pathway leading to the formation of TFE. This may also lead to the formation of cyclo-octafluorobutane (c-OFB, $c\text{-}C_4F_8$), a potent greenhouse gas with a GWP of 9 540, and, in the presence of oxygen, epoxides, ethers and carboxylic acids including TFA. TFE, c-OFB, HFP, $CF_3(CF_2)_{1\text{-}12}COOH$ (PFCA), $CF_3O(CF_2)_{1\text{-}7}COOH$, TFA, monofluoroethane (MFA) and difluoroethane (DCM) were all experimentally identified by Ellis et al. (2001) in the thermal decomposition of PTFE at 500 °C and 360 °C.

The process, as proposed by Ellis et al. (2001), is shown, simplified, in Figure 6.3. In this scheme, TFA is one of the final products.

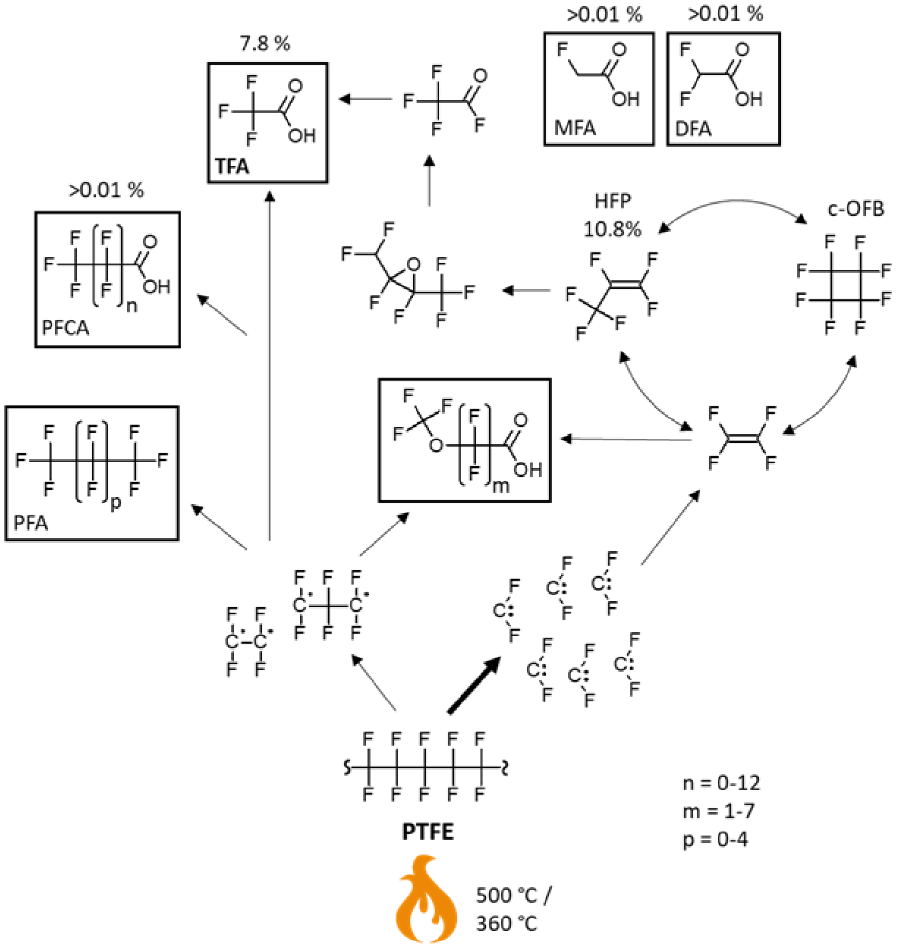

Figure 6.2. The proposed thermal degradation pathway summarises many of the pathways and products proposed by Garcia et al. (2007), Koch (2002) and Simon and Kaminsky (1998). The primary route is to the right indicated by the thicker arrow. When percentages are given, the species was also quantified. PFAs were not identified in experiments, while TFE, HFP and c-OFB were the major gases produced.

Source: modified from Ellis et al. (2001)

With respect to the formation of ODS, during incineration of general household waste containing fluorinated polymers or the incineration of fluorinated polymers on their own, the ubiquitous presence of chlorine can cause their formation.

Any fluorinated compound containing the C-CF_3 group may degrade to TFA under certain circumstances and TFA can be a significant stable product in the mineralisation of certain fluorinated polymers such as 1,1,1-tetrafluoroethane (HFC-134a, CF_3CH_2F), 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124, CF_3CHFCl) and 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123, CF_3CHCl_2) – note: all have the C-CF_3 group.

TFA is water soluble and readily washed out of the atmosphere by rain into the sea, rivers, lakes and ground water. Due to its characteristics as a very strong acid, it is likely to exist in its ionic-free formiate form (CF_3COO^-). An additional source that causes natural enrichment in seawater was long suggested to be TFA formation near hydrothermal systems with an estimated 6 000 kg annual input (Scott et al., 2005). It must be noted, however, that most of the TFA in surface waters likely comes from anthropogenic sources. Further, Joudan et al., (2021) suggest that there is insufficient scientific evidence to conclude that TFA occurs naturally at all and that there exists no reasonable mechanism of natural formation of TFA.

Box 6.2 Sources of TFA

One major anthropogenic source of TFA is the degradation of HCFCs, HFCs, HFOs and HCFOs that are mainly used as refrigerants and foam-blowing agents. The most relevant substances in this context are 1,1,1,2-tetrafluoroethane (HFC-134a) and 2,3,3,3-terafluoropropylene (HFO-1234yf). While other gases, such as HCFC-123 and HCFC-124 are practically entirely converted to TFA during atmospheric degradation (Kotamarthi et al., 1998), they are much less used and consequently emitted than many HFCs and HFOs. HFC-134a was until recently the major refrigerant in air-conditioning systems of passenger cars and light commercial vehicles. Following MAC-Directive (2006/40/EC), the gas contained in such systems may not exceed a GWP of 150. This applies to the use in all new vehicles in the EU, starting from 2017. Since HFC-134a has a global warming potential of 1 300, it has been replaced by the unsaturated low GWP gas HFO-1234yf. While HFC-134a has a molar yield of TFA in the course of its atmospheric degradation of around 7–20% (Wallington et al., 1996), HFO-1234yf degrades entirely to TFA (Hurley et al., 2008). Other HFCs and HFOs show a varying degree of TFA-yield, ranging from zero to 100%, depending on the intermediate degradation products. While trifluoroacetyl fluoride (CF_3CFO) is converted entirely to TFA, trifluoroacetaldehyde (CF_3CHO) is estimated to yield TFA of up to 10% on a molar basis (WMO, 2010).

For halogenated propylenes, the intermediate is determined by the atom that is bound to the central carbon (WMO, 2014). If fluorine is bound to it, then CF_3CFO and consequently TFA are the degradation products. This applies to HFO-1234yf. On the other hand, if hydrogen is bound to the central carbon, then CF_3CHO is the intermediate product and the TFA yield will be much smaller. This applies to 1,1,1-3-tetrafluoropropylene (HFO-1234ze) and 1-chloro-3,3,3-trifluoropropene (HCFC-1233zd), both gases that are marketed by industry as replacements of HFCs as refrigerants and foam-blowing agents.

Modelling studies of future deposition rates of TFA mostly focused on HFO-1234yf as it is a key precursor gas of TFA and limited their studies to its emissions from mobile air-conditioning systems in passenger cars. Across the United States, assuming all passenger cars in 2017 were equipped with HFO-1234yf – which is not the case since many older cars with HFC-134a are still in use but to gauge the effect once this conversion is completed – a fallout of 0.24 kg/km² of TFA was modelled (Luecken et al., 2010). For Europe, Henne et al., (2012) also assumed a complete conversion from HFC-134a to HFO-1234yf in passenger cars in 2020 – which is also not the case but, again, intended to assess the future effect – and estimated an average TFA deposition rate of 0.65–0.76 kg/km² per year. Maxima of up to 2 kg/km² per year were estimated for northern Italy.

Other major sources for TFA include the metabolic and environmental degradation of pesticides and pharmaceuticals carrying CF_3-groups, more than 1 million chemicals, mostly found in sludge and rural effluents. The total contribution to existing amounts of TFA in the ocean as a result of the continued use of HCFCs, HFCs and HFOs up to 2050 is estimated to be a small fraction, <7.5% of the approximately 0.2 µg acid equivalents/L estimated to be present at the start of the millennium, indicating the presence of major additional sources (Solomon et al., 2016). The replacement of perfluorinated compounds with polyfluorinated ethers may, for example, induce enhanced UV degradability although with significant $-CF_3$ production (Bentel et al., 2020).

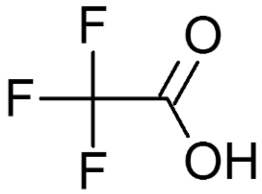

Figure 6.3. Structure of TFA.

Source: Own illustration

cont.

Freeling et al. (2020) carried out a nationwide measuring programme of trifluoroacetate in precipitation in Germany. They concluded that in February 2018–January 2019, the precipitation-weighted average concentration of trifluoroacetate in wet deposition was 0.335 µg/l, which corresponds to an annual flux of 190 µg/m^3 or around 68 tonnes (Freeling et al., 2020). Given the exceptionally dry conditions in 2018, the wet deposition flux would amount to around 98 tonnes based on the average precipitation for 1981–2010. This exceeds previously measured trifluoroacetate concentrations in Bayreuth, Germany in 1995–1996 (Jordan and Frank, 1999) and Switzerland in 1996–1997 (Berg et al., 2000) by a factor of three to five. Given the strong seasonality of the annual trifluoroacetate concentration and flux measured by Freelin g et al. (2020), precursors of TFA and trifluoroacetate are likely volatile compounds, such as HFCs and HFOs.

Several studies on the ecotoxicity of TFA in water media, as well as some risk assessment studies of TFA have been conducted. Box 6.2 summarises that TFA readily dissociates upon contact with water and builds highly stable and unreactive salts (Solomon et al., 2016). Tests on different species found a generally low toxicity of TFA salts, with the most sensitive species being the freshwater microalgae *Raphidocelis subcapitata* (formerly *Selenastrum capricornutum* and *Pseudokirchneriella subcapitata*). Adverse growth effects were detected at concentrations above 0.12 mg/L (Boutonnet et al., 1999). A new study performed by INERIS in 2017, however, found a no-effect concentration (NOEC) of 2.5 mg/L, which subsequently led to the predicted no-effect concentration (PNEC) of 0.56 mg/L TFA in freshwater according to ECHA (2020).

Due to its complete water miscibility, TFA does not bioaccumulate or biomagnify up the food chain.

6.5.2 Municipal incineration of fluorinated polymers and other perfluoroalkyl chemicals wastes

Municipal waste containing fluorinated polymers, such as end-of-life consumer products, is often incinerated in Europe (Table 6.4). Only limited amounts of fluorinated polymer waste can be incinerated in municipal waste incinerators due to the high corrosiveness of the hydrofluoric acid formed in incineration (Dams and Hintzer, 2017). There is, however, a lack of data concerning actual emissions of a variety of volatile PFAS from municipal incinerators. Studies would be highly useful to get data, both when the incinerators are operated at low-temperatures, such as during start-up or if energy consuming materials are added, and at optimal high-temperature conditions.

Aleksandrov et al. (2019) found that German municipal waste contained 0.01–0.035% fluorine. If, however, it is assumed that a fluorine content of 0.01% is a conservative estimate and that it is all PTFE, estimates of PFAS emissions are challenged by concerns on the usability of the data from this study ([37]). Further, alternative, more volatile PFAS formation, as shown in Figure 6.2, is not taken into account.

A review on PFAS emissions from waste incinerators has been published by RIVM (Bakker et al 2021). There is a lack of measurement data of PFAS in the recovered carbon dioxide and in cleaned flue gases. Measurements of PFAS in these streams are recommended in the review for better understanding of the risks of transmission of PFAS from incinerators.

The household waste produced by European countries is shown in Table 6.5, with the countries ranked by the volume of waste produced per person. The Scandinavian countries, with the exception of Iceland, show the highest incineration/energy recovery rates at 48–53%.

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[37] In the study by Aleksandrov et al., (2019) the level of PFOA in the blanks exceeded the levels of PFOA in the samples, which were apparently not corrected for the background levels. This questions the reliability of the conclusions of the Aleksandrov et al. (2019) study.

Table 6.5. Waste generation rates in the 25 highest ranking European countries, 2018, kilograms per person.

Country	Waste generated (kg/person)	Disposal – landfill and other (kg/person)	Recovery – energy recovery (kg/person)	Recycling – material (kg/person)	Recycling – composting (kg/person)	Incinerated with energy recovery (%)
Denmark	814	9	397	263	143	49
Norway	739	23	378	229	72	51
Switzerland	703	0	334	217	152	48
Malta	640	550	0	42	0	0
Germany	615	5	189	305	110	31
Luxembourg	610	38	266	171	136	44
Austria	579	13	224	147	187	39
Finland	551	4	314	161	72	57
Montenegro	530	464	0	27	1	0
France	527	110	183	132	100	35
Netherlands	511	7	213	138	147	42
Portugal	508	247	91	62	85	18
Italy	499	107	92	144	105	18
Slovenia	486	47	47	207	79	10
Spain	475	242	62	87	84	13
Lithuania	464	114	58	113	131	13
United Kingdom	463	69	176	126	78	38
Albania	462	353	13	85	-	3
Sweden	434	3	232	130	69	53
Croatia	432	286	0	97	12	0
Turkey	424	347	0	47	2	0
Slovakia	414	229	29	111	39	7
Belgium	411	4	174	143	82	42
Bulgaria	407	249	30	121	7	7
Latvia	407	240	8	78	25	2

Source: EUROSTAT (accessed 21 August 2020)

Wastes generated by such occupational activities as medical waste or waste from firefighting gear contain a larger share of materials containing fluorinated polymers. This may include devices and tubing along with containers for drugs and solutions. All medical waste is considered hazardous and in Europe is disposed of through licensed high temperature incinerators in which the temperature should ensure the complete mineralisation of the polymers to HF.

The overall picture on the incineration of waste containing fluorinated polymers is as follows.

- There is a high risk that fluorinated polymers degrade to both highly volatile and ionic/water soluble PFAS if the combustion temperature is not high enough to ensure the complete mineralisation of fluoropolymers to HF. Also, if degradation is incomplete, highly persistent TFA and HCFs with high GWPs may be formed.
- The levels of volatiles formed in incineration depends on combustion/flue gas temperature, oxygen and residence time.
- It is likely that some fluorinated polymer containing wastes are sent to municipal waste incineration plants. However, there is lack of reliable information on amounts PFAS actually emitted in flue gases from municipal waste incineration plants.
- No information is available on incineration conditions of waste treated outside EU

6.5.3 Kiln incineration of fluorinated polymers and other PFAS wastes

The Yamada and Taylor (2003) study was one of the first to assess the temperatures required for PFOS destruction at more than 900 ºC. The United Nations Environment Programme (UNEP) POPs guide on PFOS is a reference for destruction at 1100 ºC based on the work on PFOS in isolation cited by the United States Environmental Protection Agency (US EPA).

Wang et al. (2015a) demonstrated that PFOS destruction catalysed by calcium could be at much lower temperatures, possibly due to the calcium stripping of the fluorine shifting the reaction equilibrium.

Cement kilns are fairly criticised globally for their fossil fuel use, emissions of CO_2 and nitrogen oxides (NO_x), and the possible formation of chlorinated and brominated compounds (Karstensen, 2012). While fluorine is also a halogen, it behaves entirely differently simply due to the stripping effect of the high proportions of calcium and the permanent capture as calcium fluorine (Ca-F). (Patterson and Dastgheib, 2020, Wang et al 2015a)

Overall, cement kilns are seeking to improve their energy use and emissions, will be in operation for at least some decades longer than society will need to dispose of PFAS waste, and represent the best available technology for its destruction given:

- very large safety margins of temperature and residence times in the normal cement clinker production process;
- catalyses PFAS destruction at lower temperatures in all parts of the process;
- fluorine stripping and permanent capture as inert CaF_2.
- no additional energy expenditure above normal operating conditions and possible energy savings;
- no special modification of the kiln operation needed as fuel is introduced mixed into waste oil;
- no effect on the quality of cement – fluorine has long been used to improve cement hardness.

There are some organisations that are philosophically strongly opposed to cement kilns but on a net-benefit analysis they cannot justify the alternative that has a much higher risk of PFAS emissions, large energy expenditure of hazmat incineration and the cost of neutralising and disposing of the fluoride waste produced.

In conclusion there may be new techniques that can increase the removal of PFAS from incineration exhaust, which would be beneficial to investigate further also in Europe.

6.5.4 Uncontrolled burning of wastes

Some electronic and electrical components such as wire is insulated with PTFE and PVDF. In less developed countries4, the recovery of the copper from this wire, using low-technology methods such as burning, may release PFAS into the atmosphere (Figure 6.4).

Figure 6.4. Low temperature combustion of polymers associated with wire and printed circuit boards along with other e-waste at Agbogbloshie, Ghana, 2018.

Photo: S.Mudge

Studies conducted on backyard burning systems by Lemieux et al. (2000) only observed temperatures in excess of 500 °C on one occasion, suggesting that temperatures will usually be lower. Additionally, there is no information on the emission rates of any fluorinated compounds in their study. Oxygen may be a limiting factor in such systems as well and there may be a wider range of compounds formed than indicated in a study by Aleksandrov et al. (2019). In the absence of further information, this probably represents a conservative estimate of the PFOA and of other volatile PFAS emissions in low temperature combustion conditions, as shown in Figure 6.2.

6.6 Knowledge gaps

Following knowledge gaps have been identified:

- lack of information on actual handling and management of fluorinated polymer-containing products used in many applications, such as in vehicles and electronics, in the production of chemicals and use in renewable energy applications;
- detection limits used in the literature for analysis of emissions;
- number of substances included varies in studies;
- standardisation of monitoring of emissions – sampling and analytics;
- no data available on the current recycling rates of products;
- lack of information on release mechanisms of PFAS from landfills, degradation/transformation in landfill conditions and the fate of leachates;
- lack of information on cost efficient wastewater treatment systems for landfill leachate;
- assessment of past and present sludge/waste management and the disposal practices of users of fluorinated polymers, such as paper factories, carpet factories or factories producing Teflon-coated kitchenware, bearing the large-scale contamination in Baden-Württemberg, Germany in mind (Goldenman et al., 2019);
- situation of landfills where the organofluorine and fluorinated polymer industries have disposed of their waste over the last 50 years;
- situation of landfills where users of fluorinated polymers, such as paper factories, carpet factories or factories producing Teflon-coated kitchenware, have disposed of their production wastes;
- potential export beyond Europe of end-of-life products containing critical raw materials outside for metal recovery.

7 Overall impacts along the lifecycles

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Key messages:

- Potential impacts along the lifecycle of fluorinated polymers that support or conflict with the goals of EU strategies were identified.
  - Circular economy:
    - support: durable, longevity, miniaturisation of products generating less waste;
    - conflict: fluorspar on list of critical raw materials, no information on recycling, minimal recycling identified.
  - Low carbon economy:
    - support: use in renewable energy applications, reduced energy need – lighter vehicles, etc.;
    - conflict: feedstocks with the potential to emit GHG used in production.
  - Zero Pollution Ambition/toxic-free environment
    - support: longevity;
    - conflict: use of toxic feedstocks potentially emitted in production, use and end of life.
  - Other considerations may include benefits to human health such as high performing medical utensils and diagnostic instruments, protective clothing for occupational use, or use of protective textiles to minimise risks for medical staff and patients from exposure of infectious agents in medical treatment.

7.1 Approach

In this chapter impacts are analysed in the light of EU policies, which were introduced with the European Green Deal in 2019 by European Commission President Ursula von der Leyen. As a consequence of the European Green Deal, a number of strategies and action plans to reduce human and environmental health degradation have been launched, including on the CE, resource efficiency and raw materials, the low-carbon economy and the Zero Pollution Ambition for a toxic free environment.

- The CE aims to foster an economy that retains as much of the value of materials as possible, for as long as possible (EEA, 2016). To achieve a transition to a CE, action needs to address all products' lifecycle stages, and therefore needs to go beyond waste management and improved recycling. Also the growing waste generation from renewable energy sets need to implement CE principles by applying circular business models to maintain producer responsibility and facilitating reuse and material recovery from renewable energy applications after use .(EEA, 2021)
- The low-carbon economy aims to minimise emissions of GHG to the atmosphere. Focus areas include shifting from fossil fuels to renewable sources of energy, such as wind and solar power, and promotion of energy efficient products and processes.
- The Zero Pollution Ambition for a toxic-free environment, and the Chemicals Strategy for Sustainability towards a toxic-free environment (CSS) (EC, 2020), both aim to avoid harm from pollution to people and the environment. The CSS emphasises the need to prevent further pollution by substances of concern, particularly for those that accumulate or cause effects that accumulate in people or the environment. Persistent chemicals such as PFAS (EC, 2020b), bioactive chemicals, such as endocrine disrupters, and mixtures of chemicals (EC, 2020c) are highlighted examples.

The New Circular Economy Action Plan was launched in 2020 and focusses on sustainable resource use, especially in resource-intensive and high impact sectors such as electronics and information and communications technology (ICT); batteries and vehicles; packaging; plastics; textiles; construction and buildings; food; water and nutrients. Fluorinated polymers are, with the exception of the food, packaging, water and nutrients sectors, relevant to these sectors. Examples of measures mentioned are as follows:

- make sustainable products, with a focus on the safety of consumers and the environment;
- ensure less waste;
- make circularity work for people, regions and cities;
- assess potential impacts of recycling practises;
- lead global efforts on the circular economy.

The New Circular Economy Action plan contains a legislative initiative proposal to widen the Eco-Design Directive to the broadest possible range of products rather than just energy-related ones. The new Action Plan announces initiatives along the entire lifecycle of products, targeting, for example, their safe and sustainable design, promoting CE processes, fostering sustainable consumption, and aiming to ensure that resources used are kept within the EU economy for as long as possible. It introduces legislative and non-legislative measures targeting areas in which action at the EU level brings real added value.

In relation to the EU raw materials initiative, the European Commission has created a list of critical raw materials that are important to the European economy but are also associated with supply risks (European Commission, 2020). One of the listed materials is fluorspar, which is used as input in the production of fluorinated polymers. Increased recycling would be one way of reducing dependence on imports, as well as improving material efficiency and reducing the lifecycle environmental impacts of applications. Currently, fluorspar is recycled but only to a small extent since it is transformed to other chemicals when used, and recycling is currently complex (British Geological Survey, 2010).

This chapter builds on findings presented in previous chapters. The outcome of the analysis is presented for different stages of the fluorinated polymer lifecycle. Benefits and challenges related to the circular economy and resource efficiency, climate effects and toxic-free environment are assessed qualitatively.

7.2 Focus on the circular economy, resource efficiency and the EU raw material strategy

Fluorinated polymers can provide useful properties to products used in various sectors. According to information presented in literature (Améduri, 2020, 2018; WOOD, 2020), fluorinated polymers can, for instance, contribute to material or energy savings, while some of their uses can be considered essential for society with regard to protecting human or environmental health. In this context, a use that is essential to society providing, for example, important health functions, is one for which the fluorinated polymer cannot be substituted by other materials, products or services delivering comparable performance at the time of assessment. Conversely, a non-essential use, whether beneficial or not, is one that can be replaced with a non-fluorinated product or service with a comparable performance. With time, innovation of alternatives may render previously essential uses, non-essential. Some examples of fluorinated polymer materials which have a range of non-essential to essential uses are provided in Cousins et al. (2019) while a wider list of fluorinated polymers uses is provided in Glüge et al. (2020). Some examples of useful fluorinated polymers – but not necessarily essential ones – are presented below.

- Electronics: dielectric properties of fluorinated polymers have enabled the miniaturization of components and final products, and hence to savings in raw materials. Fluorinated polymers can also provide fire safety; high transmission speeds; and ease of installation and reliability of wires, as well as optical and data transmission cables. As an example, a report published by the United States fluoropolymer industry (WOOD, 2020) states that the use of fluorinated polymers in electronic applications may prolong their lifetimes by up to three times. The calculations and boundary conditions for this statement have not, however, been evaluated in this report.
- Transport: prolonging component/product lifetimes in the automotive and aerospace industries due to fluorinated polymers having high resistance against heat, cold, fire, smoke, aggressive fluids, fuels, humidity, vibrations and compressions. Improved functionality due to high reliability, engine efficiency, weight reduction and emission control, and fuel efficiency. The report published

by the United States fluoropolymer industry (WOOD, 2020) presents the following examples of benefits in two applications: in cars, the use of fluorinated polymers contributed to a 48% increase in fuel efficiency, calculated on the average fuel use per kilometre travelled in American cars in 1980–2016 (WOOD, 2020). In aerospace, a 93% corrosion reduction in cargo bays and avoided friction damage in helicopters has been demonstrated for the use of a specific product (WOOD, 2020). Again, the calculations and the boundary conditions used for these benefits have not been evaluated in this report.

- Medical utensils: prolonging lifetimes of surgical implantable devices, the reduction in complications and failures due to clogging of medical pumps and catheters. Fluorinated polymer textiles protect medical staff and patients from exposure to infectious agents. Use of fluorinated polymers provides improved reliability in the use of such medical appliances as X-rays, and magnetic resonance imaging (MRI) and computed tomography (CT) equipment (Améduri, 2020, 2018; WOOD, 2020).
- Chemical industry: reduction of corrosion and leaks, lower maintenance, safety (Améduri, 2020, 2018; WOOD, 2020).
- Building sector: durable materials that prolong lifetimes, increase fire safety and reduce maintenance needs (Améduri, 2020, 2018; WOOD, 2020).

In Table 7.1 measures or actions for achieving CE solutions listed in the new Circular Economy Action Plan are analysed for different lifecycle stages based on the information gathered in Chapters 3–6. Circular economy solutions identified in the use phase were mainly related to material and energy savings due to high functionality, safety and miniaturisation, the last of which also leads to the generation of less waste. Fluorspar is, however, a critical raw material and the recycling rate is low due to the dispersed use of fluorinated polymers in applications. For many CE measures or actions no information was available. The current practice of recycling of PTFE into microplastic (micro powder) needs detailed assessment in particular since most uses are dispersive, releasing the PTFE microplastic into the indoor or wider environment.

The expected impact was categorised on the basis of expert judgement (Table 7.1). The reasoning for the categorisation is explained within the table. Where there is uncertainty associated with the lack of information about supporting circular economy solutions, this is mentioned.

Table 7.1. Measures and action mentioned in the new Circular Economy Action Plan, including raw material initiatives along the fluorinated polymer lifecycle.

Measure/action	Mining	Production	Use	End of life
Improving product durability, reusability, upgradability and reparability, addressing the presence of hazardous chemicals in products, and increasing their energy and resource efficiency	not relevant	no data	yes, increased durability increases product lifespan (less waste)	no/yes, less waste due to miniaturisation
Increasing recycled content in products, while ensuring their performance and safety	not relevant	no data	no data	no, assessment of micro-PTFE (micro powder)
Enabling remanufacturing and high-quality recycling	not relevant	no data	no data	no
Reducing carbon and environmental footprints;	not assessed	probably	maybe, as a result of prolonged lifetime	no data
Restricting single use and countering premature obsolescence	not relevant	not relevant	not relevant	not relevant
Introducing a ban on the destruction of unsold durable goods	not relevant	no data	no data	no data
Incentivising products as a service or other business models through which producers keep the ownership of the product or	not relevant	not relevant	no data	no data

Measure/action	Mining	Production	Use	End of life
responsibility for its performance throughout its lifecycle				
Mobilising the potential of digitalisation of product information, including solutions such as digital passports, tagging and watermarks	not assessed	no data	no data	no data
Rewarding products based on their different sustainability performance. Focus on use of sustainable raw materials, substitution of materials to reduce environmental impact, energy saving	fluorspar is a critical raw material	use of feedstock with global warming and/or ODP, toxic characteristics	some products (renewable energy)	no data

7.3 Focus on the low carbon economy

Fluorinated polymers play an important role in components for high-tech products and renewable energy devices – semiconductors, displays, photovoltaic panels, fuel cells and lithium-ion batteries. As an example, the worldwide market for lithium-ion batteries is expected to grow from 78 gigawatt hours (GWh) in 2016 to 210 GWh at a compound annual growth rate of plus 13% between 2016 and 2025, with the highest growth expected in electric vehicles and industrial applications (Pillot, 2017). As the demand for electric vehicles has grown rapidly in recent years and the lifespan of their batteries is roughly 10 years, growing lithium-ion battery waste streams are expected in the near future.

Challenges related to the expected growth of these markets are related to several aspects along the lifecycle:

- raw material production;
- GHG emissions during the production process;
- GHG emissions at the end of a product's life.

In the production phase, there are risks of emissions of GHG and ODS (Chapter 4.1). In the literature, there is no information on measured or calculated emissions related to different fluorinated polymer production processes. Accurate and transparent reporting of emissions from production processes is widely lacking and thus does not allow for the monitoring and verification of reduction targets.

Reporting of GHG emissions at the end of life is often neither accurate nor transparent. Furthermore, exports of end-of-life products for further (re-)use and/or extraction of materials to areas without stringent environmental policies and standards put efforts for reductions of the carbon footprint at risk.

7.4 Focus on safety

Safety is a term used to describe either the potential risks or the observed impacts of a stressor on human or environmental health. In this context the stressor may be one or multiple chemicals. In addition, there may be other kinds of hazard, such as physical, microbiological and elements of biosafety, but these are not described here. In general terms the size of the risk/impact is determined by the hazard, how dangerous it is; and the exposure, the likelihood of being exposed to the danger: Risk = Hazard x Exposure.

There are different types of risks/impacts, since chemicals have different kinds of toxicity or hazards. Examples of hazards are carcinogenicity; mutagenicity; reproductive and developmental toxicity; sensitising and neurodevelopmental effects; metabolic; cardiovascular; and endocrine disruption. Typically, toxicological testing will determine which types of hazards chemicals have, and at which concentration level the effects will start to occur. Different species, for example, humans and animals, or between biota in an ecosystem, may experience different effects; effectively the chemicals may have different hazards for different species. The level at which the effects start to show can also differ between species and at different life stages – a developing child, for example, tends to be more vulnerable to chemical stressors than fully developed adults. People and ecosystems that are exposed to additional stressors, including heat stress, may also be less resilient in coping with the chemical stress and therefore lower levels may create impacts.

Exposure says something about how much of a chemical a person or living organism is exposed to. Exposure is a combination of the concentration levels and how frequent the exposure to the chemical(s) is(are). Chemicals that are persistent will accumulate either internally in the organism (bioaccumulative) or externally in the environment (persistent and mobile chemicals). Either will lead to increasing exposure, and thereby risk. Persistency is a combination of intrinsic properties of the molecule and the capacity of the system it is dispersed in to degrade it. This capacity may change depending on physical conditions such as temperature/climate, light, access to oxygen, surfaces that bind the chemicals, mixing of a system due, for example, to wind, and on biological conditions, such as microbes and other biota which may help to degrade the chemicals.

PFAS appearing as impurities or additives in, or as degradation products of fluorinated polymer products are examples of substances that have lately created high concern. This is due to a number of considerations and the characteristics of PFAS (Kwiatkowski et al., 2020): PFAS consist of more than 5 000 chemicals which are or form persistent degradation products; which accumulate in people and/or the environment; some PFAS are persistent and mobile in air and water; others stick to surfaces such as soil and bioaccumulate in people and biota. Furthermore, the large majority of tested PFAS are somewhat toxic either to humans, biota or Earth systems and are difficult to remove from contaminated materials, soil and water.

Identifying hazardous materials in waste streams is of great importance so that they can be removed prior to recycling. The Zero Pollution Ambition for a toxic-free environment calls for the risks posed by very persistent chemicals to be addressed rapidly. Potential hazards and their expected impacts are mainly analysed qualitatively because data are lacking on both hazards and exposure to the majority of PFAS, and particularly the risks to ecosystem health.

In the production of fluorinated polymers, feedstock chemicals containing PFAS and other substances of concern are used, including carcinogens. Toxic degradation products and by-products are also formed during the manufacturing process. Several chemicals with both high GWP and ODP are also used, but there is hardly any monitoring of these substances or reporting of emission data in the literature.

Emissions to water, soil, air and the wider environment of a large number of poly- and perfluorinated highly volatile and water-soluble by-products have been reported at sites close to fluorinated polymer production plants. The fluorinated processing aids used also create concerns. Banned toxic chemicals, such as PFOA, have been replaced to ensure decreased persistency and bioaccumulation. However, the modified molecular design, with higher volatility and higher K_{AW} values, lead to higher emissions to the atmosphere.

During fluorinated polymer production, PFAS emissions of PFOA and PFNA substitutes to air, water and soil are estimated to be about 120 t/year for Europe. The environmental degradation of fluorinated production aids, emitted during fluorinated polymer production, can lead to the formation of PFCAs and PFSAs, unstable intermediates, all forming a complex mixture of potentially harmful chemicals emitted to the environment. Biological uptake has been shown in both flora and fauna, further endangering wildlife and human health through food production. Drinking water can be polluted when some of the very water-soluble alternatives to PFOA enter the soil and water systems.

Moreover, occupational health and safety is important to consider due to the potentially toxic feedstocks and end-products, and degradation products and by-products formed during the polymer production, manufacturing and use. Inhalation of pyrolysis products of PTFE has been reported to lead to serious toxic impacts such as pulmonary edema and pneumonitis, and flu-like symptoms, sometimes called polymer fume fever (Johnson, 2018a). In animal studies, several other effects are seen such as tumors and higher mortality. In addition, studies have reported cases of pulmonary injury, for example in workers in the building industry exposed to waterproofing spray products containing fluorinated polymers (Scheepers et al., 2017; Lazor-Blanchet et al., 2004). In some cases, polymers contain a large proportion of oligomers, for example, polychlorotrifluoroethylene may consist mainly of trimers (55%) and tetramers (45%) of chlorotrifluoroethylene (Johnson, 2018a). These are very small molecules consisting of only three and four repeat-units, and thus oligomers which just qualify as polymers according to the ECHA definition (Section 2.1). According to several animal studies, summarised by Johnson (2018a) these oligomers are taken up on inhalation, bioaccumulate and form toxic degradation products.

In the use phase, the impacts are application specific. At the end-of-life stage there is a lack of information about impacts due to the dispersive use of fluorinated polymers in a variety of applications in transport and energy production as well as in, for example, coatings and insulation materials in buildings.

There is a dispersed use of products containing fluorinated polymers in numerous applications but the exposure of consumers during use is highly application specific. Examples of exposure routes from some applications include:

- inhalation of volatiles/aerosols emitted from products: overheating of kitchen utensils, spaying of impregnating agents containing fluorinated polymers, and indoor dust;
- direct human exposure from PFAS in food-contact materials leaching into food;
- dermal contact through textiles and cosmetics/personal care products but this exposure route is considered minor compared to dietary exposure and inhalation of indoor dust;
- emissions to the environment: intentional use of fluorinated microplastics, such as teflon used to lower friction in, for example, bicycles, other metal lubricants, and personal care products such as shaving foams (DK EPA, 2018), may contribute to emissions of non-degradable, persistent microplastics to the environment. Degradation of fluorinated polymers during use includes, for example, the release of fibres containing them from textiles during washing, and these end up in wastewater.

Furthermore, the risk of the dispersive use of micro-PTFE (micropowder), which amounted to about 10 000 tonnes of irradiated micropowder in 2010, also need to be assessed considering that PTFE does not degrade in the environment for centuries and might accumulate.

Some 8 300 tonnes of waste per year arise from consumer products containing fluorinated polymers, of which an estimated 1 280 tonnes is PTFE used in cooking and baking utensils (Chapter 4). Waste from consumer products is either incinerated or disposed of in landfills.

When waste containing fluorinated polymers is incinerated there is a risk that under certain conditions – low temperatures, low oxygen supply and short residence times in the burner – the polymers may degrade to TFA. This is a breakdown product of several HCFCs, regulated under the Montreal Protocol on Substances that Deplete the Ozone Layer, as well as several saturated and unsaturated HFCs, which are regulated under the EU F-gas Regulation 517/2014 and, in the case of saturated HFCs, addressed by the Kigali Amendment to the Montreal Protocol at an international level. Trifluoroacetic acid is water soluble and is readily washed out of the atmosphere by rain and enters the sea, rivers, lakes and groundwater, but generally it has low toxicity for aquatic organisms. No estimates of the emissions of TFA, particularly from the incineration of waste containing fluorinated polymers, has been reported in the literature as there are other sources of TFA emissions. No dedicated measurements of TFA and other small organofluorine molecules have been reported from incineration experiments, which largely focus on PFOS and PFOA monitoring. Considering that in pilot studies of co-incineration of PTFE, the fluorine mass balance from HF was only 56% at 870 ˚C and a 4 second residence time, and 78% at 1 020 ˚C and a 2.7 second residence time (Aleksandrov *et al.*, 2019), other potential organofluorine releases like TFA and CF_4 should be assessed in addition to the potential formation of other inorganic fluorides.

Furthermore, chemical recycling, for example pyrolysis, of plastic is increasingly promoted and due to their dispersive uses, fluorinated polymers will likely end-up in chemical recycling processes. As a result, the material flow of fluorinated polymers entering plastic pyrolysis and chemical recycling and associated releases of fluorinated GHG and ODS should be analysed.

PFOA and other PFAS can be emitted from municipal waste incineration. No reliable European data have been found but incineration of waste has increased in Europe since the ban of the disposal of biodegradable waste at landfills (EUROSTAT, 2020). Nonetheless, it can be assumed that PFOA and a broad range of other PFAS are formed, with large differences in emission volumes between the European countries, due to the burning of domestic waste with different emission factors. Additionally, the amount of fluorinated polymers present in burned waste may vary due to differences in the composition of waste collected across European countries.

The landfilling rate of municipal waste in Europe has decreased from 44% in 2006 to 23% in 2017. Annual emissions of PFAS from consumer products disposed of in landfill are estimated to be 0.43–3.7 tonnes in Europe (calculated based on population in 37 European countries). However, for a reliable assessment of releases from landfills more data from standardised monitoring programmes are needed. The emissions to air, soil and water from landfills depends on measures taken at the landfills to prevent rainwater entering the waste and minimising water transport and gas emission from the landfill body. In old landfills, seals are often missing, and leakage may occur. Waste from applications containing fluorinated polymers from the transport, chemicals and energy production sectors may, at end of life, end up in smelters if used as coatings or integrated parts in metals, or in shredder waste if used in wires or cables from, for example, vehicles.

Wastewater treatment plants are an important point source of PFAS to the surrounding environment; studies show that treated wastewater contain some level of PFAS. There is, however, a lack of information on fluorinated polymers influx to wastewater plants, and efflux of PFAS from fluorinated polymers in sludge, water and to air from wastewater treatment plants. Moreover, microplastics from the intentional use of fluoropolymers in, for example, consumer products such as personal care products and bicycle lubricants, and from degradation and abrasion of fluorinated polymer materials and surfaces may end up in wastewater plants from where these pollutants can further end up in water, soil and air. The regulation of fluorinated polymers and intentional uses of microplastics are further described in Section 8.2.

7.5 Examples of impact reductions from the replacement of fluorinated polymers

In many applications, the properties of fluorinated polymers make their replacement challenging in terms of equal performance of materials. Only a few studies have been found in literature of the reduction of environmental impacts as a result of replacing fluorinated polymers. Articles, such as on alternative materials for fluorinated polymers in fuel cells for the production of renewable energy, focus on their replacement for cost reduction purposes.

Box 7.1 provides an example of replacing materials containing fluorinated polymers in photovoltaic panels, thereby reducing their environmental impacts once they become waste. The fluorinated polymeric backsheets are used to protect the panels from moisture and adverse weathering and lengthen their operational lives (Figure 7.1). In Section 8.4.1.5, the use of PTFE in photovoltaic panels in a circular and non-toxic economy is discussed further.

Box 7.1 Comparison of end-of-life treatment of photovoltaic panels containing fluorinated and non-fluorinated polymers

The production of solar energy using photovoltaic panels, which have a lifespan of 25–30 years is expected to increase significantly in coming years. In 2016, global photovoltaic waste for the year was estimated to be 45 000 tonnes and it is likely that this will increase to 1.7 million tonnes by 2030 and 60 million tonnes by 2050 (Aryan et al., 2018). Fluorinated polymers are used as a protective layer in the backsheet of photovoltaic panels, making up roughly 3% of the backsheet material's weight or approximately 0.2% of weight of the whole panel.

A lifecycle analysis (Aryan et al., 2018) compared the environmental impacts of two potential end-of-life management scenarios – incineration and pyrolysis – of fluorinated and non-fluorinated backsheets. In the incineration scenario, the non-fluorinated backsheets showed environmental benefits in 11 of 12 impact categories evaluated – the exception being for GWP. The corresponding pyrolysis scenario showed better environmental performance for the non-fluorinated backsheets in 8 of 12 categoires. However, the pyrolysis scenario revealed a high release of HF and the presence of significant amounts of fluorine both in the form of toxic halogenated hydrocarbons and aromatic compounds in the pyrolysis products. This suggests that pyrolysis for the non-fluorinated backsheets is not as environmentally feasible as it is for of backshees containing fluorinated polymers. Additionally, pyrolysis is generally less attractive from an economic viewpoint.

The lifecycle study concludes that non-fluorinated backsheets containing bio- or polyethylene terephthalate-based alternative materials are to be recommended. For fluorinated backsheets, the preferred management option is incineration together with other waste materials in order to comply with environmental emission requirements. In addition, it is proposed that the producers should provide information on the materials in the backsheet, using, for example, ecolabels, to ensure the waste receives appropriate end-of-life treatment.

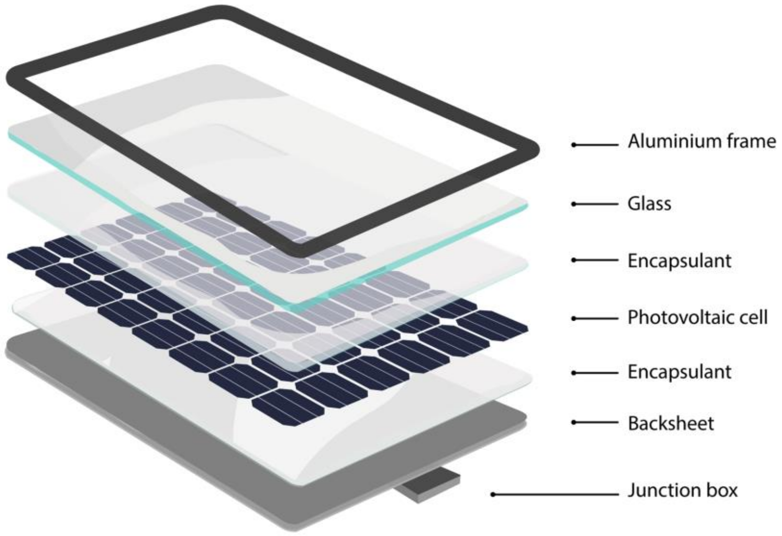

Figure 7.1. Ilustration of a photovoltaic panel.

Source: Aryan et al 2018

8 Risk governance of fluorinated polymers

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Key messages:

- The assessment of the possible risks of fluorinated polymers only during the use phase is too shallow in the framework of a CE and therefore the whole lifecycle should be considered.
- The example of PTFE illustrates that PTFE is difficult and costly to recycle or to repair. Using PTFE could hamper circular potential and is not line with the ambitions of the Commission in the Chemicals Strategy for Sustainability.
- Within the overall process of risk governance, there are different options to implement criteria for essential use.
- There is a need to unambiguously define criteria or considerations for essential use to enable application of the concept in decision making processes.

8.1 Introduction

This chapter examines to what extent the main elements in current risk governance of fluorinated polymers are in line with a CE, a low carbon economy and a toxic-free environment strategy, with a specific focus on the circular economy, using a systematic approach based on the International Risk Governance Council (IRGC) risk governance framework. More specifically, it is discussed the question whether changes are needed in the governance of substances of (potential) concern, and specifically for fluorinated polymers. Risk governance marks out institutional structures and sociopolitical processes that guide and restrain collective activities of a group, society, or international community to influence or direct the course of events or people's behaviour when dealing with risk issues (IRGC, 2017; Renn and Klinke, 2016; Klinke and Renn, 2012), Further, the concept of essential use has been introduced in the CSS. In this chapter, no difference is made between the various types of fluorinated polymers, and for illustrative purposes some examples are added.

The risk governance of fluorinated polymers in a circular economy should be seen as part of the broader discussion on the European Green Deal. As mentioned in Chapter 1, a set of policy objectives have been formulated in the European Green Deal by the European Commission with the overarching goal of making Europe climate neutral by 2050 (Commission, 2019). It provides an action plan to:

1. boost the efficient use of resources by moving to a clean CE and;
2. restore biodiversity and prevent pollution from being generated.

In a CE the amount of harmful substances will preferably be lower and no harmful substances will be released from the technosphere (production, consumption and end-of-life). Both a chemical of interest and the related product come with their own lifecycles. Chemical lifecycles span the entire supply chain for harvesting resources, synthesising, and processing a chemical, and related waste handling. Product lifecycles do not only cover the considered and other chemicals included in the same product with their respective supply chains, but also include resources used and emissions related to energy converted during, for example, product manufacturing, use, and end-of-life handling including recycling (Fantke et al., 2020).

In Section 8.2 an overview of challenges in the regulation of fluorinated polymers is given, and in Section 8.3 a short introduction to the IRGC framework is presented. This is continued with a discussion of whether fluorinated polymers fit in a CE (Section 8.4) and in what way the concept of essential use may support risk governance of fluorinated polymers and the consequences of specific implementations of the concept (Section 8.5).

8.2 Challenges in the regulation of fluorinated polymers

PFAS have become a matter of regulatory and public concern due to their persistency, bioaccumulation, and possible ecological and human health effects. To date, there is both vertical and horizontal legislation that apply to PFAS. Vertical regulations are those that address part of a lifecycle, including work-place exposure, emissions during production, risks during use, or the waste-management and end-of-life phases. The vertical regulations should comply with the REACH requirements which is a horizontal legislation.

A (non-exhaustive) summary of different international and European regulations on PFAS is presented in the Annex 3.

Fluorinated polymers are known to be extremely persistent and there is evidence that they do not degrade under environmental conditions (Ameduri, 2020). In addition, the use of the different fluorinated polymers might cause several environmental and human health risks throughout their lifecycle(s). First, the production of some fluorinated polymers, such as fine powder PTFE and PVDF, is intimately linked to the use of legacy and novel PFAS, for example, ether-based PFAS as emulsifiers during emulsion polymerization process. Most of PFAS-based processing aids are considered environmental toxicants of potential concern, of which some have been classified as SVHCs (Gebreab et al., 2020, Rice et al., 2021). Second, a variety of other PFAS, including monomers and oligomer impurities (unintentional non-polymer PFAS by-products) are emitted during the production, processing, use, and end-of-life treatment of fluorinated polymers. In general, polymer products contain residual monomers, oligomers, impurities, transformation products and often their properties drive the overall hazard of the polymer products (Chapter 4). In addition, intentionally used fluorinated polymer microplastics (PTFE microparticles) (Sections 5.5 and 5.6) may generate nanoplastics as (bio)degradation products of these microplastics that may have higher bioaccumulation potential inducing potentially adverse health effects. There are further concerns regarding the safe disposal of fluorinated polymers and their associated products and articles at the end of their life cycle. While recycling and reuse of fluorinated polymers is performed on some industrial waste repositories, only limited options exist for their recycling from consumer articles (Sections 6.1 and 6.2) (Lohmann et al., 2020). Regulating fluorinated polymers is a complex task because it needs to address all phases in the lifecycle of these chemicals.

Recently, under the REACH regulation the national authorities of Denmark, Germany, the Netherlands, Norway and Sweden have started preparing a joint REACH restriction proposal on PFAS as a group to limit the risks to the environment and human health from their manufacture and use. These authorities prefer a broad restriction covering all different PFAS substances and uses, instead of separate legislation on specific PFAS or specific uses. The broad restriction would limit as many (non-essential) uses as practically possible. This would have the greatest impact on preventing and thereby minimising human and environmental exposure to PFAS. It would also include currently unknown PFAS and uses as well as fluorinated polymers and would prevent regrettable substitution of restricted PFAS by other PFAS (RMOA, 2021 ([38])).

More specifically on fluoropolymers, while polymers are exempted from registration and evaluation in the EU under Article 2(9) of the REACH Regulation (EP and Council, 2006) they are not exempted from restriction or authorisation, and the monomers from which a polymer is formed must be registered (REACH Article 6(3)). Overall, the REACH Regulation does not exclude the future possibility of a requirement to register polymers. The Regulation has laid down that the European Commission may present criteria to characterise ‘polymers of concern (PLC)’, justify the selected criteria and may also present criteria for polymers of high concern (PHC); to propose solutions for their grouping as well as registration requirements (PRR) under REACH; and to estimate the potential risks posed by such PLCs in comparison to other chemicals based on available scientific evidence on their hazards and exposure

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[38] Assessment of regulatory needs list - ECHA (europa.eu)

(European Commission, 2018). In addition, the derogation from labelling of polymers implemented in the CLP based on a lack of bioavailability as an essential determinant for the lack of hazard concerns.

Polymers are also regulated (directly as the final product and indirectly via the monomers, additives and processing aids) by their use in specific products, such as food-contact materials (FCM) legislation EC 10/2011 for plastics. Meanwhile any other chemical in the polymer or in the finished material or article should comply with the FCM framework regulation (EC 2004/1935) which sets out the general principles of safety and inertness for all FCMs. This includes all FCMs in which fluorinated polymers may be used, such as food plastics, processing equipment, coatings, paper and board, waxes, inks, and elastomers. Other regulations which address products in which fluorinated polymers may be used include medical devices (EU Regulation on Medical Devices (MDR) (2017/745) and Regulation on In-Vitro Diagnostic Devices (IVDR) (2017/746)), cosmetics, pharmaceuticals, construction materials and toys.

To date, there is no regulation under REACH directly on fluorinated polymers. Intentionally used fluorinated polymer microplastics are, however, covered in the REACH microplastics restriction if they are placed on the market in a physical form consistent with the microplastics definition, i.e. solid particles <5mm in size. A restriction dossier concerning the use of intentionally added microplastic particles to consumer or professional products of any kind is submitted and reviewed by the Committee for Risk Assessment (RAC) and the Committee for Socio-economic Analysis (SEAC). Currently the proposed microplastic restriction is awaiting adoption by the European Commission. All uses of polymers with these properties are considered to pose a risk that is not adequately controlled if they are inevitably released to the environment when used. A much greater share of microplastics, however, is from unintentional releases. The microplastics dossier does not differentiate between different plastics/polymers in this analysis.

At an international level, fluorinated polymers are not eligible for PLC exemption from the pre-manufacture notification (PMN) review process (US EPA, 2019). In Japan, fluoro groups are designated as reactive functional groups (RFGs) preventing a polymer from being a PLC.

Risk assessment of chemicals under REACH can be performed in several ways, depending on the hazardous properties of the substance. Fluorinated polymer products can change their form during different lifecycle stages. For these reasons, conventional risk assessment approaches for chemicals may need to be modified for polymers. As the hazardous properties of fluorinated polymers are complex and, in many instances, uncertain, for example, issues surrounding physical availability, bioavailability, persistence, and degradation, a range of risk assessment paradigms could be considered, such as PBT/vPvB perspectives (non-threshold approach) and a case-by-case approach.

The hazardous potential of fluorinated polymers needs to be assessed on a case-by-case basis taking into account all relevant physical, chemical, and fate properties. In a case-by-case approach for risk assessment of fluorinated polymers, the question is what can be referred to as their extreme persistence in the environment and the potential for this to result in a non-reversible pollution stock associated with potential for environmental and/or human health risks. Overall, substantial data gaps with respect to exposure to as well as toxicity of fluorinated polymers impede risk assessments.

Currently, most studies on the potential risks of fluorinated polymers are limited to the use phase. The lack of provisions covering the whole lifecycle assessment (production/use/waste management) of fluorinated polymers and/or their feedstocks leads to insufficient regulation as shown in previous chapters of this report. Therefore, in the case of fluorinated polymers, the application of a risk governance strategy for the entire lifecycle, from development to end-of-life, is necessary to prevent potential risks.

8.3 The IRGC risk governance framework

The IRGC Framework recommends an holistic, multidisciplinary and multi-stakeholder approach to support the identification, assessment and management of risks. Furthermore, it supports processes that aim to provide and structure scientific evidence about a risk in a societal context. It helps decision makers analyse the major ambiguities and controversies that may affect the management of such risks (IRGC, 2017).

Figure 8.1 shows the IRGC risk governance framework. There is a clear division between understanding a risk, generating and evaluating knowledge, and deciding about a risk, decision making and management (IRGC, 2017, Renn, 2009). The risk governance process is structured into four distinct phases as follows:

1. The first phase is the pre-assessment of a risk. This captures and describes the various perspectives of stakeholders and society, regarding, for instance, the use of fluorinated polymers, including current approaches to the regulation of these substances. Moreover, this phase includes determining scientific conventions, looking for information through an early warning system and screening information.
2. The second phase comprises risk and concern assessment. The concern assessment includes an assessment of socio-economic impacts, an analysis of risk perceptions and of wider societal concerns.
3. The third phase focusses on knowledge characterisation and risk evaluation. In particular, risk information can be characterised as simple, complex, uncertain or ambiguous, or, most likely, a combination of these. This has implications for stakeholder participation and risk management strategies.
4. Finally, the fourth phase of the framework focusses on risk management decision making – taking action to reduce and control risks. Risk management includes the generation, assessment, evaluation and selection of appropriate management strategies, decisions about a specific strategy and alternative options, and the implementation and enforcement of such strategies. Cross cutting issues in the framework are stakeholder participation and communication.

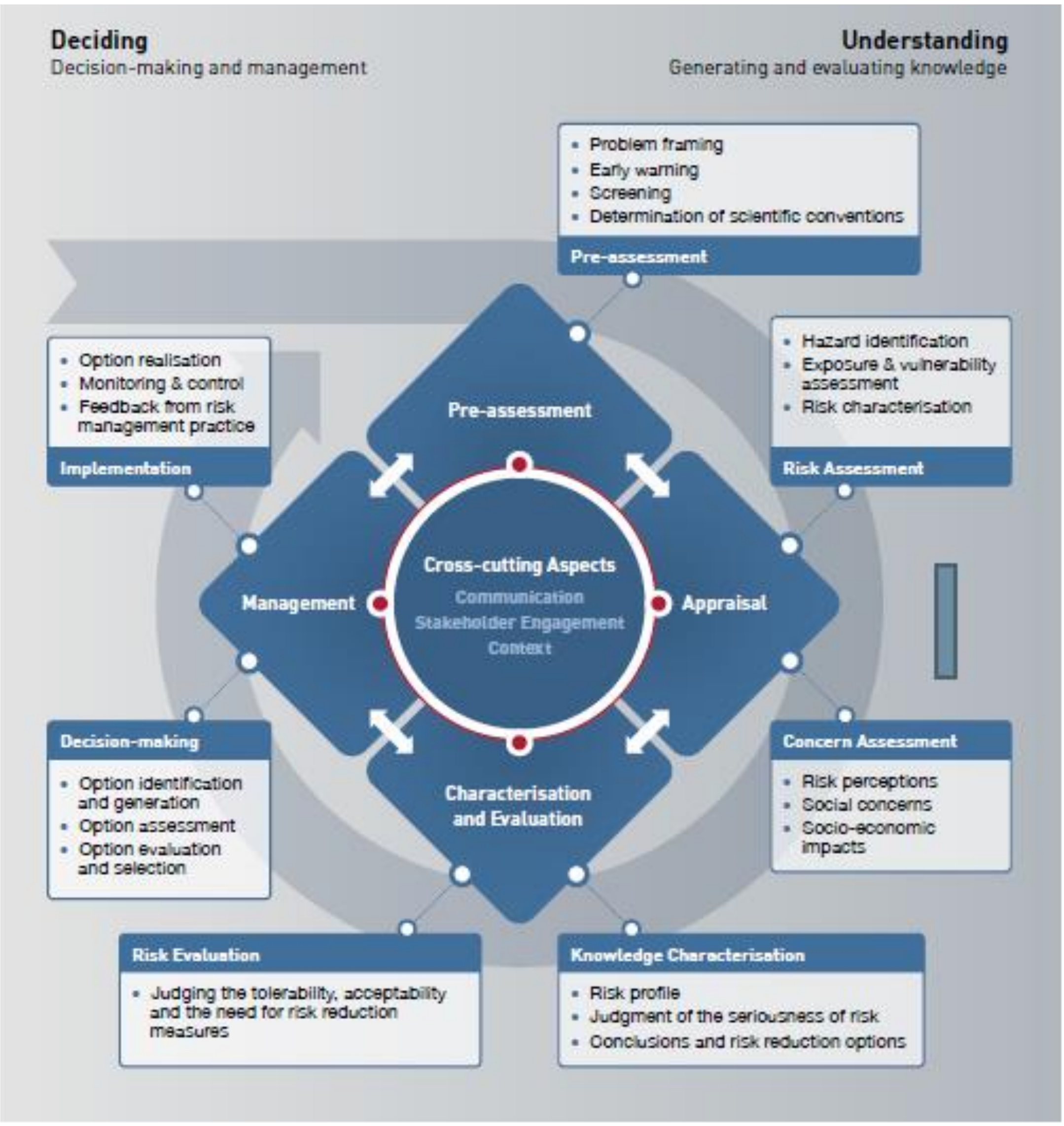


Figure 8.1. The IRGC risk governance framework.

Source: International Risk Governance Council (2017)

8.4 Assessing PTFE in the risk governance process in the context of a circular economy

As fluorinated polymers are diverse to assess, this section considers PTFE, the most used fluorinated polymer, as an example. The first focus is on PTFE in a CE. In Section 4.1.5 the entanglement between using PTFE in a CE and a low-carbon and toxic-free economy is described. These concepts are obviously linked, as one of the main drivers for a CE is to drastically cut GHG emissions, driving Europe towards the goals set by the IPCC Paris Agreement (Foundation, 2019). Additionally, a toxic free/zero pollution approach is necessary for achieving a truly sustainable CE.

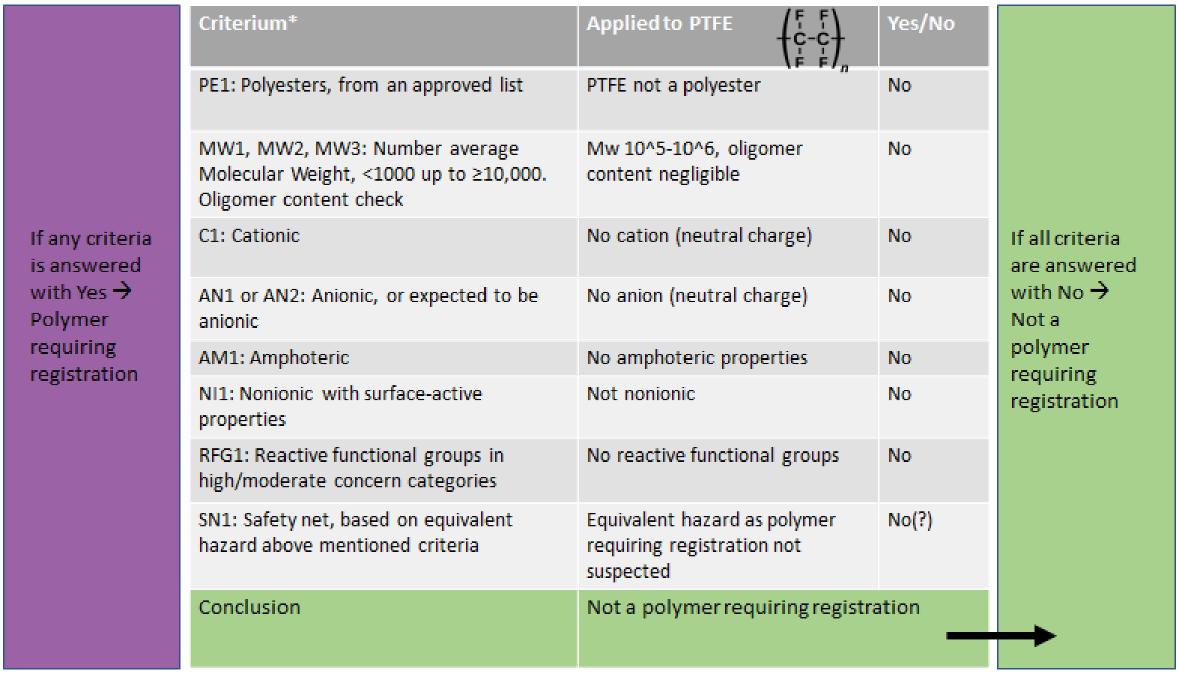
Important characteristics for realising a CE are also found at the heart of the IRGC framework: communication, stakeholder engagement and context (Figure 8.1).

8.4.1 Pre-assessment phase

PTFE is first assessed using criteria suggested by the working group on identifying polymers requiring registration under REACH (DG Environment (COM), 2020). This assessment is for the use of the polymer only, the (circular) system or lifecycle of the polymer is not considered. Next a short evaluation of PTFE in a CE is described. This is set out against the different parts of the IRGC framework. The link with a low-carbon toxic-free economy is described subsequently.

8.4.2 Appraisal phase

The assessment of PTFE by the suggested criteria identifying polymers requiring registration ('polymers of concern') is shown in Figure 8.2. From this assessment it follows that PTFE is not a polymer requiring registration when being considered in the *use phase* only.



If any criteria is answered with Yes → Polymer requiring registration

Criterium*	Applied to PTFE $\left(\begin{array}{c}F\quad F\\ -C-C-\\ F\quad F\end{array}\right)_n$	Yes/No
PE1: Polyesters, from an approved list	PTFE not a polyester	No
MW1, MW2, MW3: Number average Molecular Weight, <1000 up to ≥10,000. Oligomer content check	Mw 10^5-10^6, oligomer content negligible	No
C1: Cationic	No cation (neutral charge)	No
AN1 or AN2: Anionic, or expected to be anionic	No anion (neutral charge)	No
AM1: Amphoteric	No amphoteric properties	No
NI1: Nonionic with surface-active properties	Not nonionic	No
RFG1: Reactive functional groups in high/moderate concern categories	No reactive functional groups	No
SN1: Safety net, based on equivalent hazard above mentioned criteria	Equivalent hazard as polymer requiring registration not suspected	No(?)
Conclusion	Not a polymer requiring registration	

If all criteria are answered with No → Not a polymer requiring registration

Figure 8.2. PTFE assessment for polymer requiring registration by the criteria from the (European Commission. Directorate General for Environment. et al., 2020)

** The exact criteria can be found in the referred report.*

Source: ETC/CME

This approach for PTFE as a specific polymer indicates that it is not sufficiently risky to be of concern. As described in the next chapter, PTFE is, however, considered to be of concern in a CE.

8.4.3 Characterization and evaluation phase

From a system perspective of a CE, PTFE appears to be of concern – see, for example, Section 7.4 in which the environmental impacts of the waste stage of PTFE are described). That comes apparent when the whole life cycle of PTFE is considered. The lifecycle of fluorinated polymers, including emissions, is shown in Figure 1.2 and a more general lifecycle of material flows in a CE is shown in the Figure 8.3 below. The following areas of concern are identified.

- Production: in the production of PTFE hazardous processing aids are used, such as Gen-X, which can be released during the production, formulation or use phase (down-the-drain release from consumer products) or during incineration (Section 4.9).
- Use and biosphere recovery of products in the biological cycle: in a CE products are developed for circulating either in a biological cycle (consumption products) or a technical cycle (service products). Consumption products in this context are those at are literally consumed during their lifecycle through (physical) degradation or abrasion. Examples of biological-cycle products which may contain PTFE include lubricants, cosmetics and paper products. The use of PTFE in these causes the release of PTFE to the environment and thus does not allow its safe degradation and nutrient recovery (biosphere recovery).

- End-of-life treatment and recycling (technical cycle). First of all, the PTFE polymer has very strong chemical bonds which are not easily broken when heated. Recycling techniques used for conventional thermosetting plastics such as polyethylene cannot, therefore, be applied for PTFE. There are some innovations to tackle this issue, for example, the university of Bayreuth has developed a depolymerization process in cooperation with InVerTec and the 3M Dyneon company ([39]). It uses pyrolysis to decompose perfluorinated polymers into gaseous monomers. After cleaning the latter, they are then fed back into the manufacture of new materials; a pilot plant was built in 2015, however its current status is unclear. To the best knowledge of the authors of this chapter, there are no other industrial recycling facilities for PTFE in operation.
- The collection of PTFE polymers is challenging because it is widely used as part of a multi-layered complex products such as seals, membranes and films. Another widespread application of PTFE is as surface treatment or coating in which it is irreversibly connected with the base material, such as textile fibres. This could also hinder the recycling of the base material. Heating PTFE causes toxic fumes, therefore recycling techniques using higher temperatures may result in increased risks for workers.
- The incineration of fluoropolymers has great GHG emissions potential.

In Figure 8.3 so-called R-strategies are shown along the material flows, R1 to R6. These are developed to reduce the consumption of resources and materials in product chains and make the economy more circular. The R-strategies typically present a range of strategies ordered from high circularity (low R-numbers) to low circularity (high R-numbers), as a rule of thumb. These elaborate on the Ladder van Lansink, a tool for the priority setting of waste treatment methods (Potting et al., 2017). A more detailed explanation can be found in the report by Kishna et al. (2018) (only in Dutch) or for example in the study conducted by Morseletto et al. examining which targets can facilitate the transition to a CE (Morseletto, 2020). Since PTFE is difficult and costly to either recycle (R5) or repair/remanufacture (R4), using this material could hamper circular potential, as shown in Figure 8.3.

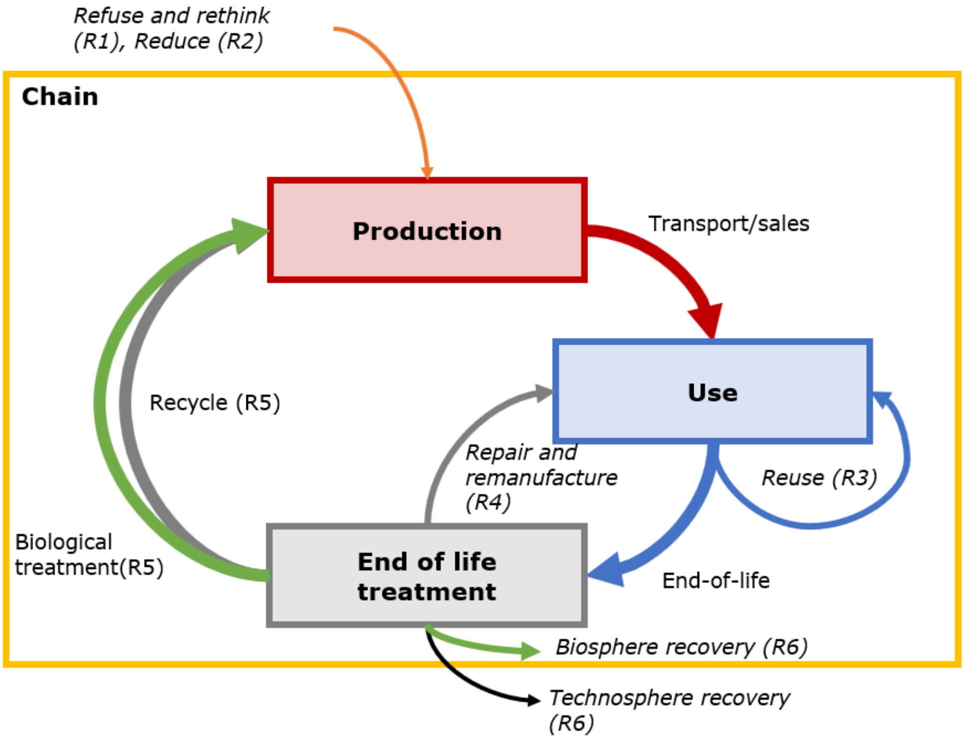


Figure 8.3. A schematic view of possible flows of materials in a circular economy.

Source: van Bruggen et al. (2021)

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[39] https://www.plasteurope.com/news/DYNEON_t230856/ (accessed July 2021)

These above mentioned considerations and R-strategies are not part of the framework for the criteria to identify and group polymers for registration/evaluation under REACH and their impact assessment (European Commission. Directorate General for Environment. et al., 2020), but should be taken in account when the use of PTFE is assessed in a CE. For a low carbon and toxic-free economy the R-strategies could also provide valuable insights.

8.4.4 Risk management phase

In a recent report by the Dutch National Institute for Public Health and the Environment (RIVM) several recommendations for the management of SVHCs in a CE have been made (van Bruggen et al., 2021; Beekman et al., 2020). These recommendations could also apply in a more general sense to other substances of concern including polymers. The Institute acknowledges that the economy is still predominantly linear and that a transition to a CE is needed. This transition provides opportunities for the management of substances of concern and the monitoring of their use. There are three challenges.

The first is the need to share information about substances throughout the entire product chain. In a circular economy products and materials, including the substances they contain, are used as inputs for a circular loop. Consequently, it is crucial that there is access to information across the product chain about the substances used and their safety. Currently, this information is available at the production phase of fluorinated polymers, but lost further down the chain.

The second challenge is for various parties in the chain to take responsibility for the safe use and re-use of substances in materials and products. Manufacturers have a responsibility for safe and sustainable design. This implies that products are designed with the aim of safe use and re-use depending on their predetermined application. Moreover, users and companies further down the chain have a responsibility for safe use and recycling and they must be enabled to take it.

As becomes clear from the description of the different phases of the IRGC Framework in the governance of substances in a CE, communication and stakeholder participation is needed in all phases of the process. The description above shows that this also holds for the processes needed for risk management in a CE. Although the IRGC framework is not specifically designed for one, the communication and stakeholder participation in the framework support the challenges identified.

The third and final challenge concerns the responsible management of substances in a CE, when phasing out is impossible or no longer possible. Within these substances, a distinction is made between:

a. legacy substances: those that are no longer allowed in new products but are still present in products in circulation, such as the presence of PFOA in existing sprinkler installations;
b. essential uses: for certain applications – certainly in the short and medium term – substances of concern are necessary because of their specific functionality and therefore cannot be phased out completely;
c. as yet unknown substances of concern: harmful effects usually only become clear (long) after the introduction of new substances – as knowledge continues to develop, substances that are not yet a cause for concern may, in the future, be classified as SVHCs;
d. changes in the use of essential substances of concern due to developments in society: as a result of the rapid development of innovations, but also due to changing requirements imposed by society, there may be shifts in the demand for and supply of substances.

In Beekman et al. (2020) several examples are given of the above mentioned categories (Beekman et al., 2020).

The above mentioned RIVM report also provides an analysis of possible indicators and sources of information for monitoring SVHCs in a CE. A distinction is made between process indicators and effect indicators. Some of these may be operational in the short term because they are based on information which is currently available. Others call for the active collection of additional information that is currently not available or only partially. To obtain a comprehensive picture of hazardous substances in a CE, it is important to start monitoring wherever possible and, at the same time, work on obtaining additional information that is not yetavailable. In a sequel report, a method for the monitoring of hazardous substances (Dutch, ZZS) in a CE is proposed (van Bruggen et al., 2021).

Monitoring fluoropolymers, or PFAS, in a CE is necessary because of environmental and possible human hazards as mentioned in Section 4.1.3, and because of related GHG emissions over their lifecycle as shown in this report. To make just considerations on their human and environmental impacts of material/product flows, transparent data is essential. Probably several indicators are needed and identified knowledge gaps along the lifecycle of fluorinated polymers (Table 9.1) should be filled as soon as possible.

8.4.5 PTFE use in solar photovoltaic panels

PTFE has many applications including use in renewable energy applications (Sections 6.1; 7.3; and 7.5). For example, many solar photovoltaic (PV) panels have a backsheet coated with PTFE. The PTFE on the backsheet is difficult to recycle which hampers the circular possibilities of a solar PV panel. The backsheet material can also be from glass or (bio)PET alternatives, which do not need a PTFE coating. Using glass might initially be more expensive, but it improves the recyclability of the panel significantly, and thereby its circular potential, decreasing the overall environmental burden. Significant GHG are produced in the production and end-of-life treatment of the PTFE in solar PVs, just like in a linear economy. This does not fit well with the aim of a low carbon economy minimising emissions of GHG. Next to that, difficulties to properly recycle or reuse the PTFE makes it difficult to keep it in different product cycles, without being wasted. And, as already mentioned, the widespread use of PTFE is a real challenge and difficult to justify in a toxic-free economy. The transition towards renewable energy is obviously necessary but the perspective of the whole system should be considered all along the way. Sustainable applications should be able to be circular and toxic-free over their *entire* lifecycles. This holds especially for such non-crucial parts as a solar PV backsheet for which circular design is already an option (Contreras-Lisperguer et al., 2021).

To realize the EU Green Deal ideals of a circular, low carbon and pollutant-free economy, renewable energy solutions should be safe and sustainable by design (see the CSS) (EC, 2020). Using a material like PTFE in solar PV solutions seems not to be in line with these ambitions.

Examples of (truly) sustainable energy production provide a link between the concept of essential use and the concepts of a low-carbon, circular and toxic-free economy. Benefits and burdens of PTFE use can only be compared by performing an integrated assessment covering the environmental and human impacts during the whole lifecycle.

8.5 Applying the concept of essential use in the risk governance process

8.5.1 The concept of essential use in the European Chemical Strategy for Sustainability towards toxic free environment

The concept of essential use has been introduced in CSS, a document of the European Commission (EC, 2020) providing a long-term vision for the EU chemicals policy. The CSS suggests the adoption of a generic approach to risk management of particularly harmful chemicals used in consumer products unless their use is deemed to be essential. Specific attention is given to the use of PFAS due to their ubiquitous use and global exposure which is considered to lead to expected yearly health related costs of EUR 52-84 billion (Goldenman et al. 2019).

In the CSS, the European Commission proposes a ban of PFAS manufacture and use within Europe, exempting those uses that are considered essential from a societal perspective (EP, 2021). This, obviously, presupposes that criteria of essentiality can both be defined and operationalized in a non-ambiguous way. Regarding the definition of and possible criteria for defining essentiality, the CSS refers to the Montreal Protocol, a multilateral environmental agreement for phasing-out ozone-depleting substances, in which criteria for essential use have been specified and applied to a few exceptional cases (Protocol, 1987) ([40]). Specifically, the Protocol states in Decision IV/25 that "*a use of a controlled substance should qualify as 'essential' if and only if (i) it is necessary for the health, safety or is critical for the functioning of society (encompassing cultural and intellectual aspects); and (ii) there are no available technically and economically feasible alternatives or substitutes that are acceptable from the standpoint of environment and health*" (Figure 8.4).

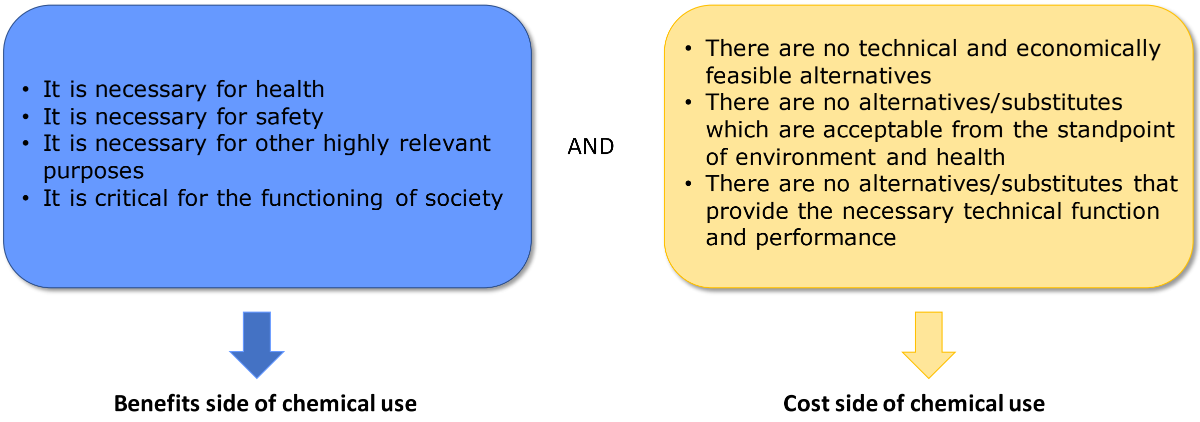

Figure 8.4. Criteria for essential use of chemicals as specified in the Montreal Protocol.

Source: Montreal Protocol (1987).

This implies that exemptions from control measures such as bans lead to societal benefits because of the essentiality and must be balanced against the consequences of such exemptions, in particular the costs of switching to safe(r) chemicals or technologies and negative impacts due on-going emissions. Identifying the use of a chemical of concern as essential is, therefore, a sufficient but not a necessary condition for its ongoing use. The obvious need for balanced decision making has also been adopted in REACH (ECHA, 2011; 2008), under which detailed information about alternative substances and technologies is mandatory in order to come to an informed decision about authorisation – the formal approval to continue one or several uses of a SVHC for a defined period) – and is used in the decision-process to assess the benefits and costs of the proposed restriction – the enforcement of control measures to eliminate the risks from producing, manufacturing or marketing a substance – of chemicals.

For PFAS in particular, Cousins et al. (2019) suggested to distinguish essential from substitutable and non-essential uses. While the first two categories differ only with regard to the availability or lack of alternative substances and technologies, the latter category denotes uses that are "*purely driven by market opportunity*" (Cousins et al., 2019). Similar to the Montreal Protocol, they assume chemical uses contributing to health and safety, for example occupational medical clothing, are likely to be essential. Dental floss or ski waxes, on the contrary, are considered non-essential because these uses do not contribute to health and safety purposes. In contrast to the Montreal Protocol, Cousins et al. (2019) do not consider the economic and technical feasibility (functionality) of alternatives, and the potential environmental implications of alternative chemicals or technologies.

So far, there is no consensus on the criteria for determining essential use, and how to distinguish essential from non-essential ones of chemicals in consumer products. While criteria such as health and safety have already been adopted in the Montreal Protocol and are also likely to receive broad acceptance for risk governance of harmful chemicals in consumer products, it is largely unclear whether there are other criteria reflecting societal preferences or values considered essential. In addition, it is unclear what criteria could identify uses that are critical for the functioning of society. Other relevant questions are who should decide on these criteria, and how to assess whether or not one or several criteria are met. Moreover, it has been recognised that societal opinions about what defines the use of a harmful chemical as essential

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[40] https://ozone.unep.org/treaties/montreal-protocol/

or critical are probably not static but can change over time and are influenced by culture (Bouman et al., 2021, EuropeanCommission, 2020). Addressing these issues is, therefore, not trivial because, obviously, the identification of criteria is value-driven and the consequences of an implementation of any criteria can have substantial impacts on society. Note that these challenges are not new, and different scientific disciplines, including social psychology and economics, have proposed methodologies of how the underlying challenge of value, preference elicitation and prioritization, can be approached (Schwartz, 2017; Schwartz, 2012; Dietz et al., 2005; Cameron et al., 2002; Fischhoff, 1996).

While discussing the practical implementation of the concept of essential use for risk governance of fluorinated polymers does not seem not meaningful in the absence of relevant criteria, it is possible to discuss possible implications of using the concept in the risk governance process using the risk governance framework suggested by the IRGC as reference. In particular, the implications of essential use considerations implemented early or late in the risk governance process are included.

One possible option for improving current risk governance and legislation, such as REACH, of fluorinated polymers is the implementation of the essential use concept in the risk management procedure. The IRGC framework could be used as a reference with the aim of providing a balanced overview of the implications of applying the concept of essential use.

8.5.1.1 Pre-assessment phase

An inventory of the uses of fluorinated polymers can be conducted during the pre-assessment phase. Assuming that criteria reflecting a societal consensus on essential uses of fluorinated polymers can be defined, and that these are based on a societal consensus, the uses which are, according to these criteria, not essential, can be identified. Defining non-essential uses early in the risk governance process implies that time- and resource-demanding follow-up steps such as hazard identification, exposure/vulnerability assessment and risk characterisation (first part of the appraisal phase) may no longer be required for these uses. Furthermore, an assessment of impacts could become redundant. The expectation is that this will simplify and accelerate the risk governance process. Hence, filtering out some uses of fluorinated polymers early in the risk governance process may be resource saving and accelerate risk management decision making about these substances. It should be noted, however, that considering uses of fluorinated polymers to be non-essential could also imply that possible benefits of these uses will be lost. This, however, occurs at the expense of in-depth insights into positive and negative impacts of such uses. In other words: non-essentiality criteria define a use to be socially irrelevant from the outset. This implies that the spheres of understanding and deciding (Figure 8.2) that are traditionally well delineated will become entangled.

8.5.1.2 Appraisal phase

If non-essential uses are excluded in the pre-assessment phase, a detailed assessment of concerns would then focus on essential uses only in the appraisal phase of risk governance. A concern is a multi-dimensional concept and includes a proper understanding of stakeholder perceptions and a systematic analysis of socio-economic impacts of the use of fluorinated polymers. It is important to note that impacts do not only arise from an on-going use of fluorinated polymers, but can also emerge from implementing risk management measures, for example through the use of alternative substances or technologies. Consequently, identifying fluorinated polymer uses that are deemed to be essential does not overcome the need to assess and balance different types of impacts in order to approve a continued use. In particular, essentiality is not a cutoff criterion for unbound continued use. Rather, acknowledging that criteria of essentiality reflect the benefits side of chemical use (i.e. the societal goals or values to which a certain use contributes), these benefits must be contrasted with the negative impacts of a use on human health, the environment or the economy. Likewise, assessing costs and impacts of potential alternative substances and technologies remains crucial to stimulate innovation towards safe(r) alternatives on one hand, and to prevent regrettable substitution on the other.

Another option is to introduce criteria of essential use slightly later in the risk governance process; in the appraisal phase. The question is, then, in what way criteria of essential use can complement or support the assessment of concerns and socio-economic impacts. Under REACH, socio-economic analysis (SEA) has become a well-established toolbox for conducting such assessments for REACH authorisation and restriction procedures, but also beyond (García-Ayllón, 2019; Georgiou et al., 2018; Pery et al., 2013). Adopting a social welfare perspective, SEA is a comprehensive and comprehensible assessment toolbox that seeks to assess and compare all impacts with an expected welfare effect. In applications for authorisation, SEA is informed by an analysis of alternatives (AoA), in which applicants have to identify available alternatives and provide an assessment of their technical and economic feasibility and the time scale for the implementation of possible alternatives (ECHA, 2021). In reality, however, impacts have not always been straightforward to quantify and to monetise. Specifically, environmental impacts have often been assessed qualitatively only due to a lack of data and a lack of methodological integration of the available information about chemical properties into economic methods (Gabbert and Hilber, 2020). While in the absence of quantitative data the use of qualitative reasoning is a legitimate way forward, it still requires that the key characteristics of a concern, such as high or extreme persistence, are appropriately transported in the overall balancing of impacts. Similarly, the quality of AoA's have often been a matter of debate since applicants have not always been able to convincingly show that alternatives were lacking, or not feasible from a technical or economic point of view (Navin-Jones, 2019). This led to criticism of some decisions on granting authorisation to chemicals, and of exemptions from restrictions (Tickner and Jacobs, 2016), as it was argued that these uses were not necessary for social health and safety. This implies that there is probably scope for improvement of specific components in SEAs. Environmental impact assessment in SEAs, for example, could be strengthened by developing integrated methods linking environmental data and assessments using economic methods (Gabbert and Hilber, 2020). This requires, first and foremost, close interdisciplinary collaboration.

Where it is possible to address all relevant impacts quantitatively, for example, by means of a cost-benefit analysis, it is debatable whether the underlying efficiency argument of welfare economics is always the best or only argument for deciding about chemicals' use. In law and ordinary moral reasoning, the avoidance of harm, the benefits of risk management measures, can have priority over the provision of costs (Geistfeld, 2019; Keating, 2018,). Within the welfare economic SEA approach such preferences can be reflected by attaching higher weight to the benefits compared to the costs involved in taking measures to avoid risks and, ultimately, damage.

Prioritising the avoidance of harm may be regarded as the added value of essential use in comparison to existing regulatory frameworks. This holds predominantly for those regulatory frameworks which lack a transparent, method-based approach for assessing and balancing impacts such as a SEA, for example the European Biocidal Products Regulation ([41]). It can also reflect different normative perspectives on how to manage the risks arising from chemicals' use. Research on expert roles in policy advice illustrates that there exist different interpretations of precaution, and can therefore also reach different conclusions on how to deal with risk and uncertainty (Spruijt et al., 2016; Silva and Jenkins-Smith, 2007; Weiss, 2003). This depends on the decision context and the specific problem at hand. By including the concept of essential use in regulatory frameworks, in particular for most hazardous substances in a CE, the (societal) voice of those who prefer to act on the side of caution may be strengthened.

8.5.1.3 Characterization and evaluation phase

In the risk evaluation phase, the evidence based on the risk and concern assessment is combined with a thorough evaluation of other factors which have not already been included in the analysis of concern. Such factors can include societal values, economic and political considerations provided that they have not explicitly been addressed in the assessment of concerns. Risks can be acceptable (no risk reduction needed), tolerable (because of benefits, but risk reduction measures are needed) or intolerable (risks should simply be avoided). Again, criteria of essential use can provide information about basic,

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[41] EUR-Lex - 32012R0528 - EN - EUR-Lex (europa.eu)

undisputable social values. If applied in the evaluation phase of the risk governance process, the concept of essential use does not impact the hazard, risk or impact assessment process. Rather, it can provide an alert to policy-makers to explicitly consider these values when adopting risk management decisions.

8.5.1.4 Risk management phase

Based on the considerations above, Figure 8.5 illustrates two options for the implementation of the concept of essential use. The first option (Figure 8.5a) requires an *a priori* definition of criteria, based on a societal consensus. If applied early in the risk governance process, this might help to reduce resources required for a hazard, risk or impact assessment, and might speed up decision making. At the same time, this approach will lead to less information about hazardous effects, risks and impacts of chemicals. Furthermore, regular and EU-wide update-assessments of essentiality criteria will be needed to ensure objectivity and relevance of the concept over time.

In Figure 8.5b criteria of essential use are defined after the regulatory assessments. The benefit of such an approach could be that the concept of essential use is only needed for uses without good alternatives; many issues might already have been solved in the socio-economic assessment in the appraisal phase. This will answer the needs of those who prefer precaution over the balancing of positive and negative impacts in risk management, as it corrects undesirable outcomes of a SEA. Moreover, with this order it is possible to keep the distinction between the understanding and deciding spheres in risk governance. The disadvantage is that this is a case-by-case approach in which the assessment of hazards, risks and impacts is not accelerated.

Figures 8.5a and b illustrate two possible options for the implementation of the concept of essential use. Other options, including parallel or iterative assessments, could be explored. As shown, the way the concept of essential use is implemented, will affect other parts of the management of the risks of (hazardous) chemicals.

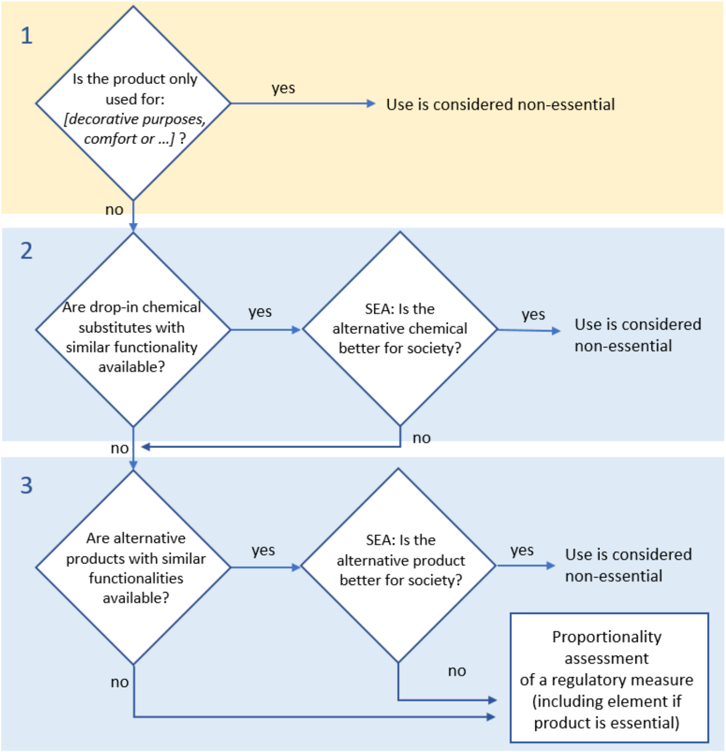

Figure 8.5a. Adding essential use (in yellow) – partly – before regular assessments.

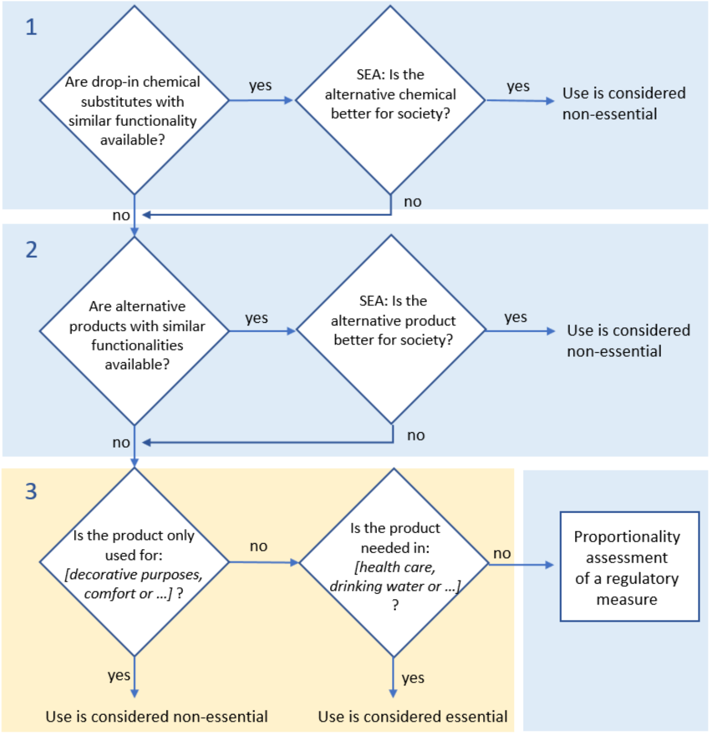

Figure 8.5b. Adding essential use (in yellow) after regulatory assessments.

8.6 Discussion and Conclusion

This chapter discussed key elements of risk governance of fluorinated polymers in a CE and reflected on possible options for applying the concept of essential use.

The IRGC framework supports the idea that the inclusion of stakeholders during all phases of the governance process is needed in a CE. This need is amplified by the assessment of PTFE using the proposed criteria for evaluation of polymers of concern. In there, only the possible hazards of the polymer during the use phase are assessed. It shows that this is too shallow in the framework of a CE. Therefore, the whole lifecycle should be assessed, including, for example, persistency and leakage to the biosphere. To realise the EU Green Deal ideals of a circular, low carbon and chemical pollution-free economy, the benefits and burdens of, for example, PTFE use could only be assessed using an integrated assessment. This should cover the environmental and human impacts of the chemical's entire lifecycle, including GHG potential. An integrated assessment also provides a link between the concept of essential use and the concepts of a low-carbon, circular and toxic-free economy.

Linking the concept of essential use to risk governance, it is concluded that there can be different options in implementing criteria of essential use, assuming that they have been defined unambiguously. Specifically, criteria can be applied at an early stage, even prior to a case-by-case hazard, risk or impact assessment. This can help to reduce resources, time and, ultimately, costs because chemicals in non-essential uses can be removed from the market immediately. The assessment of hazards, risks and socio-economic impacts will, then, focus on those chemicals which are part of essential uses. Well-defined criteria of essential use could, therefore, provide more opportunities for risk governance of fluorinated polymers than are currently used in the EU. This also implies, however, less information and data about hazards, risks or impacts for chemicals in non-essential uses. There can, therefore, also be arguments in favour of using criteria for essential use at a later stage of the risk governance process. Given this trade-off, decision making on what route to take requires a thorough assessment of all impacts that can be expected under either route. The discussion also highlights that criteria of essential use cannot not overcome the need for assessing the impacts of possible regulatory decisions on harmful chemicals. Furthermore, while applying the concept of essential use may strengthen the inclusion of societal norms and perspectives, its operationalisation largely depends on the specification of suitable criteria of essentiality or non-essentiality. Finally, assuming those criteria have been defined, regular and EU-wide updates of societal preferences on essential uses are needed to ensure the objectivity and relevance of the concept in the long-run.

9 Key gaps in knowledge

In previous chapters the impacts of fluorinated polymers along their lifecycles have been evaluated mainly based on data from literature. Fluorinated polymers may currently have important uses related to renewable energy and increasing the durability and performance of products that create benefits for society. As illustrated in the report, however, the fluorinated polymer lifecycle also shows risks for the environment and human health, including some related to climate change impacts, which question their overall benefits. At this stage the information is rather limited on both the benefits and the risks, but the severity of the potential impacts, including the immensely high GWP of fluorinated gases, warrants further studies on lifecycle emissions. These would help to assess whether fluorinated polymers contribute or block goals of a circular, toxic-free and low-carbon economy, and whether uses really can be considered essential. Reliable information is needed on flows, amounts, markets, exposures to human and the environment, replacement alternatives, and economic aspects related to different use areas for potential action on risk governance of fluorinated polymers at different stages. Knowledge gaps along the lifecycle have been collated in Table 9.1.

Key gaps in knowledge and regulations, and need for action were identified as follows.

- Data streams on feedstock and intermediate chemicals at product or at least industry level in Europe, as well as for products imported into Europe.
- Studies/research/monitoring on substances (feedstock, synthesis by-products, impurities and degradation products) that are emitted from all types of activities along the lifecycle of fluorinated polymers (production, manufacturing of products, incineration/thermal degradation/wastewater treatment, etc.). Key knowledge gaps are analyses of volatile fluorinated gases and oligomers.
- Research on degradation pathways of these fluorinated substances, to assess to which extent degradation products with high GWP are formed. Degradation during production, use, end-of-life and in the environment are relevant for such studies.
- Studies to assess whether the GWP can be calculated based on the emissions along the lifecycle of a chemical and not only on the chemical itself, as it is done now.
- More systematic studies on emissions of FTOHs and other PFAS from, for example, wastewater treatment plants and manufacturing sites.
- Research and demonstration of technologies to recycle fluorinated polymers from waste, both during the production phases and from end-of-life products. Demonstrations would have to consider how recycling is done in practice, including for wastes shipped outside Europe.
- Systematic and in-depth analyses on benefits and risks associated with the use of fluorinated polymers in different applications. Potentially, tools and criteria, which currently are being developed for ensuring safe and sustainable design, can be used in combination with a framework for essential *versus* non-essential uses. Fluorinated polymers could serve as a test case for such studies.
- Research and development of alternatives for the replacement of fluorinated polymers in product development which do not use, produce or incidentally form substances of concern along their lifecycles. Safe and sustainable by design assessments could be applied to ensure that benefits and risks related to potential replacements are assessed.
- Labelling of products containing fluorinated polymers, to enable safe waste management of end-of-life products.
- Awareness raising among various stakeholders, including product designers, for consideration of material choices, authorities and enforcement bodies, and consumers.
- Studies to assess to what extent current chemical risk management can consider lifecycle assessments, for multiple impacts across numerous policy domains, and whether updates of both chemicals, product, waste, environmental and F-gas regulations are needed to consider such systemic impacts.

Table 9.1. Identified knowledge gaps along the fluorinated polymer lifecycle.

Lifecycle	Further information needs	Links to risk governance
Mining	Potential recycling from other industries – to which extent will these (e.g. fertiliser by-products)	Fluorspar is listed as a critical raw material
	Pollution at mine location, during extraction of fluorspar	Assessment of risks to the environment and human health
Production of fluorinated polymers	Data on amounts of different fluorinated polymers produced and used in various applications	Categorisation of applications as essential or non-essential
	Information on use of fluorine-containing FP production aids Emission data of fluorine-containing FP production aids (PFOA and PFNA alternatives) and other emitted PFAS Emission data of PFAS emissions during production of fluorine-containing FP production aids Information on physico-chemical properties of PFOA and PFNA alternatives including bioaccumulation potential and persistency Information on use of poly- and perfluorinated sidechains and their physico-chemical properties Measurement and analysis of fate of PFAS released to soil, air and water near production facilities (using harmonised sampling protocols)	Need for reliable data on feedstocks and emissions in production of fluorinated polymers for the assessment of climate effects and toxic emissions to water, air and soil
Manufacturing of fluorinated polymer containing products	Data on toxic degradation products and by-products formed during the manufacturing process, data on exposure of workers and emission to air	Very little addressed in literature (only Teflon flue)
Use (note: limited focus in this report)	Replacement of fluorinated materials with alternative materials, and safety of short chain fluorinated alternatives	Information on alternatives crucial for discussion on risk governance
End of life	Data on potential recycling of fluorinated polymers in applications	Links to reduction of exposure/release from production
	Identification of key end-of-life applications containing fluorinated polymers and possible waste management options	Information for identification of options with low impacts
	Conditions in incineration of fluorinated polymers containing products	Risks of TFA formation
	Monitoring data from landfills, release behaviour	Data for risk assessment
	Information on fluorinated polymers as a source of PFAS in wastewater treatment plants (product use, degradation)	Data for risk assessment
	Technologies for capture of released PFAS in landfill leachates	Management of low-emission landfills
	Data on fluorinated polymers (volumes and types) produced/used/exported in/from Europe	Impact assessment
	Waste exported from Europe for resource recovery (Cf. smoldering)	

List of abbreviations

Acronyms, general

AFFF	Aqueous fire-fighting foam
AoA	Analysis of alternatives
AOP	Advanced oxidation process
CAS	Chemical Abstracts Service
CE	Circular economy
CEAP	Circular Economy Action Plan
CLP	European Commission's Classification, Labelling and Packaging Regulation
CMR	Carcinogenic, mutagenic or toxic for reproduction
CRF	Common Reporting Format of the United Nations Framework Convention on Climate Change
CSS	Chemicals Strategy for Sustainability towards a toxic-free future
CT	Computed tomography
CTA	Chain transfer agent
DOC	Dissolved organic carbon
DWR	Durable water-repellent
ECHA	European Chemicals Agency
EEA	European Environment Agency
EFSA	European Food Safety Authority
EOF	Extractable organic fluorine
E-PRTR	European Pollutant Release and Transfer Register
ETC	European Topic Centre
ETC/CMC	European Topic Centre on Climate Change Mitigation and Energy
ETC/WMGE	European Topic Centre on Waste and Materials in a Green Economy
EU	European Union
FABS	Semiconductor fabrication plants
FCM	Food-contact materials
GHG	Greenhouse gas
GWP	Global warming potential; carbon dioxide has a GWP of 1
HTC	High-temperature conversion
ICT	Information and communications technology
IED	Industrial Emissions Directive (of the European Union)
IPCC	Intergovernmental Panel on Climate Change
IRGC	International Risk Governance Council
IVDR	(EU) Regulation on In-Vitro Diagnostic Devices
IWWTP	Industrial wastewater treatment plants
JRC	Joint Research Centre
K_{AW}	Air–water partition coefficient
LIB	Lithium-ion battery
LoW	European List of Waste
LRTP	Long-range transport potential

MAC	Mobile air-conditioning system
MDR	(EU) Regulation on Medical Devices
MRI	Magnetic resonance imaging
NOEC	No-effect concentration
ODP	Ozone-depletion potential
ODS	Ozone-depleting substance
OECD	Organisation for Economic Co-operation and Development
PBT	Persistent, bioaccumulative and toxic
PHC	Polymers of high concern
PLC	Polymers of concern
PM	Persistent and mobile
PMN	Pre-manufacture notification
PMT	Persistent, mobile and toxic
PNEC	Predicted no-effect concentration
POP	Persistent organic pollutant
P_{ov}	Persistence
PV	Photovoltaic
RAC	Committee for Risk Assessment
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RFG	Reactive functional group
RIVM	Dutch National Institute for Public Health and the Environment
SCIP	**S**ubstances of **C**oncern **I**n articles as such or in complex objects (**P**roducts)
SEA	Socio-economic analysis
SEAC	Committee for Socio-economic Analysis
SSBD	Safe and sustainable by design
SVHC	Substances of very high concern
TDI	Tolerable daily intake
TOP	Total Oxidizable Precursors
TWI	Tolerable weekly intake
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention of Climate Change
US	United States
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
UVB	Ultraviolet B
UWWTP	Urban wastewater treatment plants
vPvB	Very persistent and very bioaccumulative
WSR	Waste Shipment Regulation
WWTP	Wastewater treatment plant
7EAP	7th Environment Action Plan (European Commission)

Acronyms: Chemicals

Note! Annex 4 includes supplementary information on PFAS terminology, classification and origin

APFO	Ammonium pentadecafluorooctanoate
CaF_2	Calcium fluoride
ETFE	Ethylene tetrafluoroethylene
FEP	Perfluorinated ethylene-propylene
FEPM	Tetrafluoroethylene propylene
HFPO-DA	Hexafluoropropylene oxide-dimer acid (GenX)
H-PFCA	Monohydrogen-substituted perfluorinated carboxylic acid
H_2SiF_6	Fluorosilicic acid
PAP	Polyfluoroalkyl phosphoric acid esters/polyfluoroalkyl phosphates
PCTFE	Polychlorotrifluoroethylene
PFA	Perfluoroalkoxy alkane
PFAA	Perfluoroalkyl acid
PFAE	Perfluoroalkylether
PFAS	Per- and polyfluoroalkyl substances
PFBA	Pentafluorobenzoic acid
PFBS	Perfluorobutane sulfonate
PFDA	Perfluorodecanoic acid
PFDcA	Perfluorodecanoic acid
PFDoA	Perfluorododecanic acid
PFECA	Per- or polyfluoroalkyl ether carboxylic acids
PFESA	Polyfluoroalkyl ether sulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate
PFIB	Perfluoroisobutylene
PFNA	Perfluorononanoic acid
PFPAE	Perfluoropolyalkylether
PFPE	Per- and polyfluorinated polyether
PFPMIE	Perfluoropolymethylisopropyl ether
PFSA	Perfluoroalkane sulfonic acid
PFTECA	Perfluoro triether carboxylic acid
PFTrA	Perfluorotridecanic acid
PFUnA	Perfluoroundecanic acid
PMVE	Perfluoromethyl vinyl ether
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PVF	Polyvinyl fluoride
$SbCl_xF_y$	Antimony pentahalide (with x+y=5)
SF_6	Sulphur hexafluoride
SFP	Sidechain fluorinated polymers

x H-PFCAs	Hydrogen-substituted perfluorinated carboxylic acids
5:3 FTCA	5:3 Fluorotelomer carboxylic acid

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Annex 1. Supplementary information on production of HF and environmental risks in fluorspar extraction

A1.1 From acid-grade fluorspar to hydrofluoric acid

The excavated ore, either from open pit or underground mines, are concentrated by flotation techniques. The ore is grounded to fine particles, for example below 150 µm. The process is conducted in a series of cells that successively concentrates the ore from the feed material (CaF_2 concentrations in the feed depends on the deposit, in the literature examples of 30–40% are mentioned) to a minimum of 97.0% CaF_2 in the final concentrate. The water in the final product is then removed in a thickener and a rotary drum filter. Tailings generated from flotation (non-recovered ore material remaining) are usually disposed of in tailings ponds as an aqueous slurry. In the tailing ponds the settled water is recycled to the plant for reuse. (Fluorine Forum 2019; Kiptanui, 2015).

As mined, fluorspar ore contains host rock and other inert impurities, together with varying amounts of lead, silver or zinc ores. The minerals that are not wanted together with impurities including also unextracted fluorine end up in the tailings ponds. An example of flows processed per operating days at Cavendish Mill (Fluorine Forum 2019) are:

- typically 1 310 tonnes per day of polymetallic fluorspar ore containing 28% CaF2 is processed (impurities: 1.79% lead);
- 250 tonnes of acid grade fluorspar concentrate are produced per day (together with 20 tonnes of lead, 40 tonnes of barytes and 300 tonnes of crushed stone aggregate are formed as by-products);
- about 700 tonnes of tailings are generated per day containing 5% CaF2 in coarse fraction (250 tonnes/day) and 12% CaF2 in fine fraction (450 tonnes/day).

After flotation, the acid grade fluorspar is transported to plants for the production of HF. In the process, the fluorspar is reacted with sulphuric acid (H_2SO_4) in an endothermic process to form HF. The hot solid calcium sulphate residues are removed and neutralised at the opposite end of the HF reactor. Gypsum is sold to the building industry for use as a floor-levelling material, building blocks and as a retarder in the cement industry. (BUSS ChemTech, n.d.; Eurofluor, n.d.)

A1.2 Environmental and health impacts from extraction of fluorspar – examples

Sustainable sourcing is recognised as important in the EU in the manufacture of products starting from raw material extraction and it takes into account environmental and health concerns as well as social and economic issues. Uncontrolled mining activities, such as small-scale unregualted mining and a lack of use of tools for protecting of health and safety, are also linked to the lack of environmental protection measures. Google Maps' images of Mongolia show dust deposition ranging several kilometres downwind of mining areas, and also evidence of large animal herds using tailings ponds as their main source of drinking water (Baatar and Grayson, 2009; Grayson, 2009).

A special health impact relates to the intake of drinking water with ahigh fluoride content from the ion exchange processes and the weathering of the rock. At mining sites, dust formation related to mining activities (for example, spillage and tailings) increase the exposure of human and animals, although, in the literature, this is only reported for coal rather than fluorspar mining. For example, in Mongolia fluoride concentrations around 2 mg/l in drinking water ([42]) occur in concentrations which cause health problems such as dental fluorosis – in several areas near deposits about half of the children have dental fluorosis – and skeletal fluorosis, which is not curable. Elevated fluoride may also lead to intellectual deficits that can be considerable (Grandjean, 2019; Grayson et al., 2016).

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[42] The World Health Organization (WHO) recommends for fluoride concentration in drinking water should not exceed 1.5 mg/l

A special concern also relates to the stability of tailings. A few acciditents involving leackage from tailings ponds have been reported. In 1985, a tailings dam of the Prestavel fluorite mine, near Tesero (Trento) in northern Italy, failed, causing a disastrous mudflow involving 180,000 m3 of semi-fluid tailings which rapidly flowed over 4.2 km along the Stava Valley until it reached the river. In this catastrophe, 268 lives were lost and 20 people injuried (Luino et al., 2012; Chandler et al., 1995). Another, tailings pond accident happened 2007 at the Derby fluorine mine in UK where a failure in a tailings dam caused a release of 20 000 m3 tailings, slightly increasing concetrations in soil immediately beneath the tailings deposit (Anon. 2007).

The host rock of fluorspar may contain impurities, such as lead, arscenic and zinc, that ends up in the tailings, along with non-extractive fluorine remains. Tailings are disposed in tailings pond; typically tailings are pumped as a slurry to huge tailings ponds from which leaks may occur into the surrounding environment. It is also possible that the tailings from fluorspar are acid generating ([43]) which affects the aquatic ecosystem and produce contamination and even health effects on humans and livestock. It is important that ponds are covered when they are full to avoid risk of dust spreading into the environment.

Underground fluorite mining produces a relatively large volume of polluted water that need to be removed from the mines during the extraction operation. If these effluents are discharged into a water body untreated, the water body may become polluted with heavy metals and fluoride. In Asturias situated in northwest Spain each year, for example, approximately 200 000 m3 of wastewater from a fluorspar mine is discharged into a nearby stream, which results in fluoride concentrations of up to 4.8 mg/l (Roqueñí et al, 2005).

The faulty exploitation of some Chinese deposits that has caused some mine closures due to environmental concerns is mentioned in the SCRREEN report (Karhu et al., 2018), but without further details.

The following are examples of environmental and health impacts connected with heavy metal pollution presented in recent literature.

- Spain: Forján et al. (2019) found that the former and current fluorspar mining on the northern coast of Spain has resulted in increased levels of mercury in soils and sediments near the mine as a result of the inappropriate disposal of processing waste.
- Kenya: increased levels of fluoride have been found in animal meat and plants around a fluorspar mine in Kenya – the exposure was assumed to result from poorly treated wastewater from the mine (Kibet et al., 2019). Fluorite mining there has had major impacts on the physical environment with changes in topography and vegetation cover.
- Tunisia: an old fluorite ($CaF2$) and barite ($BaSO4$) mine is located in Hammam Zriba, northern Tunisia. As a result of the wind erosion of the tailings and their subsequent wind transport, extreme concentrations were measured in soils near to the tailings dumps: 5% barium, 4% strontium, 7% sulphur, 1% fluorine, 0.8 % zinc and 0.2% lead. Concentrations of the major pollutants decrease with distance, but they were high even in the farthest samples, situated 2 km downstream from the mining wastes dumping area (Djebbi et al., 2017).
- Pakistan: Rashid et al. (2018) concluded that the groundwater in villages near a fluorspar mine was not fit to drink. Of analysed groundwater samples, 62.2 % exceeded the WHO limit value of 1.5 mg/l for drinking water. The elevated concentrations, typically 1.5–3 mg/l, were due to the weathering of rock and ion exchange processes.

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[43] Acid generation occur when sulphides in the tailings are oxides to sulphuric acid and there is a lack of neutralising minerals. Acid mining drainage (AMD) is produced when sulphide-bearing material is exposed to oxygen and water.

Annex 2. GWP and ODP data of substances linked to fluorinated polymer production

Table A.2.1. Substances involved in the synthesis of chloroform, the feedstock for chlorodifluoromethane ($CHClF_2$).

Chemical name	Formula	CAS No.	GWP	ODP
Methane	CH_4	74-82-8	25	-
Chloromethane	CH_3Cl	74-87-3	12	0.015
Dichloromethane	CH_2Cl_2	75-09-2	9	not quantified[*]
Trichloromethane (chloroform)	$CHCl_3$	67-66-3	16	not quantified[†]
Tetrachloromethane (carbon tetrachloride, CTC)	CCl_4	56-23-5	1 730	0.89

[*] There is evidence that dichloromethane contributes to ozone-depletion (Hossaini et al., 2017)

[†] There is evidence that trichloromethane contributes to ozone-depletion (Fang et al., 2019)

Table A.2.2. Substances involved in the synthesis of chlorodifluoromethane, the feedstock for tetrafluoroethylene (TFE).

Chemical name	Formula	CAS No.	GWP	ODP
Hydrogen fluoride	HF	7664-39-3	-	-
Trichloromethane (chloroform, TCM)	$CHCl_3$	67-66-3	16	-
Trifluoromethane (fluoroform, HFC-23)	CHF_3	75-46-7	12 400	-
Dichlorofluoromethane (HCFC-21)	$CHCl_2F$	75-43-4	148	0.036
Chlorodifluoromethane (HCFC-22)	$CHClF_2$	75-45-6	1 760	0.024–0.034
Tetrafluoroethylene	$CF_2{=}CF_2$	116-14-3	-	-

Table A.2.3. Some substances (raw materials) involved in the synthesis of TFE from chlorodifluoromethane or trifluoromethane.

Chemical name	IUPAC name	Formula	CAS No	GWP	ODP
Hydrogen fluoride	Fluorane	HF	7664-39-3	-	-
Hydrogen chloride	Chlorane	HCl	7647-01-1	-	-
Chlorodifluoromethane (HCFC-22)	Chloro(difluoro)methane	$CHClF_2$	75-45-6	1 760	0.024–0.034
Trifluoromethane (fluoroform, HFC-23)	Fluoroform	CHF_3	75-46-7	1 2400	-
Hexafluoropropylene (HFP)	1,1,2,3,3,3-Hexafluoroprop-1-ene	$CF_3CF{=}CF_2$	116-15-4	<1	-
Perfluoroisobutylene (PFIB)	1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)prop-1-ene	C_4F_8	382-21-8	?	-
Octafluorobutane (PFC-318)	1,1,2,2,3,3,4,4-Octafluorocyclobutane	c-C_4F_8	115-25-3	9 540	
Tetrafluoroethylene	1,1,2,2-Tetrafluoroethene	$CF_2{=}CF_2$	116-14-3	-	-

Table A.2.4. Some halogenated radical-generating initiators used in the polymerisation of tetrafluoroethylene (TFE).

Chemical name	Formula	CAS No	GWP	ODP
Bis(pentafluoropropionyl) peroxide	$C_6F_{10}O_4$	356-45-6	?	-
Bis(2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-1-oxopropyl)peroxide	$C_{12}F_{22}O_6$	56347-79-6	?	-
Bis(3-chloro-2,2,3,3-tetrafluoropropionyl) peroxide	$C_6Cl_2F_8O_4$	88505-66-2	?	?
Bis(trifluoromethyl) peroxide	$C_2F_6O_2$	927-84-4	?	-
Bis(trichloroacetyl) peroxide	$C_4Cl_6O_4$	2629-78-9	?	?
Oxygen difluoride	F_2O	7783-41-7	?	-
Lead(4+) tetrakis(trifluoroacetate)	$C_8F_{12}O_8Pb$	16656-82-9	?	-
Sulfur chloride pentafluoride	SF_5Cl	13780-57-9	?	?
Caesium fluoride	CsF	13400-13-0	?	-
Silver(2+) difluoride	AgF_2	-	?	-
Chromic fluoride	CrF_3	-	?	-
Lead tetrafluoride	PbF_4	-	?	-

Table A.2.5. Some fluorinated solvents/carriers used in the polymerisation of tetrafluoroethylene (TFE).

Chemical name	Other names	Formula	CAS	GWP	ODP
1,1,2-Trichloro-1,2,2-trifluoroethane	CFC-113, R113, Freon 113	$Cl_2FC-CClF_2$	76-13-1	5 820	1
1,1,1,2,2,3,4,5,5,5-Decafluoropentane	HFC-43-10mee, HFC-4310mee, R4310	$C_5H_2F_{10}$	138495-42-8	1 650	-
Chloro(difluoro)methane	HCFC-22, R22, Freon 22	CF_2ClH	75-45-6	1 760	1
Perfluoro-1,2-dimethylcyclobutane		C_6F_{12}	28677-00-1	?	-
Perfluoro-1,3-dimethylcyclohexane		C_8F_{16}	335-27-3	?	-
Perfluoro-N-methylmorpholine		$C_5F_{11}NO$	382-28-5	?[*]	-
Bis(perfluoro-n-butyl)sulphide		$C_8F_{18}S$	-	?	-
Arsenic trifluoride		AsF_3	7784-35-2		-

[*] There is a study but no results available (probably potent GHG): https://www.esrl.noaa.gov/gmd/publications/annual_meetings/2017/abstracts/61-170407-B.pdf

Table A.2.6. Overview of some dipsersants (surfactants) used in the polymerisation of TFE (tetrafluorothylene).

Chemical name	CAS No	Formula	GWP	ODP
Perfluorodimethylcyclohexane	355-02-2[*]	C_8F_{16}	?	-
1,2-Dichlorohexafluorocyclobutane	356-18-3	$C_4F_6Cl_2$ (R316c(Z))	5 400[†]	0.49–0.54[†]
1-Chloro-6-hydroperfluorohexane	307-22-2	$C_6F_{12}ClH$	?	?
1,2-Dichlorotetrafluoroethane	76-14-2	$C_2F_4Cl_2$ (R114)	8 590	1
Perfluorokerosene	-	$CF_3CF_2(CF_2CF_2)_nCF_2CF_3$	9 300 (n=1)	-
Perfluorocarboxylic acids and salts (APFO, NaPFO)	-	$C_nF_{(2n+1)}CO_2Na$ or NH_4	?	-
Chlorofluorocarboxylic acids	-	$C_nF_mCl_pH_qCO_2H$	?	?
Perfluoroether (PFPE)-based carboxylic acids (PFECAs) (F.ex. HFPO-DA (GenX), HFPO-TA)	62037-80-3 13252-14-7	$C_5F_{11}OCO_2H$ $C_3F_7OC_2F_5OC_2F_4COO^-$		-
Perfluoropolyether (PFPE)-based carboxylic acids (F.ex. ADONA)	958445-44-8	$C_6F_{12}O_2CO_2H$		
Perfluoro-chloropolyether (PFClPE)-based carboxylic acids (F.ex. perfluoro acetic acid, α-substituted with the copolymer of perfluoro-1,2-propylene glycol and perfluoro-1,1-ethylene glycol, terminated with chlorohexafluoropropyloxy group)	329238-24-6	$ClC_3F_6-O-[CF_2CF(CF_3)O-]_n-[CF(CF_3)-O-]_m-CF_2-CO_2-$ n ranges from 1 to 4 and m from 0 to 2		
PFESAs PERFLUOROSULFONIC ACID-PTFE COPOLYMER; sulfonated tetrafluoroethylene based fluoropolymer-copolymer, Nafion copolymer	66796-30-3	$C_7HF_{13}O_5S$. C_2F_4		
Perfluoro-n-pentane sulfonic acid	-	$C_5F_{11}SO_3H$	?	-
Chlorendic acid (HET acid)	115-28-6	$C_9H_4Cl_6O_4$		

[*] Perfluoro-1,3-dimethylcyclohexane has CAS 335-27-3, 355-02-2 is Perfluoromethylcyclohexane (C_7F_{14})

[†] Papadimitriou et al. (2013)

Table A.2.7. HFCs used as chain transfer agents (CTAs) in the polymerisation of TFE to PTFE.

Chemical name	Formula	CAS No	Monomer relative quantities (mol %)	GWP
Difluoromethane (HFC-32)	CH_2F_2	75-10-5	0.01-2.5	677
Trifluoromethane (fluoroform, HFC-23)	CHF_3	75-46-7	0.01-10	12 400
1,1-Difluoroethane (HFC-152a)	CH_3CHF_2	75-37-6	0.01-0.5	138

Table A.2.8, Relevant substances involved in the synthesis of polyvinylidene fluoride (PVDF).

Chemical name	IUPAC name	Formula	CAS No	GWP	ODP
1,2-Dichloroethane (DCE)	1,2-Dichloroethane	$ClCH_2CH_2Cl$	107-06-2	1.4[*]	-
Trichloroethylene (TCE, Tri)	Trichloroethene	$CCl_2=CHCl$	79-01-6	<1[*]	<0.004
Tetrachloroethylene (perchloroethylene, PCE)	Tetrachloroethene	$CCl_2=CCl_2$	127-18-4	5.9[*]	-
HCFC-132b	1,2-Dichloro-1,1-difluoroethane	CF_2ClCH_2Cl	1649-08-7	320[*]	0.062
HCFC-142b	1-Chloro-1,1-difluoroethane	CH_3CF_2Cl	75-68-3	1 980	0.023–0.057
HFC-143a	1,1,1-Trifluoroethane	CH_3CF_3	420-46-2	4 800	-
Vinylidene fluoride (VDF)	1,1-Difluoroethene	$CF_2=CF_2$	75-38-7	?	-
Polyvinylidene fluoride (PVDF)	Poly(1,1-difluoroethylene)	$-[CH_2CF_2]_n-$	24937-79-9	?	-

[*] WMO (2018)

Table A.9: 100-year GWP relative to CO_2.
Adapted from https://ghgprotocol.org/sites/default/files/ghgp/Global-Warming-Potential-Values%20%28Feb%2016%202016%29_1.pdf, Accessed on October 30th 2020.

The following table includes the 100-year time horizon GWP relative to CO_2. This table is adapted from the IPCC Fifth Assessment Report, 2014 (AR5) (44). The AR5 values are the most recent. For more information, please see the IPCC website (www.ipcc.ch). The use of the latest (AR5) values is recommended. Please note that the GWP values provided here from the AR5 for non-CO_2 gases do not include climate-carbon feedbacks.

Table A.2.9. 100-year GWP relative to CO_2.

Industrial designation or common name	**Chemical formula**	**GWP values for 100-year time horizon (based on AR5)**
Carbon dioxide	CO_2	1
Methane	CH_4	28
Nitrous oxide	N_2O	265
Substances controlled by the Montreal Protocol		
CFC-11	CCl_3F	4 660
CFC-12	CCl_2F_2	10 200
CFC-13	$CClF_3$	13 900
CFC-113	CCl_2FCClF_2	5 820
CFC-114	$CClF_2CClF_2$	8 590
CFC-115	$CClF_2CF_3$	7 670
Halon-1301	$CBrF_3$	6 290
Halon-1211	$CBrClF_2$	1 750
Halon-2402	$CBrF_2CBrF_2$	1 470
Carbon tetrachloride	CCl_4	1 730
Methyl bromide	CH_3Br	2
Methyl chloroform	CH_3CCl_3	160
HCFC-21	$CHCl_2F$	148
HCFC-22	$CHClF_2$	1 760
HCFC-123	$CHCl_2CF_3$	79
HCFC-124	$CHClFCF_3$	527
HCFC-141b	CH_3CCl_2F	782
HCFC-142b	CH_3CClF_2	1 980
HCFC-225ca	$CHCl_2CF_2CF_3$	127
HCFC-225cb	$CHClFCF_2CClF_2$	525
Hydrofluorocarbons (HFCs)		
HFC-23	CHF_3	12 400
HFC-32	CH_2F_2	677
HFC-41	CH_3F	116
HFC-125	CHF_2CF_3	3 170
HFC-134	CHF_2CHF_2	1 120
HFC-134a	CH_2FCF_3	1 300
HFC-143	CH_2FCHF_2	328
HFC-143a	CH_3CF_3	4 800
HFC-152	CH_2FCH_2F	16
HFC-152a	CH_3CHF_2	138
HFC-161	CH_3CH_2F	4
HFC-227ea	CF_3CHFCF_3	3 350
HFC-236cb	$CH_2FCF_2CF_3$	1 210
HFC-236ea	CHF_2CHFCF_3	1 330
HFC-236fa	$CF_3CH_2CF_3$	8 060
HFC-245ca	$CH_2FCF_2CHF_2$	716

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[44] Myhre, G., Shindell, D., Bréon,F.-M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D., Lamarque, J.-F., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G., Takemura T. and Zhang, H. 2013. 'Anthropogenic and Natural Radiative Forcing'. In: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung,J., Nauels, A., Xia, Y., Bex, V. and Midgley, P.M. (eds.)]. Cambridge University Press, Cambridge, UK.

Industrial designation or common name	**Chemical formula**	**GWP values for 100-year time horizon (based on AR5)**
HFC-245fa	$CHF_2CH_2CF_3$	858
HFC-365mfc	$CH_3CF_2CH_2CF_3$	804
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	1 650
Perfluorinated compounds		
Sulfur hexafluoride	SF_6	23 500
Nitrogen trifluoride	NF_3	16 100
PFC-14	CF_4	6 630
PFC-116	C_2F_6	11 100
PFC-218	C_3F_8	8 900
PFC-318	c-C_4F_8	9 540
PFC-31-10	C_4F_{10}	9 200
PFC-41-12	C_5F_{12}	8 550
PFC-51-14	C_6F_{14}	7 910
PCF-91-18	$C_{10}F_{18}$	7 190
Trifluoromethyl sulfur pentafluoride	SF_5CF_3	17 400
Perfluorocyclopropane	c-C_3F_6	9 200
Fluorinated ethers		
HFE-125	CHF_2OCF_3	12 400
HFE-134	CHF_2OCHF_2	5 560
HFE-143a	CH_3OCF_3	523
HCFE-235da2	$CHF_2OCHClCF_3$	491
HFE-245cb2	$CH_3OCF_2CF_3$	654
HFE-245fa2	$CHF_2OCH_2CF_3$	812
HFE-347mcc3	$CH_3OCF_2CF_2CF_3$	530
HFE-347pcf2	$CHF_2CF_2OCH2CF3$	889
HFE-356pcc3	$CH_3OCF_2CF_2CHF_2$	413
HFE-449sl (HFE-7100)	$C_4F_9OCH_3$	421
HFE-569sf2 (HFE-7200)	$C_4F_9OC_2H_5$	57
HFE-43-10pccc124 (H-Galden 1040x)	$CHF_2OCF_2OC_2F_4OCHF_2$	2 820
HFE-236ca12 (HG-10)	$CHF_2OCF_2OCHF_2$	5 350
HFE-338pcc13 (HG-01)	$CHF_2OCF_2CF_2OCHF_2$	2 910
HFE-227ea	$CF_3CHFOCF_3$	6 450
HFE-236ea2	$CHF_2OCHFCF_3$	1 790
HFE-236fa	$CF_3CH_2OCF_3$	979
HFE-245fa1	$CHF_2CH_2OCF_3$	828
HFE 263fb2	$CF_3CH_2OCH_3$	1
HFE-329mcc2	$CHF_2CF_2OCF_2CF_3$	3 070
HFE-338mcf2	$CF_3CH_2OCF_2CF_3$	929
HFE-347mcf2	$CHF_2CH_2OCF_2CF_3$	854
HFE-356mec3	$CH_3OCF_2CHFCF_3$	387
HFE-356pcf2	$CHF_2CH_2OCF_2CHF_2$	719
HFE-356pcf3	$CHF_2OCH_2CF_2CHF_2$	446
HFE-365mcf3	$CF_3CF_2CH_2OCH_3$	<1
HFE-374pc2	$CHF_2CF_2OCH_2CH_3$	627
Perfluoropolyethers		
PFPMIE	$CF_3OCF(CF_3)CF_2OCF_2OCF_3$	9 710
Hydrocarbons and other compounds - direct effects		
Chloroform	$CHCl_3$	16
Methylene chloride (dichloromethane)	CH_2Cl_2	9
Methyl chloride	CH_3Cl	12
Halon-1201	$CHBrF_2$	376

IPCC data sources for more information: Fifth Assessment Report values: https://www.ipcc.ch/site/assets/uploads/2018/02/WG1AR5_Chapter08_FINAL.pdf (p. 73-79)

Source: https://ghgprotocol.org/sites/default/files/ghgp/Global-Warming-Potential-Values%20%28Feb%2016%202016%29_1.pdf (Accessed on30 October 2020).

Annex 3. A non-exhaustive list of of different international and European regulations on PFAS

International and EU legislation provides a means of controlling PFAS pollution and protecting the environment and human health. Table A10 provides a (non-exhaustive) summary of different international and European legislation on PFAS. Since the detection of PFAS in human and environmental samples in the 1970s, European Directives and Regulations have provided indirect protective measures by establishing general rules for a range of PFAS, particularly PFOA and PFOS. These include the 1986 Sewage Sludge Directive (86/278/EEC); the 1998 Drinking Water Directive (DWD) (98/83/EC); the 2000 Water Framework Directive (WFD) (2000/60/EC); the 2004 Food Contact Materials Regulation (No. 1935/2004); the 2004 Persistent Organic Pollutants Regulation (No850/2004 in 2004); and the 2006 Groundwater Directive (2006/118/EC).

Furthermore, the EU legislative restrictions, including amendments of previous frameworks as well as future strategies, specifically mention PFAS. The main legislative documents are the following.

- In 2008, EC No 1272/2008 Regulation on Classification, Labelling and Packaging of substances and mixtures (the CLP Regulation), the WFD (2008/98/EC) and Environmental Quality Standards Directive (EQSD) (2008/105/EC).
- In 2010, the EU Industrial Emissions Directive (IED) (Directive 2010/75/EU), covering the management of the PFAS emissions from industrial sources.
- In 2011, the Plastic Materials Regulation (No 10/2011).
- In 2013, the Directive 2013/39/EU, which amended the WFD and the EQSD, provided harmonised guidelines for risk assessment and monitoring of priority substances.
- In 2017, first REACH restriction on PFOA.

Table A10. Overview of some of European Economic Area legislation covering PFAS.

Regulation	Description	How PFAS are regulated
European Regulation (EC) No. 1272/2008 on classification, labelling and packaging of substances and mixtures (the CLP Regulation)	The CLP Regulation harmonises the criteria for classification (CLH) of substances and mixtures, and the rules for labelling and packaging of these hazardous substances and mixtures. The classification of a substance can also determine how substances are covered under other 'downstream' legislation.	A few PFAS (e.g. PFOA, PFDA, PFNA) are subject to harmonised classification under the CLP.
The Public Activities Coordination Tool (PACT)	Provides an overview of the substance-specific activities being undertaken by authorities under the REACH Regulation and the CLP Regulation.	21 different PFAS species are listed on the PACT list.
Council Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work (the Chemical Agents Directive (CAD))	Outlines the minimum requirements for the protection of workers' health and safety arising, or likely to arise, from the effects of chemical agents in the workplace or the use of chemical agents at work. Indicative occupational exposure limit values (IOELVs) are set at a European Economic Area (EEA) level.	10 individual PFAS are covered by the CAD.
Plant Protection Products Regulation (EC) No 1107/2009		Several PFAS (approximately 37) for active substances in plant protection products for which the CLH process has been finished or is still ongoing. Three of those 37 are listed as being active substances in plant protection as well as biocidal products.
Biocidal Product Regulation (EU) No 528/2012 and amendments		11 biocidal active substances contain an aliphatic CF2- or CF3- unit

Regulation	Description	How PFAS are regulated
		(PFAS). Nine of these substances are currently approved as biocidal active substances and include the product types PT18 (insecticides), PT08 (wood preservatives), PT14 (rodenticides), PT07 (film preservatives), PT09 (fibre, leather, rubber and polymer preservatives) and PT10 (building material preservatives) and/or PT 21 (antifouling agents).
Directive 2008/98/EC (the Waste Framework Directive)	Lays down the measures to prevent or reduce the adverse impacts of the generation and management of waste by reducing resource use and improving efficiency of use. The properties of waste which render it hazardous are outlined in Annex III.	Several PFAS (including PFHxS, PFBA, PFPeA, PFHxA, PFHpA and PFBS) meet the criteria for properties of waste which render it hazardous under Annex III of the WFD.
Directive 2013/39/EEA as regards priority substances in the field of water policy (the Water Framework Directive)	Sets environmental quality standards (EQS) for priority substances listed under the WFD.	PFOS and PFOA are listed as priority hazardous substances and have set EQS values.
Directive 98/83/EC on the quality of water intended for human consumption (the Drinking Water Directive)	EU Member States to set quality standard values for the parameters that are set in Annex I, be that microbial or chemical. Regular monitoring is a requirement of this Directive, as is remedial action.	>70 individual PFAS species covered by the DWD.

REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals

The European chemicals legislation REACH includes two complementary regulatory instruments for managing the risks of hazardous chemicals: (a) authorisation, which is a formal approval to continue a specific use of a substance being classified as an SVHC ([45]) for a defined period, and (b) restriction, which is the adoption of measures to reduce or eliminate the risks from production, manufacture and marketing of a substance at an European-wide level. An authorisation is initiated by companies, who can apply for permission to continue using an SVHC beyond a pre-defined end date. Restriction procedures can be initiated by Member States' regulatory authorities or by the ECHA at the request of the EC and can be applied to any substance, including, but not necessarily, SVHCs. For both regulatory instruments the European Commission takes the final decision on adopting risk management measures, based on the written opinions of the ECHA's RAC and SEAC.

The EU restricted the industrial manufacture and use of PFOS and then PFOA under the REACH Regulation (No 1907/2006, No 522/2009; Commission Regulation 2017/1000). On 4 July 2020, based on the SVHC Candidate List, restrictions on the use, import and production of PFOA, its salts and derivatives came into effect with thresholds specific to their applications (No 2019/1021, No 2020/784).

The SVHC Candidate List also includes other PFAS (PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFTDA) due to their vPvB or PBT properties. PFHxA and PFHxS, the latter used as alternative to PFOA, have been proposed as candidates for the list under the REACH restrictions. Two more PFAS were proposed for eventual inclusion in the Restriction Annex XIV of REACH within the SVHC Candidate List: PFBS and 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propionic acid, its salts and acyl halides (HFPO-DA), which have been used as substitutes of PFOS and PFOA, respectively (ECHA, 2020; 2020b). Further safety measures to

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[45] SVHCs are chemicals which are classified as one of the following (a) carcinogenic, mutagenic or toxic for reproduction; (b) persistent, bioaccumulative or toxic (PBT) or very persistent and very bioaccumulative (vPvB), (c) endocrine disrupters; or substances that (d) give "rise to an equivalent level of concern" (EC 2006, Article 57).

protect from hazardous substances, including PFOA, PFNA, PFDA and APFO, have been established by the CLP Regulation (No 1272/2008) that aligns the European system of classification and labelling rules to the Globally Harmonised System (GHS).

Other REACH restrictions on PFAS include the following.

- In October 2017 the German and Swedish authorities proposed restricting the manufacture, marketing and use of perfluorocarboxylic acids with 9–14 carbon atoms (PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFTeDA). This regulatory procedure is completed and the restriction will enter into force in February 2023.
- A restriction proposal for PFHxS (perfluorohexanesulfonic acid, C6) was submitted by the Norwegian authorities in April 2019 and was discussed in ECHA's RAC and SEAC. The final RAC/SEAC Opinion was published in autumn 2020.
- In December 2019, a German proposal to regulate PFHxA (perfluorohexanoic acid, C6) was submitted and was discussed in the ECHA committees.
- ECHA has registered an intention to submit a restriction 1 October 2021 for the use PFAS in fire-fighting foams.

The POPs Regulation EC 850/2004

The EU has implemented the POPs Regulation (EC 850/2004, recast under Regulation EC 2019/1021) which acts to implement the provisions of the Stockholm Convention across EEA Member States.

PFOS was originally included in the restricted substances list of REACH. However, since its addition to the Stockholm Convention in 2009, it has been regulated under the POPs Regulation. PFOS, its salts and perfluorooctanesulfonyl fluoride (PFOSF) are listed under Annex I of the POPs Regulation, specifying the following exemptions for unintentional trace contaminants (UTCs):

i. substances or preparations (<10 mg/kg);
ii. semi-finished products or articles, or parts (<0.1 % by weight calculated with reference to the mass of structurally or micro-structurally distinct parts that contain PFOS or, for textiles or other coated materials, if the amount of PFOS is lower than 1 μg/m^2 of the coated material).

PFAS in sector-specific legislations

EU Industrial Emissions Directive

The Industrial Emissions Directive (Directive 2010/75/EU) regulates pollutant emissions from large industrial installations in the EU, including emissions of PFAS from sites where they are produced or used. Industrial activities which exceed production thresholds listed in the IED's Annex I must obtain a permit from the competent authorities in the relevant Member State. Sector 4 of Annex I covers the chemical industry ([46]), including the facilities that are currently producing fluorochemicals and fluorinated polymers. Releases of PFAS to the environment can also occur during the manufacture of products in which PFAS are used. Some of these activities are also listed in the IED's Annex I: for example, the production of textiles, pulp, paper and cardboard.

The permits are based on the best available techniques (BATs) described in BAT Reference Documents (BREFs). The Commission adopts the BAT conclusions as Implementing Decisions and Member States use them as a reference to define the permit conditions. In particular, the BAT associated emission levels (BAT-

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[46] The parts of Annex I Sector 4 that are relevant for PFAS are:
4.1 Production of organic chemicals such as…
(f) halogenic hydrocarbons,…
(h) plastic materials (polymers, synthetic fibres and cellulose-based fibres), …
(k) surface-active agents and surfactants.
4.4 Production of plant protection products or of biocides.
4.5. Production of pharmaceutical products including intermediates.

AELs) stated in BAT conclusions must not be exceeded when competent authorities set Emission Limits Values (ELVs) in permits. Annex II of the IED lists the polluting substances for which ELVs must be set in the permits and it indirectly covers some PFAS ([47]). In addition, Article 14(1)a of the IED requires ELVs to be set in permits "*for other polluting substances, which are likely to be emitted from the installation concerned in significant quantities, having regard to their nature and their potential to transfer pollution from one medium to another*".

Waste treatment facilities are covered by the IED and these can emit PFAS. The BAT conclusions for waste treatment ([48]) address PFOA and PFOS, but not other PFAS. Permits are given to waste treatment plants on condition that they implement the obligations within four years of the publication of a BAT conclusion. Authorities can consider setting emissions limits for all other PFAS as well as for PFOS and PFOA.

EU regulation on food-contact materials

Seventeen categories of FCM exist and fluorinated polymers are relevant to at least food plastics, coatings, paper and board, waxes, inks and elastomers. Five of the 17 uses, including food plastics, have specific regulations. The 12 other materials are so-called non-harmonised materials. The EU Plastics Regulation on Food Contact Materials (EU 10/2011) is a positive list which covers monomers and polymer production aids as well as *migration from* the final polymer article. This includes non-intentionally added substances (NIAS) at levels above the threshold of toxicological concern, which currently is set at 10 µg/kg food. These substances go through authorisation by the EFSA, based on hazard and risk criteria which are more than 30 years old (Muncke et al. 2017). While CMR and persistent chemicals in general should be avoided in FCM, many are allowed due to old authorisations or if it can be shown to be likely, for example, by migration modelling (Brandsch et al., 2015; Simoneau et al., 2011), that migration to food will not occur in amounts of toxicological concern. Modelling can be applied if the assumptions are fulfilled, for instance, that the substances in question are homogeneously distributed in the polymer, but in practice these assumptions may not be fulfilled. The FCM Regulation including the Framework Regulation (EC) No. 1935/2004, the Good Manufacturing Practices Regulation (EC) No. 2023/2006, the Plastics Regulation (EU) No. 10/2011 are currently being revised. Limit values related to either specific migration or total migration will finally be set, or a limit of non-detectability is set – a default is currently defined as 10 µg/kg food.

Examples of fluorinated polymers used in FCMs are metal coatings for non-stick pans, and baking and kitchen utensils used by consumers or in industrial food production. Fluorinated elastomers are typically used in tubing, membranes, baking trays and conveyor belts in industrial food production. Per- and polyfluorinated polyether polymers, according to the ECHA definition, are used in oil pumps and as lubricants in food production facilities. They, and fluorinated side-chain polymers, are also used as coatings and sizing agents in paper and board single-use food packaging and as food kitchen utensils such as bowls (Lohman et al., 2020; Dimzon et al., 2015; Trier et al., 2018; Trier et al. 2011, Kärrman et al., 2019).

EU Regulation on cosmetics

Regulation (EC) No 1223/2009 on cosmetic products lays out the rules that cosmetic products must comply with if they are to be made available on the market. Annex II lists the substances that are prohibited for use in cosmetics; PFOS and PFOA and their salts are prohibited, although they are found as impurities in some products. All prohibited substances are included in Annex II of the Cosmetics Regulation: Cosing_Annex II_v2 ([49]).

Detergents

Detergents are typically intentional mixtures of surfactants, consisting of a hydrophic (water repellent) tail and a hydrophilic (water soluble) polar head. These detergent mixtures are made up of so-called homologue series which vary in the lengths of their hydrophobic tails. When the hydrophobic tail are chains of (monomer) repeat units, they qualify as polymers and are exempted from REACH (Krafft and

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[47] Annex I includes PFAS identified as CMRs and PBTs.

[48] Commission Implementing Decision 2018/1147 of 10 August 2018.

[49] https://ec.europa.eu/growth/tools-databases/cosing/pdf/COSING_Annex%20II_v2.pdf

Riess, 2015). The Regulation on Detergents (EU 648/2004) and its amendments set requirements and describe methods to test detergents' ability to biodegrade initially (primary degradation) and ultimately (also called mineralisation). Since 2012, the Regulation also limits the content of phosphates, a nutrient affecting water systems, but the regulation neither assesses other impacts on human or environmental health, nor impacts along a detergent's lifecycle.

Fluorinated detergents/cleaning agents may be used as graffiti removers, and PFPEs have been used as spreading/wetting agents in floor detergents and waxes (Glüge et al., 2020).

European-Pollutant Release and Transfer Register

The European Pollutant Release and Transfer Register (E-PRTR) ([50]) makes emission data reported by Member States on major industrial activities publicly accessible. It covers emissions from the activities defined in Annex I of the E-PRTR Regulation ([51]), which largely equates to Annex I of the IED. Some of these activities are sources of PFAS related to fluorinated polymers, for example, in the chemical industry, surface treatment of metals, waste and waste water management, and the production of textiles and leather.

EU Regulations on waste

Waste are classified as hazardous or non-hazardous ([52]). The waste classification has several implications. There are numerous EU Regulations setting special requirements for waste defined as hazardous, for example, the Waste Shipment Regulation (WSR) requires permits for the export/import of hazardous waste both within EU and between EU and OECD countries beyond the EU. Waste classified as hazardous can only be disposed of in hazardous waste landfills meeting the acceptance criteria. Furthermore, the IED and the Environmental and Impact Assessment Directive concern the management of hazardous waste.

F-gas Regulation

There is a specific regulation on fluorinated GHGs (EU) No 517/2014). Since the mid-1990s ODS have been substituted by certain F-gases, in particular HFCs. Regulation (EU) No. 517/2014 aims to reduce 2030 industrial emissions by 70% compared to 1990. This reduction is to be realised by three means.

1. The gradual phase-down of the quantities of HFCs used by means of quotas. The phase-down only applies to HFCs and not to perfluorocarbons (PFCs) or SF_6.
2. Prohibitions on use and placement on the market of F-gases, insofar as is technically feasible and more climate-friendly alternatives are available.
3. Continuation and expansion of the scope of regulations concerning leak tests, certification, disposal and labelling.

Annex I Section I of the F-gas Regulation lists a number of HFCs, whereas Section 2 lists a number of PFCs that may overlap with the current restriction proposal under development.

Specifically, HFC-23 is a known by-product from fluoropolymer production (HCFC-22), as also described in Chapter 4. Twenty-seven fluorinated ethers and one perfluorinated polyether are also listed as GHGs which potentially could be used or formed during the lifecycle of fluorinated ether polymers, such as the PFPEs.

Chemicals Strategy for Sustainability

Taking a forward-looking perspective, the Chemicals Strategy for Sustainability towards toxic-free environments under the European Green Deal pays special attention to PFAS, considering numerous cases

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[50] https://ec.europa.eu/environment/industry/stationary/eper/legislation.htm
https://prtr.eea.europa.eu/#/home

[51] https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1583400375088&uri=CELEX:32006R0166

[52] Hazardous waste is a waste that due to its (intrinsic) chemical or other properties poses a risk to the environment and/or human health. The classification is primarily based on the European List of Waste (2014/955/EU) or on its hazardous properties. The European Commission Regulations Nos. 1357/2014 and 2017/997 define the properties for hazardous waste classification referring to assessment methods developed in CLP.

of environmental contamination (COM(2020) 667 final). Therefore, the strategy adopted a PFAS group approach under relevant legislation for water as well as banning them in fire-fighting foams and other non-essential uses. Further aims include enhanced policy dialogues and international forums, support for the development of innovative remediation methodologies and safe PFAS substitutes.

GLOBAL LEGISLATION AND MAJOR LEGISLATION OUTSIDE EUROPE

his section covers the most relevant global-scale legislation on PFAS.

Stockholm Convention and Persistant Organic Pollutants Regulation

The Stockholm Convention on Persistant Organic Pollutants is an international treaty that aims to eliminate or restrict the production and use of these substances in order to protect human health and the environment.

The POP Regulation (EC 2019/1021) transfers the resolutions of the Stockholm Convention into EU measures/law.

Currently, the most horizontal and widest legally-binding PFAS regulations of are in the Stockholm Convention. At global level, the Convention imposed restrictions (Annex B) on the use of PFOS ([53]), its salts and PFOSF in specific products (Decision SC-4/17) in 2009, and in 2019 included PFOA ([54]), its salts and related compounds for elimination from specific uses (IISD, 2019). After being placed on the POPs list in 2009, there was an increase in the number of countries that put legal and administrative measures in place to control PFOS production, import, export and use. Perfluorohexane sulfonic acid(PFHxS), its salts and related compounds have been proposed for listing in the Annex A of the Convention without specific exemptions (Stockholm Convention, 2019). Potential toxicity of PFAS precursors has also been highlighted by the OECD (OECD, 2007).

Montreal protocol

The Montreal Protocol on Substances that Deplete the Ozone Layer is the landmark multilateral environmental agreement transferred in Regulation (EC) No 1005/2009 that regulates nearly 100 man-made chemicals referred to as ODS. The protocol regulates production, import, export, placing on the market, use, recovery, recycling, reclamation and destruction of ODS. Adopted on 15 September 1987, the Protocol is to date the only UN treaty that has been ratified by all UN Member States.

Predominantly CFCs and HCFCs are covered by the Montreal Protocol, ranging from C1-C3 as core, partly or fully halogenated. HCFCs are gases used worldwide in refrigeration, air-conditioning and foam applications, but they are being phased out under the Montreal Protocol. They are both ODS and powerful GHGs: the most commonly used HCFC is nearly 2,000 times more potent than CO_2 in terms of its GWP.

The quantitative limits and allocating quotas for substances controlled under EC Regulation No 1005/2009 are updated yearly by means of a decision which lists the amounts, the addressees and the quota per group of companies. The latest ones are Decisions (EU) Nos. 2019/2079 and 2018/2029. A number of substances that are used as process agents are derogated from the restrictions. Thus, substances such as chlorofluorocarbon 113 (CFC113) and HCFC22, which are used as intermediates in the production of fluoropolymers, are not phased out.

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[53] The Stockholm Convention covers PFOS, salts and PFOSF. In the EU POPs Regulation, the definition of the scope is *"Perfluorooctane sulfonic acid and its derivatives (PFOS) C8F17SO2X (X = OH, metal salt (O-M+), halide, amide, and other derivatives including polymers)"*.

[54] Commission Delegated Regulation (EU) 2020/784 of 8 April 2020 amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council.

The Montreal Protocol also makes important contributions to the realisation of the UN Sustainable Development Goals.

Overall, the Montreal Protocol phased out the use of ozone-depleting CFCs except for certain essential uses, and also defined the concept of essential use in Decision IV/25 ([55]). As a result, the Montreal Protocol's concept of essential use has been put forward as an approach for reducing exposure to PFAS by phasing out all non-essential uses.

United States

Until very recently, PFAS have been largely unregulated at the federal level. Several US states have, however, set their own drinking-water guideline levels for PFOA and PFOS ([56]). The Interstate Technology and Regulatory Council (ITRC) indicated the significant variation in PFAS regulations by identifying the states that have different guideline for PFOA and/or PFOS levels in drinking- and groundwater from US EPA's health advisories (HAs) ([57]). From 2006 to 2015, the US EPA worked with eight major chemical manufacturers to voluntarily phase out production and use of so-called long-chain PFAS and their precursors (PFOA Stewardship Program) (U.S. EPA 2020a). The eight companies participating in the PFOA Stewardship Program met its goals ([58; 59]) At the federal level, the US EPA set a non-enforceable lifetime HA level for PFOA and PFOS, individually or combined, of 70 parts per trillion (ppt) in drinking water in 2016, (US EPA 2020b). This lifetime HA is based on the latest information on health effects for cancer and other diseases. The HA is not a legally enforceable federal standard and is subject to change as new information becomes available. That action was criticised for having no enforcement mechanism, for only addressing two compounds and for promulgating a maximum PFAS concentration that does not adequately protect human health. Some states have decided to set lower advisory levels while others have implemented enforceable maximum contaminant levels (MCLs) at the state level for specific PFAS chemicals.

In 2019, US EPA released its National PFAS Action Plan to provide both short-term solutions and long-term strategies to address this important issue. This Plan is designed to support the Safe Drinking Water Act (SDWA), which addresses PFAS in drinking water. In addition, the PFAS Action Act of 2019 requires the US EPA to establish destruction and disposal guidance for a range of materials, including landfill leachate, biosolids, and "*solid, liquid, or gas waste streams*" from facilities that manufacture or use PFAS ([60]). The legislation requires that, over a five-year period, the US EPA reviews all other PFAS chemicals and decides whether to list them under Superfund. This is designed to investigate and clean-up sites contaminated with hazardous substances ([61]).

In February 2020, the US EPA proposed regulating PFOA and PFOS under the Safe Drinking Water Act. In June 2020, a PFAS Significant New Use rule (SNUR) issued under Toxic Substance Control Act (TSCA) came into force affecting the importation of PFAS.

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[55] United Nations, Montreal Protocol on Substances that Deplete the Ozone Layer, Montreal, Canada, 1987

[56] Abunada, Z., Alazaiza, M.Y. and Bashir, M.J. 2020. 'An Overview of Per-and Polyfluoroalkyl Substances (PFAS) in the Environment: Source, Fate, Risk and Regulations'. *Water* 12(12):3590.

[57] ITRC. 2020. *PFAS Technical and Regulatory Guidanace Document and Fact Sheet PFAS-1*. Interstate Technology and Regulatory Council, Washington, DC, US.

[58] US EPA. 2010. *Assessing and Managing Chemicals Under TSCA Fact sheet: 2010/2015 PFOA Stewardship Program*. United States Environmental Protection Agency, Washington, DC, US."
https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program (accessed 28 October 20102021))

[59] US EPA. 2020c. *Risk management for per- and polyfluoroalkyl substances (PFASs) under TSCA*. United States Environmental Protection Agency, Washington, DC, US. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfas

[60] https://19january2021snapshot.epa.gov/pfas/epas-pfas-action-plan_.html

[61] Dean, W.S., Adejumo, H.A., Caiati, A., Garay, P.M., Harmata, A.S., Li, L., Rodriguez, E.E. and Sundar S.A. 2020. 'Framework for Regulation of New and Existing PFAS by EPA'. *J. Sci. Policy Governance* 2020;16.

The classification of 160 PFAS chemicals as hazardous chemicals under Emergency Planning and Community Right to-Know Act (EPCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) increases the pressure on US EPA to take a stricter stance in applying TSCA restrictions in the manufacturing of new and existing PFAS.

In December 2020, US EPA released interim guidance for PFAS disposal under National Defense Authorization Act.

In addition, within the National Defense Authorization Act, 2019, the Pentagon will be restricted in purchasing PFAS foams (FFF) after 2022, and prohibited from using PFAS foams after 2023.

Recently, the State of California's Department of Toxic Substances Control (DTSC) uses the P-sufficient approach as the rationale for regulating PFAS as a chemical class in certain consumer products ([62]). The idea behind the P-sufficient approach is that the persistence of PFAS is a sufficient basis to warrant regulation regardless of other hazard traits such as the chemicals' bioaccumulation potential or toxicity.

Canada

Canada has implemented a combination of regulatory and voluntary actions to reduce the risks from certain PFAS. The Canadian Government has been involved in developing regulations and guidance for certain PFAS since the early 2000s. Several federal departments are involved in different aspects of this work. Significant PFAS work is carried out under the Federal Contaminated Sites Action Plan (FCSAP) which is largely related to the PFAS resulting from aqueous film-forming foams (AFFF) use. The FCSAP program develops guidelines and guidance to assess and manage federal PFAS-contaminated sites.

The Chemicals Management Plan (CMP) is another program with significant involvement in the assessment and management of certain PFAS. The CMP has an environmental monitoring and surveillance program for air, water, sediment and biota that provides data on certain PFAS to support risk assessment and risk management tools.

Environment and Climate Change Canada (ECCC) and Health Canada (HC) are jointly responsible for assessing chemical substances in Canada to determine their risks to the environment and human health, and develop risk management instruments to address the identified risks, including through regulation. Health Canada recently published maximum acceptable concentrations (MACs) for PFOS ([63]) and PFOA ([64]) as well as drinking water screening values (DWSV) for other PFAS.

In 2006, Canada launched their Action Plan for the Assessment and Management of Perfluorinated Carboxylic Acids and their Precursors. For their regulatory approaches, Canada has prohibited the manufacture, importation, use, sale, and offer for sale ([65]) of four fluorotelomer-based substances and PFOS with some exemptions.

In 2008, the Government of Canada published regulations for PFOS and its salts that prohibit the manufacture, importation, sale, offer for sale and use of PFOS or products containing PFOS. At the time, there were some exemptions for their continued use by selected sectors at reduced concentrations. More

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[62] Bălan, S.A., Mathrani, V.C., Guo, D.F. and Algazi, A.M. 2021. 'Regulating PFAS as a chemical class under the California Safer Consumer Products Program'. *Environmental Health Perspectives*. 129(2):025001.

[63] Health Canada. 2018a. *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Perfluorooctane Sulfonate (PFOS)*. Health Canada, Ottawa, ON, Canada.

[64] Health Canada. 2018b. *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Perfluorooctanoic Acid (PFOA)*. Health Canada, Ottawa, ON, Canada.

[65] Health Canada. 'Water talk - drinking water screening values: perfluoroalkylated substances'. Retrieved from https://www.canada.ca/en/services/health/publications/healthy-living/water-talk-drinking-water-screening-values-perfluoroalkylated-substances.html

recently, in 2018, Canada proposed removing, or providing time limits, for the previous exemptions for PFOS, its salts and precursors ([66]).

In 2016, the Government of Canada published regulations that prohibit the manufacture, importation, use, sale and offer for sale of PFOA and long-chain Perfluorocarboxylic acids (LC-PFCAs C8 ≤ n ≤ C20), their salts, and their precursors with exemptions for specific uses [67].

Currently, the Government of Canada has regulations in place that prohibit the manufacture, use, sale, offer for sale, or import of PFOS, PFOA, and long-chain perfluorocarboxylic acids (LC-PFCAs), as well as their corresponding salts and precursors, and products containing these substances, with a limited number of exemptions. These regulations are under review with the objective of removing or further limiting exemptions for specific uses.

In 2018, the Canadian Federal-Provincial-Territorial Committee on Drinking Water and the Federal-Provincial-Territorial Committee on Health and the Environment released a technical guideline document, which reviewed and assessed all identified health risks associated with PFOS and PFOA in drinking water. It incorporated available studies and approaches and took into consideration the availability of appropriate treatment technology. Based on the review, the drinking water guideline for PFOS and PFOA was set at a MAC of 0.6 µg/l (600 ppt) and 0.2 µg/l (200 ppt) based on the general population.

In June 2019 Transport Canada allowed airports to use PFAS-free firefighting foam, which shows a more precautionary approach as it targets the whole class of PFAS.

Canadian federal guidelines or screening values to protect human health are now available for 11 PFAS, while values to protect ecological receptors are available for PFOS.

Australia

PFAS are not manufactured in Australia. The country’s approach to risk reduction is a combination of regulatory, policy and voluntary approaches focused on reducing the importation and use of some PFAS, such as long-chain non-polymer PFAS, and on preventing and responding to PFAS contamination consistently, using best practice.

The PFAS National Environmental Management Plan (NEMP), January 2020, from the National Chemicals Working Group of the Heads of EPAs Australia and New Zealand (HEPA) and Australia’s Department of the Environment and Energy (DoEE), provides nationally agreed guidance on the management of PFAS contamination in the environment. The NEMP is an appendix to the Intergovernmental Agreement on a National Framework Responding to PFAS Contamination and is designed to achieve a clear, effective coherent and nationally consistent approach to the environmental regulation of PFAS.

The NEMP reflects the current state of knowledge and is updated regularly to provide an evidence-based approach that will be adapted to reflect increasing scientific knowledge relevant to environmental regulation of PFAS. The plan mainly provides guidance about PFOS, PFOA, PFHxS and their direct and indirect precursors, as these are the most widely studied and recognise them as primary indicators of a broad range of PFAS, including short-chain and other long-chain PFCA and PFSA.

Australia will continue to participate in the Stockholm Convention’s processes and to address any domestic implementation requirements that may result if PFHxS or other PFAS are listed. In the meantime, the

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[66] Government of Canada. 2018. ‘Proposed amendments to the prohibition of certain toxic substances regulations’. Consultation document
https://www.canada.ca/en/environment-climate-change/services/canadian-environmental-protection-act-registry/proposed-amendments-certain-toxic-substances-2018-consultation.html

[67] Government of Canada. 2016. ‘Substance prohibition summary for PFOA, long-chain PFCAs and related substances’.
https://www.canada.ca/en/environment-climate-change/services/canadian-environmental-protection-act-registry/substance-prohibition-summary-perfluorooctanoic-acid.html (accessed 28 October 2021)

globally accepted standards outlined in the Convention for the use and management of POPs are a fundamental point of reference for the guidance provided in the NEMP.

Environmental Regulatory Efforts in Asia

There is significantly less governmental regulation of PFAS in Asia compared to that in Europe or the United States. In countries such as Bangladesh, India, Indonesia, and Malaysia, PFAS are essentially unregulated and not monitored. Japan has taken measures to regulate PFOA, PFHxA, PFHxS and PFOS in manufacturing with no maximum levels for any PFAS set for drinking water water in the country. Additionally, PFOS and its salts are listed in Class I Specified Chemical Substances under the Chemical Substances Control Law (CSCL).

In 2008, the Ministry of Environmental Protection (MEP) in China released Substances listed under the High Pollution, High Environmental risk Product Catalogue, which includes high temperature melting membrane fluorine resin coating used on non-stick cookware, kitchenware and food processing machinery, based on the potential residual PFOA in the products to establish financial and environmental protection priorities.

In 2011, the National Development and Reform Commission in China issued an Industrial Reconstructing Guide Directory Restriction on the production of PFOS and PFOA and support for research and development on alternatives to these substances. In 2014, the MEP issued Announcement No.[2014]21, banning production, transportation, application, imports and exports of PFOS, its salts and PFOSF, except for specific exemptions and acceptable uses.

Since 2013, South Korea addressed PFOS, its salts and PFOSF as restricted substances under the Persistent Organic Pollutants Control Act. Under the Act, any manufacture, import, export and use of PFOS, its salts and PFOSF are restricted except for specific exemptions and acceptable uses defined in the Stockholm Convention.

Annex 4. PFAS list

SUPPLEMENTAL

PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES IN THE ENVIRONMENT: TERMINOLOGY, CLASSIFICATION, AND ORIGINS

Table of Contents

PART 1 – FAMILIES OF SUBSTANCES (NON-POLYMERS)

NAME OF FAMILY	FORMULA	ACRONYM
Perfluoroalkyl substances	Generic name: See main paper	PFASs
Perfluoroalkyl acids	Includes perfluoroalkyl carboxylic, sulfonic, sulfinic, phosphonic and phosphinic acids	PFAAs
Perfluoroalkyl carboxylic acids	$C_nF_{2n+1}COOH$	PFCAs
Perfluoroalkane sulfonic acids	$C_nF_{2n+1}SO_3H$	PFSAs
Perfluoroalkane sulfinic acids	$C_nF_{2n+1}SO_2H$	PFSIAs
Perfluoroalkyl phosphonic acids	$O=P(OH)_2C_nF_{2n+1}$	PFPAs
Perfluoroalkyl phosphinic acids	$O=P(OH)(C_nF_{2n+1})(C_mF_{2m+1})$	PFPIAs

NAME OF FAMILY	FORMULA	ACRONYM
Perfluoroalkyl iodides	$C_nF_{2n+1}I$	PFAIs
(n:2) Fluorotelomer iodides	$C_nF_{2n+1}CH_2CH_2I$	(n:2) FTIs
(n:2) Fluorotelomer olefins	$C_nF_{2n+1}CH=CH_2$	(n:2) FTOs
(n:2) Fluorotelomer alcohols	$C_nF_{2n+1}CH_2CH_2OH$	(n:2) FTOHs
(n:2) Fluorotelomer acrylates	$C_nF_{2n+1}CH_2CH_2OC(O)CH=CH_2$	(n:2) FTACs
(n:2) Fluorotelomer methacrylates	$C_nF_{2n+1}CH_2CH_2OC(O)C(CH_3)=CH_2$	(n:2) FTMACs

Polyfluoroalkyl phosphoric acid esters / Polyfluoroalkyl phosphates / (n:2) Fluorotelomer phosphates	$(O)P(OH)_{3-x}(OCH_2CH_2C_nF_{2n+1})_x$	PAPs
Polyfluoroalkyl phosphoric acid monoesters	$(O)P(OH)_2(OCH_2CH_2C_nF_{2n+1})$	monoPAPs
Polyfluoroalkyl phosphoric acid diesters	$(O)P(OH)(OCH_2CH_2C_nF_{2n+1})(OCH_2CH_2C_mF_{2m+1})$	diPAPs
Semi-fluorinated *n*-alkanes	$F(CF_2)_n(CH_2)_mH$	SFAs
Semi-fluorinated *n*-alkenes	$F(CF_2)_nCH=CH(CH_2)_{m-2}H$	SFAenes
(n:2) Fluorotelomer (saturated) aldehydes	$C_nF_{2n+1}CH_2CHO$	(n:2) FTALs
(n:2) Fluorotelomer unsaturated aldehydes	$C_{n-1}F_{2n-1}CF=CHCHO$	(n:2) FTUALs
Perfluoroalkyl aldehydes	$C_nF_{2n+1}CHO$	PFALs
Perfluoroalkyl aldehyde hydrates	$C_nF_{2n+1}CH(OH)_2$	PFAL.H_2Os
(n:2) Fluorotelomer (saturated) carboxylic acids	$C_nF_{2n+1}CH_2COOH$	(n:2) FTCAs
(n:2) Fluorotelomer unsaturated carboxylic acids	$C_{n-1}F_{2n-1}CF=CHCOOH$	(n:2) FTUCAs
[Biotransformation product of (n+1):2 FTOH]	$C_nF_{2n+1}CH_2CH_2COOH$	n:3 Acid
[Biotransformation product of (n+1):2 FTOH]	$C_nF_{2n+1}CH=CHCOOH$	n:3 UAcid
(n:2) Fluorotelomer sulfonic acids	$C_nF_{2n+1}CH_2CH_2SO_3H$	(n:2) FTSAs

NAME OF FAMILY	FORMULA	ACRONYM
Perfluoroalkane sulfonyl fluorides	$C_nF_{2n+1}SO_2F$	PASFs
Perfluoroalkane sulfonamides	$C_nF_{2n+1}SO_2NH_2$	FASAs
N-Methyl perfluoroalkane sulfonamides	$C_nF_{2n+1}SO_2NH(CH_3)$	MeFASAs
N-Ethyl perfluoroalkane sulfonamides	$C_nF_{2n+1}SO_2NH(C_2H_5)$	EtFASAs
N,*N*-Dialkyl perfluoroalkane sulfonamides	$C_nF_{2n+1}SO_2N(C_mH_{2m+1})(C_pH_{2p+1})$, with m, p = 1 or 2	Me_2FASAs, Et_2FASAs, MeEtFASAs
Perfluoroalkane sulfonamidoethanols	$C_nF_{2n+1}SO_2NHCH_2CH_2OH$	FASEs
Perfluoroalkane sulfonamidoacetic acids	$C_nF_{2n+1}SO_2NHCH_2COOH$	FASAAs
N-Methyl perfluoroalkane sulfonamidoethanols	$C_nF_{2n+1}SO_2N(CH_3)CH_2CH_2OH$	MeFASEs
N-Ethyl perfluoroalkane sulfonamidoethanols	$C_nF_{2n+1}SO_2N(C_2H_5)CH_2CH_2OH$	EtFASEs
N-Methyl perfluoroalkane sulfonamidoacetic acids	$C_nF_{2n+1}SO_2N(CH_3)CH_2COOH$	MeFASAAs
N-Ethyl perfluoroalkane sulfonamidoacetic acids	$C_nF_{2n+1}SO_2N(C_2H_5)CH_2COOH$	EtFASAAs
N-Methyl perfluoroalkane sulfonamidoethyl acrylates	$C_nF_{2n+1}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	MeFASACs
N-Ethyl perfluoroalkane sulfonamidoethyl acrylates	$C_nF_{2n+1}SO_2N(C_2H_5)CH_2CH_2OC(O)CH=CH_2$	EtFASACs
N-Methyl perfluoroalkane sulfonamidoethyl methacrylates	$C_nF_{2n+1}SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$	MeFASMACs
N-Ethyl perfluoroalkane sulfonamidoethyl methacrylates	$C_nF_{2n+1}SO_2N(C_2H_5)CH_2CH_2OC(O)C(CH_3)=CH_2$	EtFASMACs

PART 2 – SELECTED INDIVIDUAL COMPOUNDS (NON-POLYMERS)

Chlorocarbons	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Tetrachloromethane (carbon tetrachloride)	CCl_4	56-23-5	CTC
Chloromethane (methyl chloride)	CH_3Cl	74-87-3	MC
Dichloromethane (methylene chloride)	CH_2Cl_2	75-09-2	DCM
1,2-Dichloroethane	$C_2H_4Cl_2$	107-06-2	1,2-DCE
Tetrachloroethylene	$CCl_2=CCl_2$	127-18-4	Perc

Fluorocarbons (FCs)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Difluorocarbene	CF_2^{2-}	None available	
Trifluoromethyl	CF_3^-	None available	
Carbon tetrafluoride (tetrafluoromethane)	CF_4	75-73-0	PFC-14
Tetrafluoroethylene	C_2F_4	116-14-3	TFE
Hexafluoroethane	C_2F_6	76-16-4	PFC-116
Hexafluoropropylene	$CF_3CF=CF_2$	116-15-4	HFP
Heptafluoropropyl	$C_3F_7^-$	None available	
Hexafluoro-1,3-butadiene	C_4F_6	685-63-2	
Octafluorocyclobutane	c-C_4F_8	115-25-3	PFC-318
Fluorocarbonyl	CFO	1871-24-5	
Carbonyl difluoride	CF_2O	353-50-4	
Trifluoroacetyl fluoride	C_2F_4O	354-34-7	
Hexafluoropropylene oxide	C_3F_6O	428-59-1	HFPO

Chlorofluorocarbons (CFCs)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Chlorofluoromethylene	$CClF^{2-}$	None available	
Chlorotrifluoroethylene	$CClF=CF_2$	79-38-9	CTFE
Trichloroethylene	$CClH=CCl_2$	79-01-6	TCE
Fluorotrichloromethane	CCl_3F	75-69-4	CFC-11

Hydrochlorofluorocarbons (HCFCs)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Chlorodifluoromethane	$CHClF_2$	75-45-6	HCFC-22
2,2-Dichloro-1,1,1-trifluoroethane	$C_2HCl_2F_3$	306-83-2	HCFC-123
1-Chloro-1,2,2,2-tetrafluoroethane	C_2HClF_4	2837-89-0	HCFC-124
1,2-Dichloro-1,1-difluoroethane	$C_2H_2Cl_2F_2$	1649-08-7	HCFC-132b
1-Chloro-1,1-difluoroethane	$C_2H_3ClF_2$	75-68-3	HCFC-142b
1-Chloro-3,3,3-trifluoropropylene	$CF_3CH=CHCl$	102687-65-0	HCFC-1233zd(E)

Hydrofluorocarbons (HFCs)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Poly(fluoromethylene)	CHF	36572-92-6	
Trifluoromethane (fluoroform)	CHF_3	75-46-7	HFC-23
Fluoromethane	CH_3F	593-53-3	HFC-41
Fluoroethane	C_2H_5F	353-36-6	
1,1,1-Tetrafluoroethane	$CHFCF_3$	811-97-2	HFC-134a
1,1,1-Trifluoroethane	CH_3CF_3	420-46-2	HFC-143a
1,1,2-Tetrafluoroethane	$CHFCF_2$	430-66-0	HFC-143
Vinylidene fluoride (1,1-Difluoroethylene)	$CH_2=CF_2$	24937-79-9	VDF
1,2-Difluoroethane	$C_2H_4F_2$	624-72-6	HFC-152
1,1-Difluoroethane	$C_2H_4F_2$	75-37-6	HFC-152a
1,2-Difluoroethylene	$C_2H_3F_3$	1691-13-0	
Fluoroethane	C_2H_5F	353-36-6	HFC-161
2,3,3,3-Tetrafluoropropylene	$CF_3CF=CH_2$	754-12-1	HFO-1234yf
1,3,3,3-Tetrafluoropropylene	$CF_3CH=CF$	29118-24-9	HFO-1234ze(E)

Perfluoroalkyl carboxylic acids (and selected salts)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Difluoroacetic acid	CF_2COOH	381-73-7	
Trifluoroacetic acid	CF_3COOH	76-05-1	TFAA
Perfluoropropanoic acid	C_2F_5COOH	422-64-0	PFPrA
Perfluorobutanoic acid	C_3F_7COOH	375-22-4	PFBA
Ammonium perfluorobutanoate	$NH_4^+ C_3F_7COO^-$	10495-86-0	NH_4-PFBA
Sodium perfluorobutanoate	$Na^+ C_3F_7COO^-$	2218-54-4	Na-PFBA
Perfluoropentanoic acid	C_4F_9COOH	2706-90-3	PFPeA
Ammonium perfluoropentanoate	$NH_4^+ C_4F_9COO^-$	68259-11-0	NH_4-PFPeA
Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4	PFHxA
Ammonium perfluorohexanoate	$NH_4^+ C_5F_{11}COO^-$	21615-47-4	NH_4-PFHxA
Sodium perfluorohexanoate	$Na^+ C_5F_{11}COO^-$	2923-26-4	Na-PFHxA
Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9	PFHpA
Ammonium perfluoroheptanoate	$NH_4^+ C_6F_{13}COO^-$	6130-43-4	NH_4-PFHpA
Sodium perfluoroheptanoate	$Na^+ C_6F_{13}COO^-$	20109-59-5	Na-PFHpA
Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1	PFOA
Ammonium perfluorooctanoate	$NH_4^+ C_7F_{15}COO^-$	3825-26-1	APFO (or NH_4-PFOA)
Sodium perfluorooctanoate	$^{222}Na^+ C_7F_{15}COO^-$	335-95-5	Na-PFOA
Potassium perfluorooctanoate	$K^+ C_7F_{15}COO^-$	2395-00-8	K-PFOA
Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1	PFNA
Ammonium perfluorononanoate	$NH_4^+ C_8F_{17}COO^-$	4149-60-4	APFN (or NH_4-PFNA)
Sodium perfluorononanoate	$Na^+ C_8F_{17}COO^-$	21049-39-8	Na-PFNA
Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2	PFDA
Ammonium perfluorodecanoate	$NH_4^+ C_9F_{19}COO^-$	3108-42-7	NH_4-PFDA
Perfluoroundecanoic acid	$C_{10}F_{21}COOH$	2058-94-8	PFUnDA
Ammonium perfluoroundecanoate	$NH_4^+ C_{10}F_{21}COO^-$	4234-23-5	NH_4-PFUnDA
Perfluorododecanoic acid	$C_{11}F_{23}COOH$	307-55-1	PFDoDA
Perfluorotridecanoic acid	$C_{12}F_{25}COOH$	72629-94-8	PFTrDA
Perfluorotetradecanoic acid	$C_{13}F_{27}COOH$	376-06-7	PFTeDA
Perfluoropentadecanoic acid	$C_{14}F_{29}COOH$	141074-63-7	PFPeDA
Perfluorohexadecanoic acid	$C_{15}F_{31}COOH$	67905-19-5	PFHxDA
Perfluoroheptadecanoic acid	$C_{16}F_{33}COOH$	57475-95-3	PFHpDA
Perfluorooctadecanoic acid	$C_{17}F_{35}COOH$	16517-11-6	PFODA
Perfluoroalkyl carboxylate anions	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Trifluoroacetate	CF_3COO^-	14477-72-6	TFA
Perfluoropropanoate	$C_2F_5COO^-$	44864-55-3	PFPrA
Perfluorobutanoate	$C_3F_7COO^-$	45048-62-2	PFBA
Perfluoropentanoate	$C_4F_9COO^-$	45167-47-3	PFPeA
Perfluorohexanoate	$C_5F_{11}COO^-$	92612-52-7	PFHxA
Perfluorohepanoate	$C_6F_{13}COO^-$	120885-29-2	PFHpA
Perfluorooctanoate	$C_7F_{15}COO^-$	45285-51-6	PFOA
Perfluorononanoate	$C_8F_{17}COO^-$	72007-68-2	PFNA
Perfluorodecanoate	$C_9F_{19}COO^-$	73829-36-4	PFDA
Perfluoroundecanoate	$C_{10}F_{21}COO^-$	196859-54-8	PFUnDA
Perfluorododecanoate	$C_{11}F_{23}COO^-$	171978-95-3	PFDoDA
Perfluorotridecanoate	$C_{12}F_{25}COO^-$	862374-87-6	PFTrDA
Perfluorotetradecanoate	$C_{13}F_{27}COO^-$	365971-87-5	PFTeDA
Perfluoropentadecanoate	$C_{14}F_{29}COO^-$	1214264-29-5	PFPeDA
Perfluorohexadecanoate	$C_{15}F_{31}COO^-$	1214264-30-8	PFHxDA
Perfluoroheptadecanoate	$C_{16}F_{33}COO^-$	None available	PFHpDA
Perfluorooctadecanoate	$C_{17}F_{35}COO^-$	798556-82-8	PFODA

Perfluoroalkane sulfonic acids (and selected anions and salts)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Trifluoromethane sulfonic (or triflic) acid	CF_3SO_3H	1493-13-6	TFMS
Perfluoroethane sulfonic acid	$C_2F_5SO_3H$	354-88-1	PFEtS
Perfluoropropane sulfonic acid	$C_3F_7SO_3H$	423-41-6	PFPrS
Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5 or 59933-66-3	PFBS
Perfluorobutane sulfonate anion	$C_4F_9SO_3^-$	45187-15-3	PFBS
Potassium perfluorobutane sulfonate	$K^+ C_4F_9SO_3^-$	29420-49-3	K-PFBS
Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4	PFPeS

Potassium perfluopentane sulfonate	$K^+ C_5F_{11}SO_3^-$	3872-25-1	K-PFPeS
Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4	PFHxS
Perfluorohexane sulfonate anion	$C_6F_{13}SO_3^-$	108427-53-8	PFHxS
Potassium perfluorohexane sulfonate	$K^+ C_6F_{13}SO_3^-$	3871-99-6	K-PFHxS
Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8	PFHpS
Ammonium perfluoroheptane sulfonate	$NH_4^+ C_7F_{15}SO_3^-$	68259-07-4	NH_4-PFHpS
Potassium perfluoroheptane sulfonate	$K^+ C_7F_{15}SO_3^-$	60270-55-5	K-PFHpS
Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1	PFOS
Perfluorooctane sulfonate anion	$C_8F_{17}SO_3^-$	45298-90-6	PFOS
Ammonium perfluorooctane sulfonate	$NH_4^+ C_8F_{17}SO_3^-$	29081-56-9	NH_4-PFOS
Sodium perfluorooctane sulfonate	$Na^+ C_8F_{17}SO_3^-$	4021-47-0	Na-PFOS
Potassium perfluorooctane sulfonate	$K^+ C_8F_{17}SO_3^-$	2795-39-3	K-PFOS
Lithium perfluorooctane sulfonate	$Li^+ C_8F_{17}SO_3^-$	29457-72-5	Li-PFOS
Tetraethylammonium perfluorooctane sulfonate	$N(C_2H_5)_4^+ C_8F_{17}SO_3^-$	56773-42-3	NEt_4-PFOS
Diethanolammonium perfluorooctane sulfonate	$NH_2(CH_2CH_2OH)_2^+ C_8F_{17}SO_3^-$	56773-42-3	
Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	474511-07-4	PFNS
Ammonium perfluorononane sulfonate	$NH_4^+ C_9F_{19}SO_3^-$	17202-41-4	NH_4-PFNS
Perfluorodecane sulfonic acid	$C_{10}F_{21}SO_3H$	335-77-3	PFDS
Perfluorodecane sulfonate anion	$C_{10}F_{21}SO_3^-$	126105-34-8	PFDS
Ammonium perfluorodecane sulfonate	$NH_4^+ C_{10}F_{21}SO_3^-$	67906-42-7	NH_4-PFDS
Potassium perfluorodecane sulfonate	$K^+ C_{10}F_{21}SO_3^-$	2806-16-8	K-PFDS
Perfluoroundecane sulfonic acid	$C_{11}F_{23}SO_3H$	749786-16-1	PFUnDS
Perfluorododecane sulfonic acid	$C_{12}F_{25}SO_3H$	79780-39-5	PFDoDS

Perfluoroalkane sulfinic acids	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluorooctane sulfinic acid	$C_8F_{17}SO_2H$	647-29-0	PFOSI

Perfluoroalkyl phosphonic acids	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluorohexyl phosphonic acid	$O{=}P(OH)_2C_6F_{13}$	40143-76-8	C6-PFPA
Perfluorooctyl phosphonic acid	$O{=}P(OH)_2C_8F_{17}$	40143-78-0	C8-PFPA
Perfluorodecyl phosphonic acid	$O{=}P(OH)_2C_{10}F_{21}$	52299-26-0	C10-PFPA

Perfluoroalkyl phosphinic acids	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Bis(perfluorohexyl) phosphinic acid	$O{=}P(OH)(C_6F_{13})_2$	40143-77-9	C6/C6-PFPIA
Bis(perfluorooctyl) phosphinic acid	$O{=}P(OH)(C_8F_{17})_2$	40143-79-1	C8/C8-PFPIA
Perfluoro(hexyloctyl) phosphinic acid	$O{=}P(OH)(C_6F_{13})(C_8F_{17})$	610800-34-5	C6/C8-PFPIA

Perfluoroalkyl iodides	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluoro (or pentafluoro)ethyl iodide	C_2F_5I	354-64-3	PFEI
Perfluorobutyl iodide	C_4F_9I	423-39-2	PFBI
Perfluorohexyl iodide	$C_6F_{13}I$	355-43-1	PFHxI
Perfluorooctyl iodide	$C_8F_{17}I$	507-63-1	PFOI
Perfluorodecyl iodide	$C_{10}F_{21}I$	423-62-1	PFDI
Perfluorododecyl iodide	$C_{12}F_{25}I$	307-60-8	PFDoDI
Perfluorotetradecyl iodide	$C_{14}F_{29}I$	307-63-1	PFTeDI
Perfluorohexadecyl iodide	$C_{16}F_{33}I$	355-50-0	PFHxDI
Perfluorooctadecyl iodide	$C_{18}F_{37}I$	29809-35-6	PFODI

(n:2) Fluorotelomer iodides	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer iodide	$C_4F_9CH_2CH_2I$	2043-55-2	4:2 FTI
6:2 Fluorotelomer iodide	$C_6F_{13}CH_2CH_2I$	2043-57-4	6:2 FTI
8:2 Fluorotelomer iodide	$C_8F_{17}CH_2CH_2I$	2043-53-0	8:2 FTI
10:2 Fluorotelomer iodide	$C_{10}F_{21}CH_2CH_2I$	2043-54-1	10:2 FTI
12:2 Fluorotelomer iodide	$C_{12}F_{25}CH_2CH_2I$	30046-31-2	12:2 FTI
14:2 Fluorotelomer iodide	$C_{14}F_{29}CH_2CH_2I$	65510-55-6	14:2 FTI
16:2 Fluorotelomer iodide	$C_{16}F_{33}CH_2CH_2I$	65150-94-9	16:2 FTI
18:2 Fluorotelomer iodide	$C_{18}F_{37}CH_2CH_2I$	65104-63-4	18:2 FTI

(n:2) Fluorotelomer olefins	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer olefin	$C_4F_9CH{=}CH_2$	19430-93-4	4:2 FTO

6:2 Fluorotelomer olefin	$C_6F_{13}CH=CH_2$	25291-17-2	6:2 FTO
8:2 Fluorotelomer olefin	$C_8F_{17}CH=CH_2$	21652-58-4	8:2 FTO
10:2 Fluorotelomer olefin	$C_{10}F_{21}CH=CH_2$	30389-25-4	10:2 FTO
12:2 Fluorotelomer olefin	$C_{12}F_{25}CH=CH_2$	67103-05-3	12:2 FTO

(n:2) Fluorotelomer alcohols	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2-Fluorotelomer alcohol	$C_4F_9CH_2CH_2OH$	2043-47-2	4:2 FTOH
6:2-Fluorotelomer alcohol	$C_6F_{13}CH_2CH_2OH$	647-42-7	6:2 FTOH
8:2-Fluorotelomer alcohol	$C_8F_{17}CH_2CH_2OH$	678-39-7	8:2 FTOH
10:2-Fluorotelomer alcohol	$C_{10}F_{21}CH_2CH_2OH$	865-86-1	10:2 FTOH
12:2 Fluorotelomer alcohol	$C_{12}F_{25}CH_2CH_2OH$	39239-77-5	12:2 FTOH
14:2 Fluorotelomer alcohol	$C_{14}F_{29}CH_2CH_2OH$	60699-51-6	14:2 FTOH
16:2 Fluorotelomer alcohol	$C_{16}F_{33}CH_2CH_2OH$	65104-67-8	16:2 FTOH
18:2 Fluorotelomer alcohol	$C_{18}F_{37}CH_2CH_2OH$	65104-65-6	18:2 FTOH

(n:2) Fluorotelomer acrylates	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer acrylate	$C_4F_9CH_2CH_2OC(O)CH=CH_2$	52591-27-2	4:2 FTAC
6:2 Fluorotelomer acrylate	$C_6F_{13}CH_2CH_2OC(O)CH=CH_2$	17527-29-6	6:2 FTAC
8:2 Fluorotelomer acrylate	$C_8F_{17}CH_2CH_2OC(O)CH=CH_2$	27905-45-9	8:2 FTAC
10:2 Fluorotelomer acrylate	$C_{10}F_{21}CH_2CH_2OC(O)CH=CH_2$	17741-60-5	10:2 FTAC
12:2 Fluorotelomer acrylate	$C_{12}F_{25}CH_2CH_2OC(O)CH=CH_2$	34395-24-9	12:2 FTAC
14:2 Fluorotelomer acrylate	$C_{14}F_{29}CH_2CH_2OC(O)CH=CH_2$	34362-49-7	14:2 FTAC
16:2 Fluorotelomer acrylate	$C_{16}F_{33}CH_2CH_2OC(O)CH=CH_2$	65150-93-8	16:2 FTAC
18:2 Fluorotelomer acrylate	$C_{18}F_{37}CH_2CH_2OC(O)CH=CH_2$	65104-64-5	18:2 FTAC

(n:2) Fluorotelomer methacrylates	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer methacrylate	$C_4F_9CH_2CH_2OC(O)C(CH_3)=CH_2$	1799-84-4	4:2 FTMAC
6:2 Fluorotelomer methacrylate	$C_6F_{13}CH_2CH_2OC(O)C(CH_3)=CH_2$	2144-53-8	6:2 FTMAC
8:2 Fluorotelomer methacrylate	$C_8F_{17}CH_2CH_2OC(O)C(CH_3)=CH_2$	1996-88-9	8:2 FTMAC
10:2 Fluorotelomer methacrylate	$C_{10}F_{21}CH_2CH_2OC(O)C(CH_3)=CH_2$	2144-54-9	10:2 FTMAC
12:2 Fluorotelomer methacrylate	$C_{12}F_{25}CH_2CH_2OC(O)C(CH_3)=CH_2$	6014-75-1	12:2 FTMAC
14:2 Fluorotelomer methacrylate	$C_{14}F_{29}CH_2CH_2OC(O)C(CH_3)=CH_2$	4980-53-4	14:2 FTMAC
16:2 Fluorotelomer methacrylate	$C_{16}F_{33}CH_2CH_2OC(O)C(CH_3)=CH_2$	59778-97-1	16:2 FTMAC
18:2 Fluorotelomer methacrylate	$C_{18}F_{37}CH_2CH_2OC(O)C(CH_3)=CH_2$	65104-66-7	18:2 FTMAC

Polyfluoroalkyl phosphoric acid monoesters (= fluorotelomer phosphate monoesters)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer phosphate monoester	$(O)P(OH)_2(OCH_2CH_2C_4F_9)$	150065-76-2	4:2 monoPAP
6:2 Fluorotelomer phosphate monoester	$(O)P(OH)_2(OCH_2CH_2C_6F_{13})$	57678-01-0	6:2 monoPAP
8:2 Fluorotelomer phosphate monoester	$(O)P(OH)_2(OCH_2CH_2C_8F_{17})$	57678-03-2	8:2 monoPAP
10:2 Fluorotelomer phosphate monoester	$(O)P(OH)_2(OCH_2CH_2C_{10}F_{21})$	57678-05-4	10:2 monoPAP
12:2 Fluorotelomer phosphate monoester	$(O)P(OH)_2(OCH_2CH_2C_{12}F_{25})$	57678-07-6	12:2 monoPAP
Polyfluoroalkyl phosphoric acid diesters (= fluorotelomer phosphate diesters)	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_4F_9)_2$	135098-69-0	4:2 diPAP
4:2/6:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_4F_9)(OCH_2CH_2C_6F_{13})$	1158182-59-2	4:2/6:2 diPAP
6:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_6F_{13})_2$	57677-95-9	6:2 diPAP
6:2/8:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_6F_{13})(OCH_2CH_2C_8F_{17})$	943913-15-3	6:2/8:2 diPAP
8:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_8F_{17})_2$	678-41-1	8:2 diPAP
8:2/10:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_8F_{17})(OCH_2CH_2C_{10}F_{21})$	1158182-60-5	8:2/10:2 diPAP
10:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_{10}F_{21})_2$	1895-26-7	10:2 diPAP
10:2/12:2 Fluorotel. phosphate diester	$(O)P(OH)(OCH_2CH_2C_{10}F_{21})(OCH_2CH_2C_{12}F_{25})$	1158182-61-6	10:2/12:2 diPAP
12:2 Fluorotelomer phosphate diester	$(O)P(OH)(OCH_2CH_2C_{12}F_{25})_2$	57677-99-3	12:2 diPAP
Semifluorinated n-alkanes	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
(Perfluorooctyl)ethane	$F(CF_2)_8(CH_2)_2H$	77117-48-7	F_8H_2
(Perfluorohexyl)octane	$F(CF_2)_6(CH_2)_8H$	133331-77-8	F_6H_8

(Perfluorohexyl)hexadecane	$F(CF_2)_6(CH_2)_{16}H$	133310-71-1	F_6H_{16}
(Perfluorooctyl)hexadecane	$F(CF_2)_8(CH_2)_{16}H$	117146-18-6	F_8H_{16}
(Perfluorohexadecyl)hexadecane	$F(CF_2)_{16}(CH_2)_{16}H$	137338-42-2	$F_{16}H_{16}$

Semifluorinated n-alkenes	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
(Perfluorohexyl)hexadecene	$F(CF_2)_6CH=CH(CH_2)_{14}H$	1244062-15-4	F_6H_{16}ene
(Perfluorooctyl)hexadecene	$F(CF_2)_8CH=CH(CH_2)_{14}H$	1244062-16-5	F_8H_{16}ene
(Perfluorohexadecyl)hexadecene	$F(CF_2)_{16}CH=CH(CH_2)_{14}H$	1244062-14-3	$F_{16}H_{16}$ene

(n:2) Fluorotelomer (saturated) aldehydes	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer aldehyde	$C_4F_9CH_2CHO$	135984-67-7	4:2 FTAL
6:2 Fluorotelomer aldehyde	$C_6F_{13}CH_2CHO$	56734-81-7	6:2 FTAL
8:2 Fluorotelomer aldehyde	$C_8F_{17}CH_2CHO$	135984-68-8	8:2 FTAL
10:2 Fluorotelomer aldehyde	$C_{10}F_{21}CH_2CHO$	864551-38-2	10:2 FTAL
12:2 Fluorotelomer aldehyde	$C_{12}F_{25}CH_2CHO$	None available	12:2 FTAL

(n:2) Fluorotelomer unsaturated aldehydes	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer unsaturated aldehyde	$C_3F_7CF=CHCHO$	864551-39-3	4:2 FTUAL
6:2 Fluorotelomer unsaturated aldehyde	$C_5F_{11}CF=CHCHO$	69534-12-9	6:2 FTUAL
8:2 Fluorotelomer unsaturated aldehyde	$C_7F_{15}CF=CHCHO$	58544-13-1	8:2 FTUAL
10:2 Fluorotelomer unsaturated aldehyde	$C_9F_{19}CF=CHCHO$	864551-40-6	10:2 FTUAL
12:2 Fluorotelomer unsaturated aldehyde	$C_{11}F_{23}CF=CHCHO$	None available	12:2 FTUAL

Perfluoroalkyl aldehydes	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Trifluoroacetaldehyde (fluoral)	CF_3CHO	75-90-1	
Perfluoropentanal	C_4F_9CHO	375-53-1	PFPeAL
Perfluoroheptanal	$C_6F_{13}CHO$	63967-41-9	PFHpAL
Perfluorooctanal	$C_7F_{15}CHO$	335-60-4	PFOAL
Perfluorononanal	$C_8F_{17}CHO$	63967-40-8	PFNAL
Perfluoroundecanal	$C_{10}F_{21}CHO$	63967-42-0	PFUnDAL

Perfluoroalkyl aldehyde hydrates	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluoropentanal hydrate	$C_4F_9CH(OH)_2$	355-30-6	PFPeAL.H_2O
Perfluoroheptanal hydrate	$C_6F_{13}CH(OH)_2$	64739-16-8	PFHpAL.H_2O
Perfluorononanal hydrate	$C_8F_{17}CH(OH)_2$	191528-99-1	PFNAL.H_2O
Perfluoroundecanal hydrate	$C_{10}F_{21}CH(OH)_2$	None Available	PFUnDAL.H_2O

(n:2) Fluorotelomer (saturated) carboxylic acids	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
6:2 Fluorotelomer carboxylic acid	$C_6F_{13}CH_2COOH$	53826-12-3	6:2 FTCA
8:2 Fluorotelomer carboxylic acid	$C_8F_{17}CH_2COOH$	27854-31-5	8:2 FTCA
10:2 Fluorotelomer carboxylic acid	$C_{10}F_{21}CH_2COOH$	53826-13-4	10:2 FTCA
12:2 Fluorotelomer carboxylic acid	$C_{12}F_{25}CH_2COOH$	70887-93-3	12:2 FTCA

(n:2) Fluorotelomer unsaturated carboxylic acids	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
6:2 Fluorotelomer unsaturated carboxylic acid	$C_5F_{11}CF=CHCOOH$	70887-88-6	6:2 FTUCA
8:2 Fluorotelomer unsaturated carboxylic acid	$C_7F_{15}CF=CHCOOH$	70887-84-2	8:2 FTUCA
10:2 Fluorotelomer unsaturated carboxylic acid	$C_9F_{19}CF=CHCOOH$	70887-94-4	10:2 FTUCA
12:2 Fluorotelomer unsaturated carboxylic acid	$C_{11}F_{23}CF=CHCOOH$	70887-95-5	12:2 FTUCA

Other biotransformation products of n:2 FTOHs	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:3 Acid	$C_4F_9(CH_2)_2COOH$	80705-13-1	4:3 Acid
5:3 Acid	$C_5F_{11}(CH_2)_2COOH$	914637-49-3	5:3 Acid
6:3 Acid	$C_6F_{13}(CH_2)_2COOH$	27854-30-4	6:3 Acid
7:3 Acid	$C_7F_{15}(CH_2)_2COOH$	812-70-4	7:3 Acid
5:3 Unsaturated carboxylic acid	$C_5F_{11}CH=CHCOOH$	1869-04-1 875878-70-9 (E)	5:3 UAcid
7:3 Unsaturated carboxylic acid	$C_7F_{15}CH=CHCOOH$	755-03-3	7:3 UAcid

		56017-63-1 (E) 173441-56-0 (Z)	

(n:2) Fluorotelomer sulfonic acids	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer sulfonic acid	$C_4F_9CH_2CH_2SO_3H$	757124-72-4	4:2 FTSA
6:2 Fluorotelomer sulfonic acid	$C_6F_{13}CH_2CH_2SO_3H$	27619-97-2	6:2 FTSA
8:2 Fluorotelomer sulfonic acid	$C_8F_{17}CH_2CH_2SO_3H$	39108-34-4	8:2 FTSA
10:2 Fluorotelomer sulfonic acid	$C_{10}F_{21}CH_2CH_2SO_3H$	120226-60-0	10:2 FTSA

(n:2) Fluorotelomer sulfonate anions	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
4:2 Fluorotelomer sulfonate anion	$C_4F_9CH_2CH_2SO_3^-$	414911-30-1	4:2 FTSA
6:2 Fluorotelomer sulfonate anion	$C_6F_{13}CH_2CH_2SO_3^-$	425670-75-3	6:2 FTSA
8:2 Fluorotelomer sulfonate anion	$C_8F_{17}CH_2CH_2SO_3^-$	481071-78-7	8:2 FTSA
10:2 Fluorotelomer sulfonate anion	$C_{10}F_{21}CH_2CH_2SO_3^-$	None available	10:2 FTSA

Perfluoroalkane sulfonyl fluorides	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluorobutane sulfonyl fluoride	$C_4F_9SO_2F$	375-72-4	PBSF
Perfluoropentane sulfonyl fluoride	$C_5F_{11}SO_2F$	375-81-5	PPeSF
Perfluorohexane sulfonyl fluoride	$C_6F_{13}SO_2F$	423-50-7	PHxSF
Perfluoroheptane sulfonyl fluoride	$C_7F_{15}SO_2F$	335-71-7	PHpSF
Perfluorooctane sulfonyl fluoride	$C_8F_{17}SO_2F$	307-35-7	POSF
Perfluorononane sulfonyl fluoride	$C_9F_{19}SO_2F$	68259-06-3	PNSF
Perfluorodecane sulfonyl fluoride	$C_{10}F_{21}SO_2F$	307-51-7	PDSF

Perfluoroalkane sulfonamides	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluorobutane sulfonamide	$C_4F_9SO_2NH_2$	30334-69-1	FBSA
Perfluoropentane sulfonamide	$C_5F_{11}SO_2NH_2$	82765-76-2	FPeSA
Perfluorohexane sulfonamide	$C_6F_{13}SO_2NH_2$	41997-13-1	FHxSA
Perfluoroheptane sulfonamide	$C_7F_{15}SO_2NH_2$	82765-77-3	FHpSA
Perfluorooctane sulfonamide	$C_8F_{17}SO_2NH_2$	754-91-6	FOSA
N-Methyl perfluoroalkane sulfonamides	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Methyl perfluorobutane sulfonamide	$C_4F_9SO_2NH(CH_3)$	68298-12-4	MeFBSA
N-Methyl perfluoropentane sulfonamide	$C_5F_{11}SO_2NH(CH_3)$	68298-13-5	MeFPeSA
N-Methyl perfluorohexane sulfonamide	$C_6F_{13}SO_2NH(CH_3)$	68259-15-4	MeFHxSA
N-Methyl perfluoroheptane sulfonamide	$C_7F_{15}SO_2NH(CH_3)$	68259-14-3	MeFHpSA
N-Methyl perfluorooctane sulfonamide	$C_8F_{17}SO_2NH(CH_3)$	31506-32-8	MeFOSA
N-Ethyl perfluoroalkane sulfonamides	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Ethyl perfluorobutane sulfonamide	$C_4F_9SO_2NH(C_2H_5)$	40630-67-9	EtFBSA
N-Ethyl perfluoropentane sulfonamide	$C_5F_{11}SO_2NH(C_2H_5)$	162682-16-8	EtFPeSA
N-Ethyl perfluorohexane sulfonamide	$C_6F_{13}SO_2NH(C_2H_5)$	87988-56-5	EtFHxSA
N-Ethyl perfluoroheptane sulfonamide	$C_7F_{15}SO_2NH(C_2H_5)$	68957-62-0	EtFHpSA
N-Ethyl perfluorooctane sulfonamide	$C_8F_{17}SO_2NH(C_2H_5)$ (sulfluramid)	4151-50-2	EtFOSA
N,N-Dialkyl perfluoroalkane sulfonamides	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N,N-Dimethyl perfluorooctane sulfonamide	$C_8F_{17}SO_2N(CH_3)_2$	213181-78-3	Me$_2$FOSA
N,N-Diethyl perfluorooctane sulfonamide	$C_8F_{17}SO_2N(C_2H_5)_2$	87988-61-2	Et$_2$FOSA

Perfluoroalkane sulfonamido ethanols	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluorobutane sulfonamidoethanol	$C_4F_9SO_2NHCH_2CH_2OH$	34454-99-4	FBSE
Perfluoropentane sulfonamidoethanol	$C_5F_{11}SO_2NHCH_2CH_2OH$	None available	FPeSE
Perfluorohexane sulfonamidoethanol	$C_6F_{13}SO_2NHCH_2CH_2OH$	106443-63-4	FHxSE
Perfluoroheptane sulfonamidoethanol	$C_7F_{15}SO_2NHCH_2CH_2OH$	167398-54-1	FHpSE
Perfluorooctane sulfonamidoethanol	$C_8F_{17}SO_2NHCH_2CH_2OH$	10116-92-4	FOSE

Perfluoroalkane sulfonamidoacetic acids	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
Perfluorobutane sulfonamidoacetic acid	$C_4F_9SO_2NHCH_2COOH$	347872-22-4	FBSAA
Perfluoropentane sulfonamidoacetic acid	$C_5F_{11}SO_2NHCH_2COOH$	647-43-8	FPeSAA
Perfluorohexane sulfonamidoacetic acid	$C_6F_{2n+1}SO_2NHCH_2COOH$	1003193-99-4	FHxSAA

Perfluoroheptane sulfonamidoacetic acid	$C_7F_{15}SO_2NHCH_2COOH$	1003194-00-0	FHpSAA
Perfluorooctane sulfonamidoacetic acid	$C_8F_{17}SO_2NHCH_2COOH$	2806-24-8	FOSAA

N-Methyl perfluoroalkane sulfonamidoethanols	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Methyl perfluorobutane sulfonamidoethanol	$C_4F_9SO_2N(CH_3)CH_2CH_2OH$	34454-97-2	MeFBSE
N-Methyl perfluoropentane sulfonamidoethanol	$C_5F_{11}SO_2N(CH_3)CH_2CH_2OH$	68555-74-8	MeFPeSE
N-Methyl perfluorohexane sulfonamidoethanol	$C_6F_{13}SO_2N(CH_3)CH_2CH_2OH$	68555-75-9	MeFHxSE
N-Methyl perfluoroheptane sulfonamidoethanol	$C_7F_{15}SO_2N(CH_3)CH_2CH_2OH$	68555-76-0	MeFHpSE
N-Methyl perfluorooctane sulfonamidoethanol	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	24448-09-7	MeFOSE
N-Ethyl perfluoroalkane sulfonamidoethanols	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Ethyl perfluorobutane sulfonamidoethanol	$C_4F_9SO_2N(C_2H_5)CH_2CH_2OH$	34449-89-3	EtFBSE
N-Ethyl perfluoropentane sulfonamidoethanol	$C_5F_{11}SO_2N(C_2H_5)CH_2CH_2OH$	68555-72-6	EtFPeSE
N-Ethyl perfluorohexane sulfonamidoethanol	$C_6F_{13}SO_2N(C_2H_5)CH_2CH_2OH$	34455-03-3	EtFHxSE
N-Ethyl perfluoroheptane sulfonamidoethanol	$C_7F_{15}SO_2N(C_2H_5)CH_2CH_2OH$	68555-73-7	EtFHpSE
N-Ethyl perfluorooctane sulfonamidoethanol	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	1691-99-2	EtFOSE

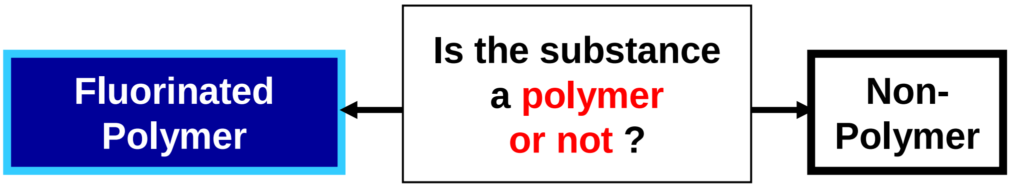
N-Methyl perfluoroalkane sulfonamidoacetic acids and salts	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Methyl perfluorobutane sulfonamidoacetic acid	$C_4F_9SO_2N(CH_3)CH_2COOH$	159381-10-9	MeFBSAA
N-Methyl perfluorohexane sulfonamidoacetic acid	$C_6F_{13}SO_2N(CH_3)CH_2COOH$	715646-50-7	MeFHxSAA
N-Methyl perfluorooctane sulfonamidoacetic acid	$C_8F_{17}SO_2N(CH_3)CH_2COOH$	2355-31-9	MeFOSAA
Potassium *N*-methyl perfluorooctane sulfonamidoacetate	$K^+ C_8F_{17}SO_2N(CH_3)CH_2COO^-$	70281-93-5	K-MeFOSAA
N-Ethyl perfluoroalkane sulfonamidoacetic acids and salts	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Ethyl perfluorobutane sulfonamidoacetic acid	$C_4F_9SO_2N(C_2H_5)CH_2COOH$	68957-33-5	EtFBSAA
N-Ethyl perfluoropentane sulfonamidoacetic acid	$C_5F_{11}SO_2N(C_2H_5)CH_2COOH$	68957-31-3	EtFPeSAA
N-Ethyl perfluorohexane sulfonamidoacetic acid	$C_6F_{13}SO_2N(C_2H_5)CH_2COOH$	68957-32-4	EtFHxSAA
N-Ethyl perfluoroheptane sulfonamidoacetic acid	$C_7F_{15}SO_2N(C_2H_5)CH_2COOH$	68957-63-1	EtFHpSAA
N-Ethyl perfluorooctane sulfonamidoacetic acid	$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$	2991-50-6	EtFOSAA
Potassium *N*-ethyl perfluorooctane sulfonamidoacetate	$K^+ C_8F_{17}SO_2N(C_2H_5)CH_2COO^-$	2991-51-7	K-EtFOSAA

N-Methyl perfluoroalkane sulfonamidoethyl acrylates	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Methyl perfluorobutane sulfonamidoethyl acrylate	$C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH{=}CH_2$	67584-55-8	MeFBSAC
N-Methyl perfluoropentane sulfonamidoethyl acrylate	$C_5F_{11}SO_2N(CH_3)CH_2CH_2OC(O)CH{=}CH_2$	67584-56-9	MeFPeSAC
N-Methyl perfluorohexane sulfonamidoethyl acrylate	$C_6F_{13}SO_2N(CH_3)CH_2CH_2OC(O)CH{=}CH_2$	67584-57-0	MeFHxSAC
N-Methyl perfluoroheptane sulfonamidoethyl acrylate	$C_7F_{15}SO_2N(CH_3)CH_2CH_2OC(O)CH{=}CH_2$	68084-62-8	MeFHpSAC

N-Methyl perfluorooctane sulfonamidoethyl acrylate	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	25268-77-3	MeFOSAC
N-Ethyl perfluoroalkane sulfonamidoethyl acrylates	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Ethyl perfluorobutane sulfonamidoethyl acrylate	$C_4F_9SO_2N(C_2H_5)CH_2CH_2OC(O)CH=CH_2$	17329-79-2	EtFBSAC
N-Ethyl perfluoropentane sulfonamidoethyl acrylate	$C_5F_{11}SO_2N(C_2H_5)CH_2CH_2OC(O)CH=CH_2$	68298-06-6	EtFPeSAC
N-Ethyl perfluorohexane sulfonamidoethyl acrylate	$C_6F_{13}SO_2N(C_2H_5)CH_2CH_2OC(O)CH=CH_2$	1893-52-3	EtFHxSAC
N-Ethyl perfluoroheptane sulfonamidoethyl acrylate	$C_7F_{15}SO_2N(C_2H_5)CH_2CH_2OC(O)CH=CH_2$	59071-10-2	EtFHpSAC
N-Ethyl perfluorooctane sulfonamidoethyl acrylate	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OC(O)CH=CH_2$	423-82-5	EtFOSAC
N-Methyl perfluoroalkane sulfonamidoethyl methacrylates	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Methyl perfluorobutane sulfonamidoethyl methacrylate	$C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$	67584-59-2	MeFBSMAC
N-Methyl perfluoropentane sulfonamidoethyl methacrylate	$C_5F_{11}SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$	67584-60-5	MeFPeSMAC
N-Methyl perfluorohexane sulfonamidoethyl methacrylate	$C_6F_{13}SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$	67584-61-6	MeFHxSMAC
N-Methyl perfluoroheptane sulfonamidoethyl methacrylate	$C_7F_{15}SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$	67939-96-2	MeFHpSMAC
N-Methyl perfluorooctane sulfonamidoethyl methacrylate	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$	14650-24-9	MeFOSMAC
N-Ethyl perfluoroalkane sulfonamidoethyl methacrylates	**FORMULA**	**CAS REGISTRY NUMBER**	**ACRONYM**
N-Ethyl perfluorobutane sulfonamidoethyl methacrylate	$C_4F_9SO_2N(C_2H_5)CH_2CH_2OC(O)C(CH_3)=CH_2$	67939-33-7	EtFBSMAC
N-Ethyl perfluoropentane sulfonamidoethyl methacrylate	$C_5F_{11}SO_2N(C_2H_5)CH_2CH_2OC(O)C(CH_3)=CH_2$	67906-73-4	EtFPeSMAC
N-Ethyl perfluorohexane sulfonamidoethyl methacrylate	$C_6F_{13}SO_2N(C_2H_5)CH_2CH_2OC(O)C(CH_3)=CH_2$	67906-70-1	EtFHxSMAC
N-Ethyl perfluoroheptane sulfonamidoethyl methacrylate	$C_7F_{15}SO_2N(C_2H_5)CH_2CH_2OC(O)C(CH_3)=CH_2$	67939-36-0	EtFHpSMAC
N-Ethyl perfluorooctane sulfonamidoethyl methacrylate	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OC(O)C(CH_3)=CH_2$	376-14-7	EtFOSMAC

Figure S1. Terminology Decision Flowcharts

How to determine nomenclature – an Overview

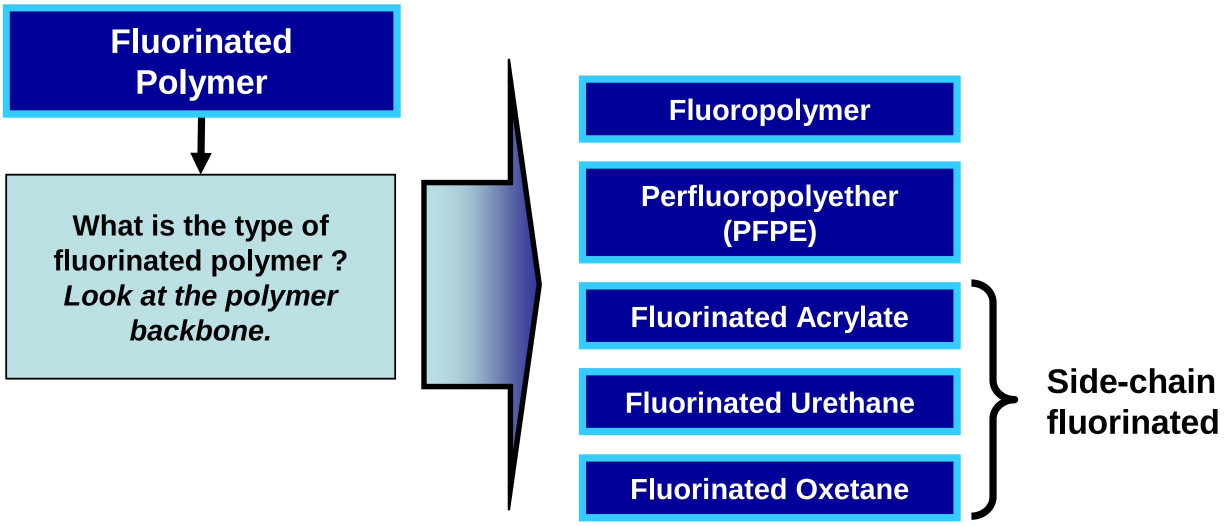


Fluorinated Polymer

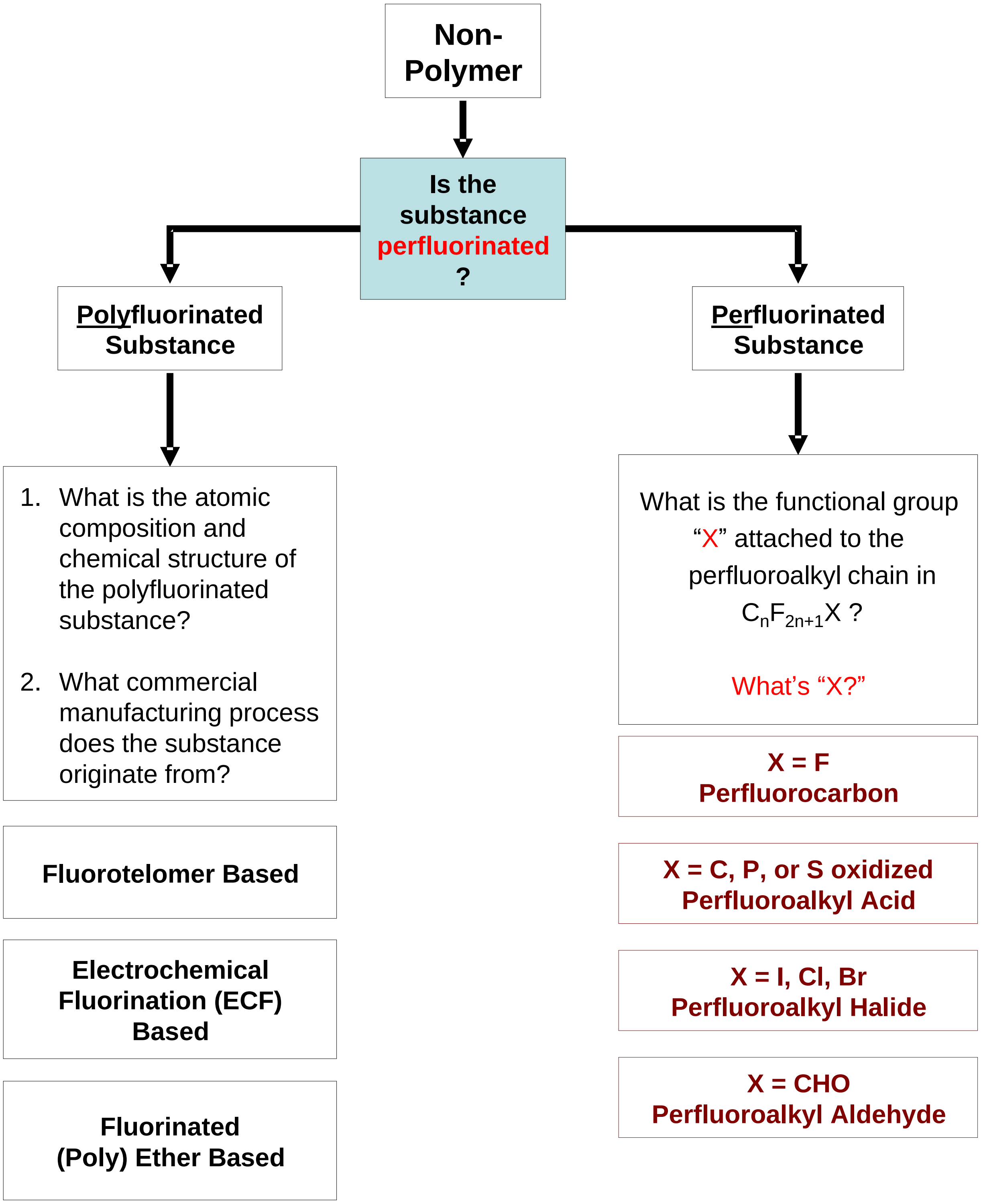
Is the substance a polymer or not ?

Non-Polymer

Fluorinated Polymer Decision



Non-Polymer Decision Tree

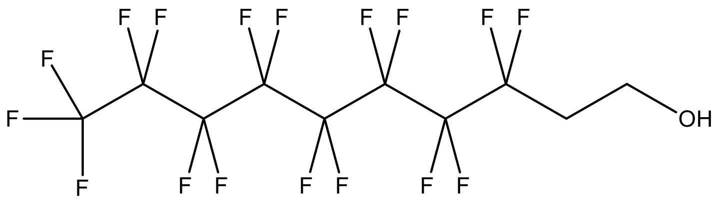


1. What is the atomic composition and chemical structure of the polyfluorinated substance?
2. What commercial manufacturing process does the substance originate from?

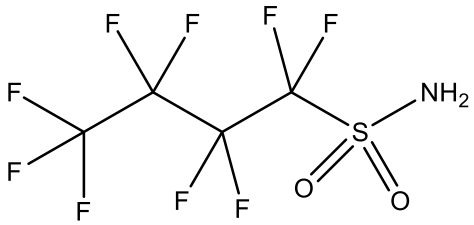
What is the functional group “X” attached to the perfluoroalkyl chain in $C_nF_{2n+1}X$?

What’s “X?”

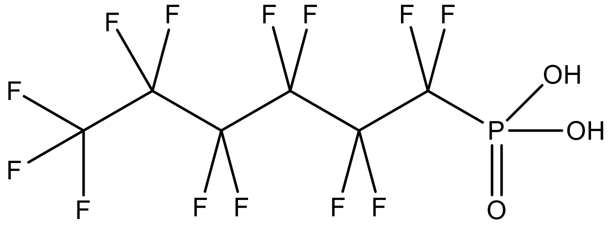
Example #1 8:2 Fluorotelomer alcohol

Substance Chemical Structure	Question	Conclusion
$F(CF_2)_8CH_2CH_2OH$ 	**Polymer or Non-Polymer?**	**Non-Polymer**
$F(CF_2)_8$ CH_2CH_2OH	**Perfluorinated?** *No. The substance has a perfluoroalkyl chain, $F(CF_2)_8$-, but all hydrogen on carbons are not replaced with fluorine*	**Poly-fluorinated**
$F(CF_2)_8$**CH_2CH_2**OH	**Process Origin?** *Perfluoroalkyl chain with an ethylene spacer (-CH_2CH_2-). Fluorotelomer origin*	**Fluoro-telomer origin**
$F(CF_2)_8CH_2CH_2$**OH**	**Functionality** *Alcohol*	**Fluoro-telomer Alcohol (FTOH)**
$F(CF_2)_8CH_2CH_2OH$	*Eight fluorinated carbons, two non-fluorinated carbons, therefore 8:2*	**8:2 Fluoro-telomer Alcohol (8:2 FTOH)**

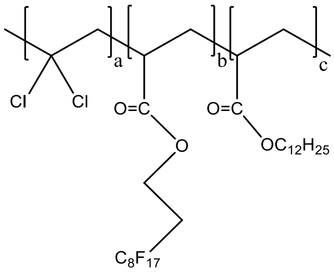
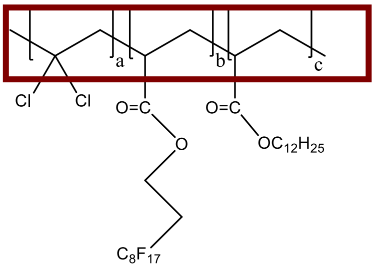
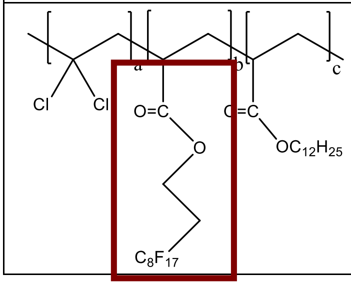
Example #2 Perfluorobutane sulfonamide

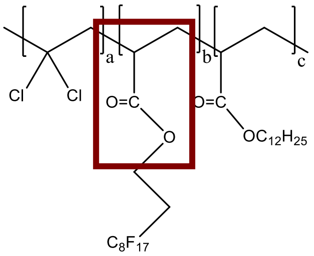
Substance Chemical Structure	Question	Conclusion
$F(CF_2)_4SO_2NH_2$ 	**Polymer or Non- Polymer?**	**Non-Polymer**
$F(CF_2)_4SO_2NH_2$	**Perfluorinated?** *Yes. All hydrogens on all four carbons are replaced with fline. Perfluorobutyl*	**Perfluorinated**
$F(CF_2)_4SO_2NH_2$	**Perfluoroalkyl Acid?** *No. Has no acid functionality*	
$F(CF_2)_4SO_2NH_2$	**Process Origin?** *Perfluoroalkyl chain with a sulfone, -SO_2-, spacer. Electrochemical fluorination (ECF) origin*	**ECF origin**
$F(CF_2)_4SO_2NH_2$	**Functionality** *Sulfonamide*	**Perfluorobutane-sulfonamide (FBSA)**

Example #3 Perfluorohexyl phosphonic acid

Substance Chemical Structure	**Question**	**Conclusion**
$F(CF_2)_6P(=O)(OH)_2$ 	**Polymer or Non- Polymer?**	**Non-Polymer**
$F(CF_2)_6P(=O)(OH)_2$	**Perfluorinated?** *Yes. All hydrogens on all six carbons are replaced with fluorine. Perfluorohexyl*	**Perfluorinated**
$F(CF_2)_6P(=O)(OH)_2$	**Perfluoroalkyl Acid?** *Yes.* *Phosphonic, $-P(=O)(OH)_2$, acid*	**Perfluoroalkyl acid**
$F(CF_2)_6P(=O)(OH)_2$		**Perfluorohexyl phosphonic acid (C6-PFPA)**

Example #4 Side-chain Fluorinated Acrylate Polymer (Fluorotelomer origin)

Substance Chemical Structure	**Question**	**Conclusion**
	**Polymer or Non-Polymer?**	**Polymer**
	**Fluoropolymer?** *No. The polymer backbone contains no fluorine bound to carbon.*	
	**Side-chain fluorinated?** *Yes*	**Side-chain fluorinated polymer**

Substance Chemical Structure	Question	Conclusion
	**Polymer Type?** *Acrylate*	**Side-chain fluorinated acrylate polymer**

References:

1. Robert C. Buck†, James Franklin*‡, Urs Berger§, Jason M. Conder||, Ian T. Cousins§, Pim de Voogt#, Allan Astrup Jensen††, Kurunthachalam Kannan‡‡, Scott A. Mabury§§, and Stefan P. J. van Leeuwen||||

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