Justification for exemption of Fluoropolymers from PFAS restriction proposal under EU REACH

PFAS (per- and polyfluoroalkyl substances) are a broad group of man-made chemicals that are characterized by strong carbon-fluorine bonds. PFAS are under regulatory scrutiny due to concerns about their presence in environment and potential adverse effects on human health. PFAS may be mobile, resistant to biodegradation, may accumulate over time in soil, water, and living organisms and may be toxic to human health and environment. However, the broad group of PFAS also includes substances or groups of substances which exhibit different physio-chemical properties, toxicological and environmental profiles. One such unique group is fluoropolymers.

Fluoropolymers should be exempted from the PFAS restriction proposal under EU REACH because of their safety and different physio-chemical, environmental and toxicological properties.

This paper differentiates fluoropolymers from other PFAS of concern and provides justification for their exemption from the wider PFAS restriction based on the following six factors:

1. Fluoropolymers are safe
2. Fluoropolymers offer high socio-economic value
3. Fluoropolymers are irreplaceable
4. Fluoropolymers do not degrade under intended use conditions
5. Fluoropolymers can be disposed safely at their end of life
6. Majority of fluoropolymers can be manufactured responsibly without the use of fluorinated polymerization aids.

Fluoropolymers are safe

Fluoropolymers are a safe, high molecular weight group of 38 substances that are inert. Fluoropolymers are thermally, biologically, and chemically stable, insoluble in water, non-mobile, non-bioavailable, non-bioaccumulative, and non-toxic. They satisfy the internationally recognized Organization for Economic Cooperation and Development (OECD) Polymers of Low Concern (PLC) criteria. Fluoropolymers are neither soluble in water nor in other solvents and biological liquids. Fluoropolymers cannot penetrate cell membranes or bio-accumulate and therefore do not pose any risk to human health or the environment.

References:

1. *(Eco)-toxicological read across on Fluoropolymers – GSI Environmental 2023*
2. *A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers – Henry et. al., 2018*
3. *A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers – Korzeniowski et. al., 2022*

Fluoropolymers offer high socio-economic value

Fluoropolymers are extremely stable, specialty materials with unique physio-chemical properties. They are chemically inert, highly resistant to temperature variability, offer good weatherability, and exhibit low flammability. They also have properties such as low coefficient of friction, dielectric strength, and

flexibility. Fluoropolymers are used in a wide variety of highly critical applications due to their valuable properties and unique combination of functionalities.

Any restriction on fluoropolymers could have far reaching adverse impacts on industry as well as society, given the essentiality of fluoropolymers to a wide range of industrial applications like:

Renewable energy: Solar panels and wind energy: various components of renewable energy installations, such as photovoltaic panels and wind turbines, require fluoropolymers.

Electric Vehicles: Fluoropolymers are critical for optimal performance of lithium-ion batteries and hydrogen fuel cells. Without fluoropolymers, decarbonization and environmental sustainability goals in the EU like EU Green Deal would be seriously compromised.

Semiconductors: Due to their resistance to harsh chemicals, fluoropolymers are essential for manufacturing semiconductors, providing an impurity-free environment. Without fluoropolymers, the semiconductor industry will be unable to produce microchips necessary for digitalization and vital for achieving autonomy in critical technologies.

Food and Water Treatment: Fluoropolymers are utilized in water filtration systems (which avoids the need to use chemicals for water treatment), and in food processing systems to guarantee adequate sanitary conditions and protect consumers from harmful contamination.

Pharmaceutical and Medical Devices: Catheters and medical implants are made of fluoropolymers due to their biological compatibility, inertness and durability. Furthermore, the production of medicines and vaccines require ultra pure conditions which can only be achieved with equipment containing fluoropolymer materials.

Chemical Process Industry: Fluoropolymers are unmatched in resistance to chemical attack and performance under wide temperature variations. They are the safest, most secure material for processing and containing chemicals. Fluoropolymers are found in all kinds of industrial equipment, as well as joints and gaskets to secure operation and ensure safety of workers.

Transport: Fluoropolymers contribute to both fuel efficiency and safety, playing a key role in systems such as brakes in cars or wing flaps in aircrafts. They are also the best option available to protect electrical cables in aircrafts, where high reliability of such cables, which can be exposed to thermal as well as chemical pressure, is fundamental.

References:

4. *Critical use of fluoropolymers in the functioning of modern society – Sales et. al., 2023*

Fluoropolymers are irreplaceable

Fluoropolymers provide a combination of highly desired properties for use in many industrial sectors. These properties, and particularly their combination in single products, make them irreplaceable in many applications. In fact, it is commonly accepted that their unique set of properties cannot be matched by alternative materials, particularly in the wide range of operability they offer. While alternatives may provide one or two properties with similar behavior, they never offer the full range of benefits.

Fluoropolymers are high-cost materials, and they are only chosen where no other material is able to match the required combination of properties. Substituting fluoropolymers with substances offering

inferior performance would negatively impact the safety of people and the environment compromising key sustainability objectives.

Fluoropolymers are currently irreplaceable for many critical applications, and existing potential alternatives would be associated with significant trade-offs that could compromise safety of workers, the general population, or the environment, either due to direct hazardous properties of the alternative, or by downgrading performance and life of key applications.

References:

5. *Technical report on Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use – Chemservice 2022*

Fluoropolymers do not degrade under intended use conditions

Fluoropolymers are polymers with a carbon-only backbone with fluorine atoms directly bonded to it. The exceptional strength of the C-F bond in fluoropolymers prevents them from degrading to small molecular weight PFAS under intended use conditions under environmental conditions. As concluded in a 2013 Danish EPA report, 'Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances', the degradation of fluoropolymers cannot lead to the formation of long chain Perfluorocarboxylic acids (PFCAs), and they are not included in the OECD list of possible precursors of short chain PFAS.

Fluoropolymers are not only different from non-polymeric PFAS, but they also exhibit completely different properties from other polymeric PFAS like side-chain fluorinated polymers, particularly in relation to possible environmental degradation into smaller PFAS. Chemservice has captured in a report the main differences between fluoropolymers, perfluoropolyethers and side-chain fluorinated polymers, highlighting how those differences justify considering fluoropolymers as chemicals posing no relevant risk for human health or the environment due to degradation to small molecule PFAS of concern.

Side-chain fluorinated polymers can degrade to hazardous non-polymeric PFAS during their intended use or under environmental conditions at the end-of-life phase of their applications due to their chemical structure. Moreover, these substances are mainly used in dispersive consumer applications like coatings on carpets, paper and textiles. OECD has published a report on side chain fluorinated polymers confirming the above.

References:

6. *Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances – Danish EPA, 2013*
7. *Differentiation of fluoropolymers from other polymeric PFAS – Chemservice, 2022*
8. *Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle - OECD Series on Risk Management, No. 73, 2022*

Fluoropolymers can be disposed safely at their end of life

Conversio report on 'Fluoropolymer Waste in Europe 2020' provides information about the end of life fate of fluoropolymer applications, products and associated waste streams. It also delivers an in-depth description on how and where fluoropolymer containing products and corresponding wastes are generated and what happens to the collected fractions at the end of life that is identification of the waste treatment route such as incineration, landfill and recycling. From the study, it was concluded that in 2020, out of about 40 kilotons of fluoropolymer materials sold in the EU, 23.5 kilotons of fluoropolymer waste was collected, either in commingle waste streams or partly in source separated waste fractions. Almost, 84% of fluoropolymer applications were incinerated at the end of their life in waste-to-energy recovery plants, 13% of the collected fluoropolymer waste was landfilled and around 3% was recycled. Overall, fluoropolymer waste is a tiny fraction of less than 0.01% by weight in comparison to the total plastic waste collected.

Waste-to-energy incineration

An experimental project was conducted by the Karlsruhe Institute of Technology (KIT) in cooperation with Société Générale de Surveillance (SGS) under supervision of the German Federal environmental Agency (UBA) along with incineration experts worldwide to assess if fluoropolymers get fully mineralized at household and industrial waste-to-energy incineration plants without any formation of short chain or long chain PFAS.

The results confirm that fluoropolymers at their end of life when incinerated under representative European waste-to-energy incineration plant conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment. The absence of organic fluorides and more specifically PFAS in tests representative of municipal waste incineration confirms complete mineralization of fluoropolymers to hydrogen fluoride and carbon-di-oxide and provides critical data for exemption of Fluoropolymers from the PFAS restriction proposal.

Landfill

Fluoropolymers are inert, non-toxic and have low to no degradation potential and therefore pose no risk when disposed of in landfills. Various studies on PTFE were performed by W.L. Gore to address potential partitioning of PFAS into water, air and soil and its leaching potential. The results support the stability of PTFE and lack of transformation to other PFAS, and that PTFE will not partition to air, water, or soil. Potential inhalation, oral or dermal exposure to PTFE for biota or the environment is highly unlikely. In another example regarding the safety of fluoropolymers with respect to their exposure to soil and water, the most common fluoropolymer, PTFE, is used as a geomembrane (lining material) in pits used for landfilling to prevent contamination of groundwater through leachates emitted from hazardous waste.

References:

9. *Pilot-Scale Fluoropolymer Incineration Study-Preliminary report – Gehrmann et. al., 2023*
10. *Summary of the PTFE studies performed with independent laboratories to investigate Persistence, Degradation, Transformation to or Release of Substances of Concern*
11. *Contamination from a leaking geomembrane—A necessary and imminent evil? – Tippett et. al., 2023*

Majority of fluoropolymers can be manufactured responsibly without the use of fluorinated polymerization aids

The true and main concern related to fluoropolymers is the use of fluorinated polymerization aids (PFAS) and their emissions thereof during the manufacturing of fluoropolymers. It is important to note that more than 50% of fluoropolymer production does not require the use of fluorinated polymerization aids. For the remaining fluoropolymers, industry has dedicated significant effort and investment toward developing Non-Fluorinated Polymerization Aid (NFPA) technology in the manufacture of fluoropolymers. Several manufacturers such as Gujarat Fluorochemicals, Solvay, Arkema and Honeywell have made tremendous progress in this direction and have committed to completely move away from the use of fluorinated polymerization aids in their fluoropolymer manufacturing processes. A recently published article in volume 6 of the International Chemical Regulatory and Law Review (ICRL) states that the technologies available today allow for the manufacture of more than 80% of fluoropolymers globally without the use of fluorinated polymerization aids.

References:

12. *Developments in fluoropolymer manufacturing technology to remove intentional use of PFAS as polymerization aids – Ameduri et.al., 2023.*

Conclusion

Summarizing, it is abundantly clear that fluoropolymers themselves are safe, do not pose any risk to human health and the environment and that the only concern related to the fluoropolymer lifecycle is the use of fluorinated polymerization aids. Therefore, regulating the use of fluorinated polymerization aids in the manufacturing of fluoropolymers removes the only true concern related to fluoropolymers, allowing industry and society to continue benefitting from fluoropolymer applications offering safety and well-being, digitalization, decarbonization and environment protection. We support the full exemption of fluoropolymers from the EU PFAS restriction proposal while including within the definition for future regulation fluorinated polymerization aids.



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FINAL

June 13, 2023

RE: Technical Support Document in Response to ECHA Annex XV Restriction Proposal for PFAS, Gujarat Fluorochemical's RAC Comment Letter

OVERALL COMMENT

In response to the Annex XV Restriction Report, proposal for a restriction on per- and polyfluoroalkyl substances (PFAS), we offer the following comments.

Overall, we find the proposal to be overly broad with respect to "PFAS", and scientifically distorted as it relates to fluoropolymers. The goal of reducing risks to the environment and human health from exposure to PFAS and/or their degradation products can be achieved without requiring a restriction on PFAS as single class – especially with PFAS having a broad range of chemical functional groups and physical/chemical properties. Furthermore, by essentially equating risk with persistence, the proposal significantly oversimplifies the approach to both hazard identification and risk assessment that has been central to risk management approaches under REACH and other EU regulatory frameworks for many years (see REACH Annex XIII). Fluoropolymers should be excluded from the proposed risk management option because they are not bioaccumulative, not mobile, and not toxic, and, therefore, do not pose a risk to the environment or human health.

SPECIFIC COMMENTS

1. **Persistence alone is not an appropriate measure of potential human health or environmental risk.**

   Some PFAS have been described as persistent because they degrade or transform to "terminal" persistent compounds. As stated in the restriction proposal (p.24), "[t]he persistence as the core concern of PFASs has also been pointed out by scientists for instance in the Helsingør Statement on PFASs (Scheringer et al., 2014) as well as the follow up Madrid statement (Blum et al., 2015)." The proposal omits an important detail, which is that neither of these statements refer to fluoropolymers. Scheringer et al. (2014) specifically referred to *non-polymer* perfluoroalkyl acids (PFAS) – perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs), including perfluorooctanesulfonic acid (PFOS). Likewise, Blum et al. (2015) references scientific studies that are exclusively on non-polymer perfluoroalkyl acids (PFAAs), rather than fluoropolymers.

   As described in REACH Annex XIII, several regulatory frameworks in Europe require the assessment of "persistent, bioaccumulative, toxic" (PBT) properties of chemicals, including refined classifications such as "very persistent and very bioaccumulative (vPvB)". Substances with PBT/vPvB properties **combine** the characteristics of strong persistence with the potential to accumulate in the environment and biota (Moermond et al., 2012, p. 2). Dating back to the Stockholm Convention on Persistent Organic Pollutants, the objective for evaluating PBT as combined characteristics is the "protection

of the environment and humans from substances that may harm these entities, either locally or globally, by accumulation in organisms where they then exert toxic effects" (Solomon et al., 2013, p. 1). Inherent in this objective is the understanding that the toxicity of a substance is contingent on the level present in the organism, and that chemicals with a lower bioaccumulation potential will present a lower risk.

Persistence in the environment does not indicate that the substance would accumulate in organisms, nor that environmental levels would rise to such an extent that exposure would result in toxicity. According to ECHA, substances that persist for long periods of time in the environment **and** have a high potential to accumulate in biota are of specific concern because their long-term effects are rarely predictable[1]. Importantly, the PBT criteria established under REACH has always considered the characteristics of **both** persistency and bioaccumulation **together**, as indicators of potential risk (i.e., toxicity). Potential for bioaccumulation is defined by REACH criteria (EC-1907-2006) as the condition when the bioconcentration factor (BCF) in aquatic species is higher than 2000.

PBT criteria have been applied consistently under numerous EU regulatory frameworks. The following are examples of applications of PBT concepts in regulatory programs over the past three decades (based on Table 3 from Moermond et al., 2012):

Time Period	Regulatory Program that Adopted or Applied PBT Concept
Late 1990s	Criteria Expert Group for Persistent Organic Pollutants develop criteria for categorization of POPs (Solomon et al. 2013)
1998	United Nations Economic Commission for Europe, the Convention on Long-range Transboundary Air Pollution (LRTAP)
2001	Stockholm Convention
2003	OSPAR Convention for the Protection of the Marine Environment of the Northeast Atlantic
2004	EU directives on Human & Veterinary Pharmaceuticals
	International Maritime Organization (IMO) International Convention for the Control and Management of Ship's Ballast Water and Sediments
2006	Registration, Evaluation, Authorisation and Restriction of Chemicals, (REACH)

Across each of these regulatory frameworks, the **combination** of chemical properties that comprise PBT criteria are consistently evaluated:

a. The chemical is evaluated for its persistence (P/vP) in the environment based on its half-life in environmental media (e.g., water, sediment, soil); **and**,

b. The chemical is evaluated for bioaccumulation (B/vB) in biota based on its BCF, octanol/water coefficient (log K_{OW}), or monitoring data; **and**,

c. The chemical is evaluated for toxicity (T) to biota based on observed adverse effects at concentrations exceeding specific exposure thresholds, or evidence of

[1] https://echa.europa.eu/understanding-pbt-assessment

carcinogenicity, mutagenicity, reproductive toxicity, or specific target organ toxicity after repeated exposure.

While there are differences in the specific criteria applied during PBT/vPvB evaluation, each regulatory framework makes clear that **no standalone criteria**, whether it be P/vP, B/vB, or T, is sufficient cause for PBT/vPvB status or environmental concern. In all cases, at least two of these three properties (P and B) must be established to identify a chemical as PBT/vPvB.

In fact, there is precedent within EU chemical legislation for not restricting chemicals based on persistence alone. For example, vinyl neodecanoate was evaluated by the PBT Working Group and classified as "P/vP" but "not fulfilling PBT and vP/vB criteria". Specifically, the assessment report states that vinyl neodecanoate: "is not considered to be a PBT substance. It does not meet the B criteria and does not meet the screening criteria for T. It does meet the screening criteria for P (and vP)."[2]

2. **Fluoropolymers are not bioaccumulative**.

   Available data indicate that fluoropolymers are not bioaccumulative. Bioaccumulation potential is generally assessed based on a prediction using the octanol-water coefficient (e.g., log K_{OW} > 3) or measurements in tissue and exposure media (e.g., BCF > 2000). Fluoropolymers such as polytetrafluoroethylene (PTFE, CASRN 9002-84-0), polyvinylidene fluoride (PVDF) homopolymer (CASRN 24937-79-9), perfluoroalkoxy alkane (PFA, CASRN 26655-00-5 and 31784-04-0), and fluoroelastomer (FKM, CASRNs 9011-17-0, 26424-79-6, and 25190-89-0) are insoluble in octanol and water (Henry et al., 2018; Korzeniowski et al., 2022). Therefore, the bioaccumulation potential of fluoropolymers cannot be reliably predicted from a log K_{OW}. Measured biota tissue, water, and sediment concentrations indicate there is a low bioaccumulation potential for fluoropolymers in aquatic food webs. Researchers examining benthic invertebrate exposure to PTFE and other polymers demonstrated that there was no evidence of bioaccumulation through the aquatic benthic community from lower trophic level filter-feeders and grazers to higher trophic level omnivores and predators in the Arctic (Sfriso et al., 2020) and in Norway (Bour et al., 2018).

3. **Fluoropolymers are not environmentally mobile.** The restriction proposal argues that the continuous release of PFAS will lead to the accumulation of these compounds in the environment, such that unknown toxicity thresholds will be exceeded at some unknown point in the future. Moreover, the proposal also suggests that "PFAS" as a class will be found in all environmental media. Neither of these arguments apply to fluoropolymers.

   Fluoropolymers are not water soluble and will not likely result in widespread groundwater impacts or exposures from drinking water. If released to the environment, fluoropolymers are likely to remain in the environmental matrix they contact following release, such as terrestrial soil or aquatic sediment. Because fluoropolymers are chemically inert, they cannot partition and are not chemically mobile between water and soil/sediment. Any potential movement of fluoropolymers in the environment will occur via mechanical

[2] https://echa.europa.eu/documents/10162/6af350f6-e259-4545-859f-293ce8515cb3

transport processes, such as overland flow from precipitation events (e.g., rainfall flows carrying fluoropolymers from soil to sediment via runoff). Indeed, Feng et al. (2022) recently demonstrated that PTFE in modelled tidal sediments showed enhanced retention and low likelihood of resuspension into the water column. Given their chemical inertness, non-volatility, and lack of water solubility, fluoropolymers are not highly mobile in the environment.

4. **Fluoropolymers present in the environment are not toxic to humans or ecological receptors.** Toxicity studies on fluoropolymers indicate that adverse effects are unlikely following exposure by human or ecological receptors to levels of fluoropolymer that may be present in the environment. A summary of available laboratory bioassays examining the toxicity of PTFE on test animals is provided by Radulovic and Wojcinski (2014). Given that fluoropolymers such as PTFE are insoluble in water and non-volatile, the most likely exposure route for PTFE is ingestion. In fact, acute oral toxicity of PTFE in rats is low, with a reported LD_{50} > 11,280 mg/kg. Researchers also found there were no observed adverse effects in rats exposed to up to 25% PTFE in rat diet for up to 90 days (Naftalovich et al., 2016; Radulovic & Wojcinski, 2014). The lack of toxicity of PTFE at 25% of the diet level fed to rats for 90 days was subsequently validated by peer review by the Scientific Review Panel of the Hazardous Substances Data Bank (TOXNET) (Naftalovich et al., 2016). Additionally, a four-week repeated dose study exposed mice to PTFE via their diet and reported no effects at any dose level, and no PTFE was detected in mice blood (Lee et al., 2022). The study supports an unbounded no-observed-adverse-effect-level (NOAEL) of 2,000 milligrams per kilogram (mg/kg) in mice, equivalent to approximately 9,720 mg/kg for a 60 kg human adult. The lack of toxicity from ingestion of PTFE and other fluoropolymers is attributed to their extremely high molecular weight, which renders absorption via the gastrointestinal tract negligible, and the fact that they are chemically inert compounds and not metabolized under physiological conditions (Naftalovich et al., 2016).

   Manufacturer Material Safety Data Sheets indicate that dermal contact with PTFE does not cause skin irritation in rabbits or humans. PTFE is not considered genotoxic and is so inert it has been used in genotoxicity protocols or test methodologies for *Salmonella typhimurium* mutagenicity testing of the US EPA Mobile Reaction Chamber (Naftalovich et al., 2016). The World Health Organization's International Agency for Research on Cancer concluded that organic polymeric materials (such as fluoropolymers) as a group are not classifiable as to their carcinogenicity to humans (Group 3) (IARC, 1999).

5. **The "P-sufficient" approach is novel and precedent setting, worldwide.** The Annex XV Restriction of all "PFAS" would be the first of its kind globally. The Restriction Report (p.24) references California EPA, Department of Toxic Substances and Chemicals (DTSC) as an example of established regulatory precedent, where a state regulatory agency has placed restrictions on all PFAS as class[3]. The referenced journal article (Bălan et al., 2021) written by California DTSC staff specifically refers to PFAS present in specific consumer products. It would be inaccurate to conclude from this one example that

[3] The Restriction report says: "It is noted that the first example of regulation of PFASs as a chemical class according to the P-sufficient approach has been introduced in California. Here a regulation of PFASs as a class is in place for certain consumer products under the California Safer Consumer Products Program (Balan et al., 2021)."

California has adopted the P-sufficient concept as a PFAS risk management strategy. Indeed, an examination of recent legislative developments in California clearly shows that the state is actually pursuing a **targeted** risk management strategy:

1. PFAS in fire-fighting foam
    - Effective 1 January 2022, this legislation prohibits the use of class B firefighting foam containing intentionally added PFAS chemicals in California.
2. PFAS in textiles
    - Effective 1 January 2024, will prohibit the sale of PFAS-containing textile articles and require least toxic alternatives when replacing PFAS.
3. PFAS in cosmetics
    - Effective 1 January 2025, prohibits sale of cosmetic products that contain intentionally-added PFAS.
4. PFAS in plant-based food packaging and cookware
    - Effective 1 January 2023, prohibits sale of various plant fiber-based food packaging that contains PFAS.
    - Requires disclosure of certain chemicals, including PFAS, in cookware starting January 2023.

Importantly, none of these legislative actions apply to industrial PFAS uses, where fluoropolymers are primarily utilized. Furthermore, these initiatives clearly demonstrate that California is pursuing targeted restrictions on PFAS used in specific consumer products.

Moreover, Bălan et al. (2021) inappropriately include fluoropolymers under their P-sufficient approach based solely on one false statement and a second statement that lacks important context:

1. “Fluoropolymers are characterized by large molecular sizes and do not degrade to PFAAs under typical environmental conditions, although they have been observed to release [perfluorocarboxylic acids] PFCAs, including [perfluorooctanoate] PFOA, when heated to temperatures between 180 °C and 800 °C (Schlummer et al. 2015; Feng et al. 2015).”

   This statement, while correct regarding the large molecular weight of fluoropolymers, is incorrect with regard to the release of PFCAs such as PFOA. When heated to temperatures greater than 300 °C, the potential transformation products of PTFE include trifluoroacetic acid (TFA, CASRN 76-05-1), hydrofluoric acid (CASRN 7664-39-3), tetrafluoroethylene (TFE, CASRN 116-14-3), hexafluoropropylene (CASRN 116-15-4), or perfluoroisobutylene (CASRN 382-21-8) (Ellis et al., 2001; Radulovic and Wojcinski, 2014; Henry et al., 2018; Tolkach et al., 2020). Heating PVDF homopolymer to temperatures greater than 300 °C may result in the formation of hydrogen fluoride (HF, CAS No. 7664-39-3) and oxides of carbon (Arkema, 2011). Similarly, thermal decomposition of PFA at temperatures exceeding 300 °C can produce HF, carbonyl difluoride (CASRN 353-50-4), carbon monoxide (CO, CASRN 630-08-0) and carbon dioxide (CASRN 124-38-9) (Inoflon Fluoropolymers, 2018). The potential transformation products of these fluoropolymers do not include PFCAs such as PFOA at intended use and end of life conditions.

2. “PFAAs are used in the manufacture of fluoropolymers and can occur as impurities in the final product.”

PFAAs such as fluorinated polymerization aids (FPAs), also referred to as fluorosurfactants, are currently used by some chemical manufacturers, albeit to a lesser extent, to facilitate the polymerization reaction that forms the final fluoropolymer product (Ameduri et al., 2023). PFOA and hexafluoropropylene oxide dimer acid (HFPO-DA, or GenX) are examples of these FPAs that have garnered widespread environmental concern. Furthermore, the substitution of non-fluorinated polymerization aids (NFPAs) for FPAs in the manufacture of the three main fluoropolymers by volume – PTFE, PVDF, and FKM – allows for the complete manufacture of these fluoropolymers without the use of FPAs and any resulting minor impurities (Ameduri et al., 2023). Therefore, by implementing the widespread use of NFPAs in fluoropolymer manufacturing, environmental contamination can be reduced to the maximum extent practicable.

Residual impurities from non-polymeric PFAS entrained in the final fluoropolymer product, such as low molecular weight (<1000 Da) leachables and residual monomers, are quantifiably low: <1 ppm in PTFE and <50 ppb in PFA (Henry et al., 2018). This low leaching potential is what allows PTFE to meet the requirements for use in the food and beverage, pharmaceutical, medical, and semiconductor industries (Olabisi and Adewale, 2015). The following table summarizes the numerous regulatory safety standards that fluoropolymers meet for US and EU regulations, demonstrating their safety for use across drinking water, food contact, and medical industries:

Regulation	Regulatory Program Description
EC 10/2011	EU Commission Regulation No 10/2011 of 14 January 2011 safety requirement on plastic materials and articles intended to come into contact with food (EU, 2011a).
21CFR 177.1550	US food contact regulation for perfluorocarbon resins (CFR, 2023).
2011/65/EU	Restriction of hazardous substances in electrical & electronic equipment (EU, 2011b).
USP Class VI	Biocompatibility testing requirements from the U.S. Pharmacopeia (USP). Includes safety standards for plastic, polymers, and elastomers to be applied in medical devices and surgical equipment. Testing includes acute systemic toxicity test, intracutaneous test, and implantation test (USP, n.d.).
3-A 20-27	Sanitary standards for multiple-use plastic materials as a product contact or cleaning solution contact surfaces in equipment for production, processing, and handling of milk and milk products. Test criteria includes their ability to be cleaned, to receive effective bactericidal treatment, and to maintain their essential functional properties (3-A, 2011).
Umwelt Bundesamt (UBA)	German Environmental Agency (UBA) evaluation criteria for any plastic and rubber products that come in contact with drinking water (UBA, 2022).

Sanitary Conformity Certification (ACS)	French mandatory certification for any device in contact with drinking water during production, treatment, storage, and distribution (ANSES, 2013; FR, n.d.).
Water Regulations Approval Scheme (WRAS)	United Kingdom's accreditation body for approval process of water fittings. It aims to prevent the misuse, waste, excessive consumption, and inaccurate measurement of water and, ensure that drinking water is free from contamination. Includes products used only after the time of supply (WRAS, n.d.).

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Critical Review

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of fluorinated substances that are in the focus of researchers and regulators due to widespread presence in the environment and biota, including humans, of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Fluoropolymers, high molecular weight polymers, have unique properties that constitute a distinct class within the PFAS group. Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability. They have negligible residual monomer and oligomer content and low to no leachables. Fluoropolymers are practically insoluble in water and not subject to long-range transport. With a molecular weight well over 100 000 Da, fluoropolymers cannot cross the cell membrane. Fluoropolymers are not bioavailable or bioaccumulative, as evidenced by toxicology studies on polytetrafluoroethylene (PTFE): acute and subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, cytotoxicity, in vitro and in vivo genotoxicity, hemolysis, complement activation, and thrombogenicity. Clinical studies of patients receiving permanently implanted PTFE cardiovascular medical devices demonstrate no chronic toxicity or carcinogenicity and no reproductive, developmental, or endocrine toxicity. This paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" (PLC). This review concludes that fluoropolymers are distinctly different from other polymeric and nonpolymeric PFAS and should be separated from them for hazard assessment or regulatory purposes. Grouping fluoropolymers with all classes of PFAS for "read across" or structure–activity relationship assessment is not scientifically appropriate. *Integr Environ Assess Manag* 2018;14:316–334. © 2018 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals, Inc. on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

Keywords: Fluoropolymer International regulation Polytetrafluoroethylene Polymer of low concern PFAS

INTRODUCTION

The carbon–fluorine (C–F) bond is the strongest bond between C and another atom, instilling substances that contain a majority of C–F bonds with stability, inertness, and persistence (Banks et al. 1994). Per- and polyfluoroalkyl substances (PFAS) are a large group of highly fluorinated synthetic substances with diverse properties that have been used in a wide variety of industrial and consumer applications since the 1950s (Buck et al. 2011). Within the group are distinct substances with different properties: polymers and nonpolymers; solids, liquids, and gases; persistent and nonpersistent substances; highly reactive and inert substances; mobile and insoluble substances; and toxic and nontoxic chemicals.

The PFAS are a large, diverse group of substances that, in some respects, challenge easy distinction for assessment and management. A clearer understanding of the origin of PFAS found in the environment and assessment of their properties is needed to be able to determine which classes of PFAS require management action. Per- and polyfluoroalkyl substances must be assessed taking into account their differences in chemical, physical, thermal, and biological properties. A single, globally harmonized system for PFAS classification has not yet been defined, resulting in a lack of distinction between PFAS. As regulatory frameworks continue to evolve, such as the Regulation (EC) No 1907/2006 of the European

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Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (RC 2006), more work is needed to distinguish classes of PFAS to ensure that regulations are appropriate in scope and proportionality.

Two long-chain nonpolymer perfluoroalkyl acids (PFAAs), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (both PFAS), found widespread in the environment and living systems, led to regulatory assessment and management efforts in several countries (Buck et al. 2011; OECD 2017; USEPA 2017a). Management actions to curtail manufacture of long-chain PFAAs, including PFOS and PFOA, and substances that may degrade to form them (also known as "precursors") have been taken (EC 2006; ECHA 2015; USEPA 2017a). Both PFOS and PFOA have been determined by regulators to be persistent, bioaccumulative, and toxic (PBT) substances (EC 2006; ECHA 2015). A current concern is the potential for certain side-chain polymer PFAS to degrade in the environment to PFOS and PFOA or lower homologues (Liu and Mejia-Avendaño 2013). In addition, PFOS (a nonpolymeric perfluoroalkyl substance) and related substances have been listed as persistent organic pollutants (POPs) under Annex B of the Stockholm Convention (UNEP 2009), and PFOA and other related substances (UNEP 2011), as well as perfluorohexane sulfonic acid (PFHxS) and related substances are being evaluated for listing (UNEP 2017a). As a result, questions about the health and environmental safety of PFAS as a group have been raised (Scheringer et al. 2014; Blum et al. 2015).

These findings have prompted expanded regulatory interest and concern about PFAS as a group, spurring additional assessment and management actions. The German Environment Agency, Umweltbundesamt (UBA), published a proposal to implement new assessment criteria and procedures for identifying persistent (P), mobile (M), and toxic (T) substances under the European Union REACH chemical registration process (UBA 2017). The UBA has concluded that PM and/or PMT substances constitute "an irreversible threat to sources of drinking water and the quality of drinking water" in Germany. This has prompted the designation of PFAS substances as posing an "equivalent level of concern" under Article 57(f) of REACH and thereby has prompted the need for a new paradigm for chemical assessment and authorization. The Swedish Chemicals Agency, Kemikalieinspektionen (KEMI), announced agreement among 37 government agencies and research institutions in the European Union (EU) to expand cooperation to reduce the risks and increase the knowledge of PFAS, thereby endorsing the UBA view on the hazards posed by all PFAS substances (KEMI Swedish Chemicals Agency 2016). The KEMI announcement indicated that all perfluoralkyl substances should be considered as extremely persistent in the environment, and many are water soluble, mobile in soil, and likely to contaminate waterways and drinking water supplies. A risk assessment report prepared by KEMI is forthcoming (ChemNews 2016).

The PFAS are divided into 2 primary categories: nonpolymers and polymers (Figure 1). Figure 1 shows that these 2 categories are divided into 5 classes of PFAS. The fluoropolymer class of PFAS is the focus of the present paper. The nonpolymer category includes perfluoroalkyl substances and polyfluoroalkyl substances. The polymer category includes fluoropolymers, perfluoropolyethers, and side-chain fluorinated polymers. Polymers generally have very different physical, chemical, and biological properties than do nonpolymer chemical substances of low molecular weight. Precise criteria that distinguish polymers from nonpolymers have been established (OECD 1993).

There are distinct differences between the 5 classes of PFAS. For example, PFOA, in the class nonpolymer perfluoroalkyl substances, is small, mobile, and persistent; has been assessed and determined to be a PBT chemical (ECHA 2015); and is in the final stage for recommendation of listing as a POP under the Stockholm Convention (UNEP 2017b). Regulatory and industry management actions on PFOA include precursor substances that may degrade to form PFOA (USEPA 2017a). An example in the class of nonpolymer polyfluorinated substances, 8:2 fluorotelomer alcohol, is known to degrade under environmentally relevant conditions to form PFOA (Liu and Mejia-Avendaño 2013). It is therefore a precursor substance to PFOA and subject to regulatory management (Liu and Mejia-Avendaño 2013). Polymers derived from 8:2 fluorotelomer alcohol are examples of the side-chain fluorinated polymers class. These polymers may degrade to form PFOA and therefore are subject to regulatory management. Lastly, perfluoropolyethers class is a complex class of PFAS, which contains O linkages in the polymer backbone.

In the present paper, we address fluoropolymers, a class of PFAS polymers (Figure 1). Fluoropolymers are high molecular weight solid plastics that have been studied extensively.

The present paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" (PLC) and to show that fluoropolymers are distinctly different enough from other classes of PFAS to not be grouped with them for hazard assessment or regulatory purposes.

PERFORMANCE CHARACTERISTICS AND USES OF FLUOROPOLYMERS

Since the discovery of polytetrafluoroethylene (PTFE) in 1938 (Plunkett 1987), the use of fluoropolymers has grown considerably to take advantage of their unique physical–chemical, thermal, and biological properties. The 4 fluoropolymers addressed in the present paper, polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), and tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (e.g., perfluoroalkoxy polymer, PFA), accounted for approximately 70% to 75% of the world fluoropolymer consumption in 2015 (IHS 2016). The representative fluoropolymer discussed in the present paper, PTFE, made up 58% (by weight) of 2015 worldwide fluoropolymer consumption (IHS 2016). Fluoropolymers are high molecular weight plastics with unique properties attributable to the strong C–F bonds, the strongest bond between C and another atom, making

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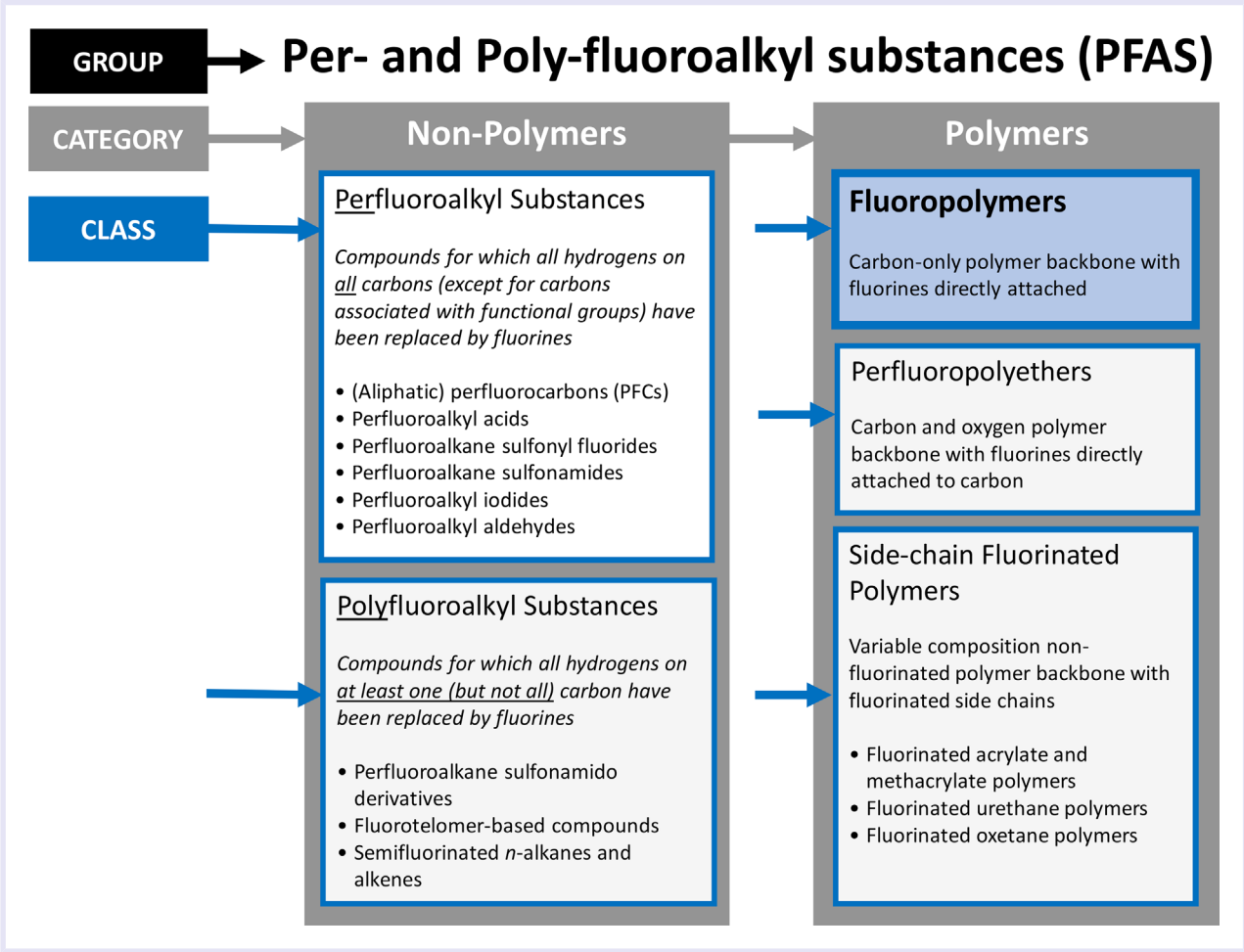


Figure 1. Per- and polyfluoroalkyl substances (PFAS).

them highly stable (Olabisi and Adewale 2015). Carbon atoms alone form the fluoropolymer backbone, each surrounded by an envelope of F atoms. Fluoropolymers are generally very high molecular weight (>100 000 Da); have high thermal, chemical, photochemical, oxidative, hydrolytic, and biological stability; have low flammability, neutral electrical charge, and resistance to degradation; have negligible residual monomers and low molecular weight oligomer content; have limited low molecular weight leachables; and have no reactive functional groups of concern (Gangal and Brothers 2015).

The unique properties of fluoropolymers include durability, mechanical strength, inertness, thermal stability in foreseeable use conditions, and resistance to chemical, biological, and physical degradation (Hougham et al. 1999). Table 1 shows performance characteristics required in various commercial fluoropolymer applications (Gangal and Brothers 2015; Dams and Hintzer 2016). For example, medical devices are successful when they are made from "biocompatible" biomaterials, that is, the material has the ability to perform with an appropriate host response in a specific situation (Williams 1987). The inertness of PTFE allows for its acceptance into the body. Moreover, PTFE flexibility and durability deliver mechanical integrity for the device's lifetime. The microstructure of PTFE can be modified to meet specific physiological needs (e.g., porous and open structure to facilitate tissue ingrowth), enhancing its utility in medical devices. In terms of end-use function, PTFE's inertness, physical properties (Ebnesajjad 2011), and the low level of residual monomer, oligomers, and low molecular weight leachables (Supplemental Data p 32–55) meet the requirements for low levels of contaminants and particulates in manufacturing environments essential for the food and beverage, pharmaceutical, medical, and semiconductor industries (Olabisi and Adewale 2015). Manufacturing applications requiring ultrapure high efficiency particulate air (HEPA) filtration use the finely controlled microporous PTFE membranes. Other components requiring a high degree of contamination control associated with patient care (e.g., dialysis tubing) also find the properties of PTFE essential. Durability in harsh conditions makes PTFE a superior material of choice in aerospace, environmental controls, energy production and storage, and electronics, as well as in technical apparel. The thermal stability of PTFE and FEP fluoropolymers provides improved fire safety risk over other polymers when used in plenums and structural

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Table 1. Fluoropolymer functionality and commercial applications

	Fluoropolymer characteristics									
	Durable		Inert		Functional			Stable		
Commercial application	Mechanical strength	Low particulation	Resistance to chemicals	Nontoxic, biocompatible, biological degradation resistant	Flexibility	Friction resistance	Low dielectric constant	Low leachables	Resistance to photolysis, oxidation, hydrolysis	Stability
Aerospace	X	—	X	—	X	X	X	—	X	X
Automotive industry	X	—	X	—	X	X	X	—	X	x
Medical devices	X	X		X	X	X	—	X	X	X
Pharmaceutical manufacture	X	X	X	X	X	—	—	X	—	X
Consumer outdoor apparel	X	—		X	X	—	—	X	—	—
Technical clothing (military, firefighters, first responders, medical personnel)	X	—	X	X	X	X	—	X	X	X
Consumer electronics	X	—	X	—	X	X	X	—	X	X
Wireless communications	X	—	X	—	X	X	X	—	X	X
Satellite navigation systems	X	—	X	—	X	X	X	—	X	X
Semiconductor industry	—	X	X	—	—	—	X	X	—	—
Building construction	X	—	—	X	X	—	X	—	X	X
Energy production and storage	X	X	—	—	—	—	X	X	X	X
Food and beverage production	X	X	X	X	X	X	—	X	X	—
Food protection and packaging	X	X	X	X	X	—	—	X		—
Drinking water filtration	—	X	X	X	—	—	—	X	X	—
Environmental protection	—	X	X	X	—	—	—	X	X	X

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geometries in aviation and standard building construction (Olabisi and Adewale 2015). In addition, chemical resistance to acids, bases, solvents, and chemical attack, combined with its unique conformable strength, makes PTFE an ideal coating for chemical process equipment, lining for process piping, sealants for gaskets and hoses, and fabricated parts for pumps, gears, and other mechanical parts that need this extreme resistance for functionality (Olabisi and Adewale 2015). The low dielectric constant of PTFE ensures the integrity of high speed–low signal loss systems as employed in the aerospace industry for flight controls, communication, and protection from extreme cold, moisture, and altitude changes (Dams and Hintzer 2016). These are lifesaving applications that are used in satellite systems for navigation, wireless communications, in-flight navigation, and shielding from electronic interference. Civil and military aviation depends on reliable performance of these systems for long service hours with minimal maintenance down times. In addition, PTFE provides reduced friction of moving parts (e.g., cable chains), preventing particulation during automated manufacturing in cleanroom environments (Dams and Hintzer 2016). This friction reduction is also uniquely beneficial in light load bearings, gears, cams, and other mechanical machine parts as well as in weaving fibers, yarns, and greases (Dams and Hintzer 2016).

ASSESSMENT OF POLYMERS

History

Prior to the mid-20th century, regulation of new chemical substances, mixtures, and polymers in general was very limited. National chemical inventories were created with notification requirements for new chemical substances, mixtures, and polymers. In the United States, new chemicals submitted to the US Environmental Protection Agency (USEPA) under the Toxic Substances Control Act (TSCA) (USC 1976) for addition to the US chemical inventory are reviewed for potential physical, chemical, and biological effects (environmental and mammalian), as well as for potential exposure to the environment and human populations. Over time, the USEPA regulatory scientists gained enough knowledge through the review of the thousands of data packages to develop tools to assist in the identification of physical–chemical properties, potential hazard, and potential exposure to assist in and expedite the chemical review and assessment process (Auer et al. 1990; Wagner et al. 1995; USEPA 2012; USEPA 2017b).

The predictive power and reliability of these approaches were tested and refined (Wagner et al. 1995). Over time, it was recognized that many of the physical–chemical properties, such as molecular weight, limit the ability of the chemical to cross the cell membrane and therefore limit its bioavailability. Further examination of general physical–chemical properties and their relationship to hazard potential of a given chemical led to the development of general principles or criteria for the identification of chemicals, including polymers, with low hazard potential. These criteria were developed for use by USEPA for its hazard evaluation of new polymers. The USEPA made this methodology available to the public to assist submitters interested in developing low hazard polymers (USEPA 1997a). In 1984, the USEPA published the polymer exemption rule to exempt low hazard polymers from certain notification requirements under the new chemicals program (USFR 1984). The polymer exemption rule incorporated the hazard criteria as part of the criteria to determine eligibility for exemption (USEPA 1997a, 2010).

The hazard criteria that support the PLC concept represent an extension of these principles and practices developed for (nonpolymeric) chemicals and rely heavily on physical–chemical properties that determine a chemical's bioavailability. In 1993, the Organisation for Economic Co-operation and Development (OECD) Expert Group on Polymers found that sufficient data existed to create a consensus document identifying the essential data elements to qualify a polymer as a PLC to human health and the environment (OECD 1993). By 2007, the OECD Expert Group on Polymers agreed that, "Polymers of low concern are those deemed to have insignificant environmental and human health impacts" (OECD 2009). Thus, there was agreement within the OECD that polymeric chemicals meeting these criteria have a low hazard potential. However, the integration of the criteria into a risk management framework may differ from country to country according to their individual regulatory mandate.

In a recent report commissioned by the European Commission (EC) (BIO by Deloitte 2015), the following countries agreed on the polymer properties predictive of adverse human health and environmental hazard: Australia, Canada, China, Japan, South Korea, Philippines, New Zealand, Taiwan, and the United States. Further, the report identified the eligibility criteria to be considered a PLC with respect to potential for adverse impact on health and the environment. The report also compiled existing polymer regulations outside the EU and proposed alternative options for EU polymer registration, including defining a category of a PLC and grouping polymers into families.

The PLC criteria are described in the following section. Note that there are some policy components, such as elemental composition, as well as the physical–chemical attributes, in the PLC criteria.

POLYMER OF LOW CONCERN CRITERIA

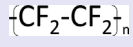
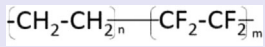
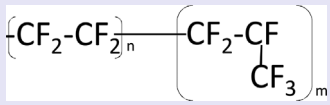
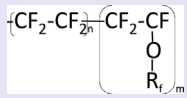
Here we describe each of the eligibility criteria for PLC and provide an assessment for the representative fluoropolymer PTFE. We will show that fluoropolymers, including PTFE, satisfy the widely accepted assessment criteria to be considered PLCs (Table 2) and therefore are considered to be of low hazard to human health and the environment.

Polymer composition

The polymer composition criterion requires structure and elemental composition of the polymer be described and identified (e.g., by Chemical Abstracts Service [CAS] number).

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Table 2. Fluoropolymers and PLC criteria

	Fluoropolymers			
	PTFE	ETFE	FEP	PFA
Assessment criteria[a]	CAS 9002-84-0	CAS 25038-71-5, 68258-85-5	CAS 25067-11-2	CAS 26655-00-5, 31784-04-0
Structure				
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to C)	Yes	Yes	Yes	Yes
Molecular weight	389 000–8 900 000[bc]	—	—	—
(M_n > 1000 Da and oligomer content < 1%)	520 000–45 000 000[bd]	530 000–1 200 000[ef]	241 000–575 000[eg]	200 000–450 000[eh]
Molecular weight distribution MW ÷ number average M_n (M_n and heterogeneity of MW distribution indicate if majority are >1000 or <1000 Da, which could penetrate the cell)	2.3[i]	1.4–2.7[f]	1.55–2.09[g]	1.7[j]
Wt % oligomer (see Figure 2) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible
Ionic character (cationic polymers associated with aquatic toxicity; polycationic with adverse human health effect)	Neutral	Neutral	Neutral	Neutral
RFGs[k] (some highly reactive functional groups associated with adverse human health and ecotoxicology effects, e.g., acrylates, isocyanates, anhydrides, aziridines)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)
FGEW[k] (typical value) (the lower the FGEW, the more reactive the polymer and the higher the potential for health and environmental impact)	$>10^5$–10^7	$>10^5$–10^6	$>10^5$	$>10^5$
Low molecular weight leachables (MW < 1000 Da able to enter cell)	<1 ppm	No active leachables by USP class VI[l] (121 °C)	No active leachables by USP class VI[l] (121 °C)	No active leachables by USP class VI[l] (121 °C)
Residual monomers (monomers have lower MW than polymers; typically more hazardous than polymers)	<1 ppm	<50 ppb	<50 ppb	<50 ppb
Ratio of residual monomers to molecular weight (typical value) (more low MW monomer content per mole increases bioavailability and hazard potential)	$\sim10^{-13}$ to 10^{-15}	$\sim10^{-13}$ to 10^{-14}	$\sim10^{-13}$	$\sim 10^{-13}$
Structural similarities to RFG of concern (increases potential risk of adverse effects)	None	None	None	None
Reference standard see also ISO 1133 (ISO 2011), ISO 12086 (ISO 2006)	ASTM D 4894 (ASTM 2015a), D 4895 (ASTM 2015b)	ASTM D 2116 (ASTM 2016a)	ASTM D 3159 (ASTM 2015c)	ASTM D 3307 (ASTM 2016b)

(*Continued*)

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Table 2. (*Continued*)

	Fluoropolymers			
	PTFE	ETFE	FEP	PFA
Assessment criteria[a]	CAS 9002-84-0	CAS 25038-71-5, 68258-85-5	CAS 25067-11-2	CAS 26655-00-5, 31784-04-0
Physical–chemical properties				
Water solubility (per USP 2011) (water solubility <10 mg/L showed generally low health concerns; 10 mL/L to 10000 mg/L had potential health concern)	Practically insoluble or insoluble (1×10^{-5} mg/L)	Practically insoluble or insoluble	Practically insoluble or insoluble	Practically insoluble or insoluble
Octanol–water partition coefficient, K_{OW} (higher K_{OW} associated with lipophilicity and a high potential to bioaccumulate or bioconcentrate)	NA	NA	NA	NA
Particle size (median mass aerodynamic diameter, MMAD, should be >5 μm)	100–500 μm (powders)	50–250 μm (powders)	50–250 μm (powders)	50–250 μm (powders)
	—	2–4 mm (pellets)	2–4 mm (pellets)	2–4 mm (pellets)
Stability				
Hydrolysis (breaking into M_n < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Light (hν) (breaking into M_n < 1 000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Oxidation (breaking into M_n < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Biodegradation (aerobic and anaerobic) (breaking into M_n < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp (°C) (breaking into M_n < 1000 Da increases hazard potential)	260	150	200	260
Meets PLC criteria[a] (Y/N)	Yes	Yes	Yes	Yes

ASTM = American Society for Testing and Materials; CAS = Chemical Abstracts Service; Da = dalton; ETFE = ethylene tetrafluoroethylene; FEP = fluorinated ethylene propylene; FGEW = functional group equivalent weight; ISO = International Organization for Standardization; MMAD = median mass aerodynamic diameter; M_n = number average molecular weight; MW = molecular weight; MWD = molecular weight distribution; OECD = Organisation for Economic Co-operation and Development; PFA = perfluoroalkoxy polymer; PFPE = perfluoropolyether; PLC = polymer of low concern; PTFE = polytetrafluoroethylene; PVDF = polyvinylidene fluoride; PVF = polyvinyl fluoride; RFG = reactive functional groups; USEPA = US Environmental Protection Agency; USP = US Pharmacopeia.

[a]See OECD 2009 and BIO by Deloitte 2015 for details on characteristics of a "polymer of low concern."

[b]Molecular weight is number average molecular weight.

[c]Berry and Peterson 1951; Doban et al. 1956.

[d]Suwa et al. 1973.

[e]Molecular weight is weight average molecular weight.

[f]Tuminello et al. 1993.

[g]Tuminello 1989.

[h]Putnam 1986.

[i]Chu et al. 1989.

[j]Frick et al. 2012.

[k]For definition of reactive functional group; lists of low-, moderate-, and high-concern functional groups; and FGEW limits, see USEPA Polymer Exemption Guidance Manual (USEPA 1997b), BIO by Deloitte 2015 (p 191–192), and USEPA 2010. See Supplemental Data.

[l]In the USP<88> testing for "class VI," 2 g of the plastic (e.g., FEP, ETFE, or PFA) were extracted at 121 °C in: 1) 0.9% sodium chloride solution, 2) sesame oil, NF, 3) alcohol saline, and d) polyethylene glycol. The acute systemic toxicity and intracutaneous reactivity tests were conducted with those extracts. The intramuscular implantation was conducted with the plastic. Passing these 3 tests indicates that any leachables were not released in concentrations capable of causing these adverse effects, but does not result in a quantitative concentration of leachables. (See USP 2018.)

Note: The following are not addressed in this paper: PFPEs, side-chain fluorinated polymers, fluoroelastomers, PVF, and PVDF.

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Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da

The number average molecular weight (M_n) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report (BIO by Deloitte 2015) states that the "most potential health concern polymers have a number average molecular weight, Mn, < 1000 Da and oligomer content >1%." The higher the oligomeric content, the more likely a polymer is to be a health or ecotoxicological (OECD 2009, p 9). In fact, when comparing the potential health concern of polymers with varying percent oligomer content, "...the distribution of potential health concern polymers showed an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD 2009, p 24).

Molecular weight (MW) is an important predictor of biological effect because very large molecules (>1000–10 000 Da) are too large to penetrate cell membranes (Supplemental Data in Beyer 1993, p 14). Because large molecular weight polymers cannot enter the cell, they cannot react with "target organs," such as the reproductive system, and are not bioavailable. "Therefore, as the M_n of a polymer increases, a reduced incidence of potential health concern effects might be expected" (OECD 2009, p 20).

An additional PLC consideration is the weight percent oligomers <1000 Da. Oligomers may be composed of, for example, dimers, trimmers, and tetramers, meaning they have 2-, 3-, and 4-monomer units, respectively. The EU report (BIO by Deloitte 2015) concluded that most potential health concern polymers have M_n of <1000 Da and oligomer content of >1%: "...the distribution of potential health concern polymers showed an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD 2009, p 24).

Molecular weight distribution (MWD), also known as "polydispersity index," measures the heterogeneity of size of polymer molecules in a polymer. The MWD is an important parameter for predicting potential biological effects of polymers because although M_n may be a large value, low MW oligomers <1000 Da may be present, which could penetrate the cell.

Electrical charge (ionic character)

Electrical charge or ionic character can be anionic, cationic, amphoteric, or nonionic. Specifically, cationic polymers have been associated with aquatic toxicity (Auer et al. 1990; USEPA 1997a). Polycationic polymers that are water soluble or dispersible are of concern due to adverse human health (inhalation) effects (NICNAS 2016).

Reactive functional groups and RFG ratio to MW

A "reactive functional group" (RFG) is defined as an atom or associated group of atoms in a chemical substance that is intended or can be reasonably anticipated to undergo facile chemical reaction (USFR 2012). Some highly reactive functional groups (or a high ratio of RFGs per mole) have been associated with adverse human health and ecotoxicology (e.g., acrylates, methacrylates, isocyanates, anhydrides, aziridines) (USEPA 2010). Methods have been demonstrated to identify the functional end groups on fluoropolymers (Pianca et al. 1999).

The functional group equivalent weight (FGEW) is used to determine if the RFGs in a polymer are substantially diluted by polymeric material to allow the polymer to be a PLC (USEPA 1997b). The FGEW of a polymer is defined as the ratio of the M_n to the number of functional groups in the polymer. It is the weight of a polymer that contains 1 formula weight of the functional group. The FGEW is used as an indication of the degree of reactivity of the polymer; the lower the FGEW, the more reactive the polymer and the higher the potential for health and environmental impact (OECD 2009, p 10).

Low MW leachables

Low MW leachables are chemical molecules, either inorganic or organic, that migrate (i.e., leach) out of the polymer. These could be residual monomers or oligomers resulting from incomplete polymerization processes, surface residues, or other chemicals used in the manufacturing processes (e.g., initiators, catalysts, chain transfer agents, surfactants). Chemical analysis, by techniques such as thermal gravimetric analysis (TGA), gas chromatography mass spectrometry (GC-MS), or liquid chromatography mass spectrometry (LC-MS) are used to identify low MW leachables.

Low MW leachables are critically important to the potential for a polymer to affect health and the environment, given that they may be able to migrate out of the polymer and cross cell membranes to potentially react with biomolecules. In a report to the EU (BIO by Deloitte 2015) the polymer policies for 10 countries around the world, including the EU REACH handling of polymers, were reviewed. The report concluded that "Polymers with <1% MW <1000 Da and low water extractivity are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant."

Monomers, by nature, are reactive. Unreacted monomer left in a polymer may migrate out of the polymer to react with biomolecules to cause potential adverse effects. Regulatory authorities (BIO by Deloitte 2015) and the OECD Expert Group on Polymers (OECD 2009) agree that the residual monomer content of a polymer is critical to determining if it qualifies to be a PLC.

Particle size

Particle size is also a PLC criterion. Particles that are small enough to reach the deep lung upon inhalation are often associated with adverse health effects. Therefore, to qualify as a PLC, median mass aerodynamic diameter (MMAD) of the polymer particle size should be greater than 5 μm.

Structural and elemental composition

In the United States, Chemical Categories of Concern are the result of the review of new chemicals by the USEPA under the TSCA (see https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/chemical-categories-used-review-new). New chemicals submitted to the USEPA

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under the TSCA for addition to the US chemical inventory are reviewed for potential chemical, physical, and biological effects (environmental and mammalian). The USEPA groups Premanufacture Notice (PMN) chemicals with shared chemical and toxicological properties into categories, enabling both PMN submitters and USEPA reviewers to benefit from the accumulated data and past decisional precedents, allowing reviews to be facilitated. The categories describe the molecular structure, boundary conditions such as MW, equivalent weight, the log of the octanol–water partition coefficient, log P, or water solubility, and standard hazard (mammalian and ecological) and (environmental) fate tests to address concerns. The categories include chemicals for which sufficient history has been accumulated so that hazard concerns and testing recommendations vary little from chemical to chemical within the category. (See Supplemental Data, p 30, for details on USEPA's chemical categories.)

Elemental composition

The elemental composition is a factor in the assessment of the eligibility of polymers for reduced notification requirements. The exclusion of polymers under this step is not a conclusion of hazard but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process. These elemental requirements differ across jurisdictions as covered in the report to the EU on global regulatory approaches to polymer assessment (BIO by Deloitte 2015). For example, in the EU under REACH it is proposed that polymers composed from among these elements, covalently bound to C, have reduced hazard: H, N, O, Si, S, F, Cl, Br, or I (BIO by Deloitte 2015). In contrast, the USEPA Polymer Exemption Rule states that a polymer is eligible for reduced agency review when it has at least 2 of the following elements: C, H, O, N, S, or Si (USFR 1995).

Water and lipid solubility and the octanol–water partition coefficient

Water solubility is the extent to which a compound will dissolve in water. According to the OECD 2009 meeting of the Expert Group on Polymers, polymers with "negligible" water solubility, or those described as "hydrophobic" have been represented with a water solubility of 0.000001 mg/L (1×10^{-6} mg/L; assigned arbitrarily) (OECD 2009). That is equivalent to 1 ppt, a very conservative definition.

Based on the data set studied, the OECD Expert Group on Polymers concluded "A higher proportion of polymers with intermediate water solubility values (10 mL/L–10 000 mg/L) displayed potential health concern. Polymers with water solubility <10 mg/L showed generally low health concerns" (OECD 2009, p 10). Although not a solubility metric, a polymer capable of absorbing its weight in water was associated with increased inhalation cancer risk in rats (OECD 2009).

The octanol–water partition coefficient (K_{OW}) is another criterion to assess chemicals and their environmental and health impact. The K_{OW} is a physical–chemical property at equilibrium to represent the lipophilic or hydrophilic nature of a chemical, the distribution of a compound in octanol, representing the lipophilic nature, to its solubility in water, representing the aqueous nature. The higher the K_{OW}, the more lipophilic the compound. Typically, a K_{OW} >5000 or a log K_{OW} >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. Numerous studies showed that K_{OW} was useful for correlating structural changes of drug chemicals with the change observed in some biological, biochemical, or toxic effect (LaGrega et al. 2010). It has been found to be related to water solubility, soil or sediment adsorption coefficients, and bioconcentration factors for aquatic life. According to the Stockholm Convention, a bioconcentration factor of >5000 and a log K_{OW} >5 is used as a criterion for bioaccumulation.

Stability

Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. As was previously described in the Polymer of Low Concern section under the *Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da* heading, molecules with M_n <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment.

Abiotic stability

Polymers are stable; monomers are not. Abiotic degradation may involve sunlight, water, or oxygen. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Hydrolytic degradation of polymers is another potential way to break the polymer bonds, creating smaller oligomers that may be bioavailable. Chemical oxidation is a reaction involving the loss of electrons from 1 atom to another.

Biotic stability: aerobic, anaerobic, and in vivo

Biotic stability is assessed by whether or not the polymer is degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic) conditions; in vitro and in vivo stability studies demonstrate this. In vivo biodegradation involves the breaking of the polymer bonds by the action of bacteria, enzymes, and oxidants within the organism.

Thermal stability

Thermal stability of a polymer can be assessed when used as intended under normal, foreseeable use conditions or in extreme temperatures during disposal, such as by incineration. Thermal stability testing may involve Thermal Gravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance.

ASSESSMENT OF FLUOROPOLYMERS ACCORDING TO PLC CRITERIA

Characteristics of a PLC have been described in the preceding section. These criteria represent the combined

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experience and knowledge of global regulatory authorities on factors demonstrated to be predictive of health and environmental hazards of polymers (OECD 2009; BIO by Deloitte 2015). Four fluoropolymers were assessed according to the PLC criteria. The results are summarized in Table 2, and an expanded discussion on specific criteria is provided in the remainder of this section.

Polymer composition

Fluoropolymers satisfy the PLC criterion of polymer composition. Polytetrafluoroethylene is a homopolymer of tetrafluoroethylene (TFE). Polytetrafluoroethylene can be a homopolymer (1 monomer) or it can be a modified homopolymer containing TFE widely and not more than 1% of another fluoromonomer (see ASTM 2015). Polytetrafluoroethylene contains only C and F having a $–CF_2–$ backbone terminated on both ends of each polymer chain with $–CF_3$. In unique cases, based on production method and ingredients used, commercial PTFE may have end groups that contain O, H, N, or S, depending on the initiator or chain transfer agent used in polymerization (Pianca et al. 1999). Polytetrafluoroethylene meets the compositional criterion to be a PLC.

Molecular weight, M_n, MWD, and % oligomer <1000

Fluoropolymers satisfy the PLC criterion of MW, M_n, MWD, and % oligomer <1000. Fluoropolymers are practically insoluble in water and all organic solvents. Therefore, standard MW methods are not applicable for fluoropolymers like PTFE and have been replaced by standardized indirect methods that use specific gravity and melt flow index to determine MW of PTFE and fluoropolymers (see Supplemental Data, p 27–28). Standard Specific Gravity (SSG) and Melt Flow Rate (MFR) are more conveniently and frequently used with fluoropolymers rather than rheological and dynamic light scattering methods (Chu et al. 1989; Starkweather and Wu 1989; Tuminello 1989; Tuminello et al. 1993). Polytetrafluoroethylene has an M_n of 500 000 to 9 000 000 Da (Berry and Peterson 1951; Doban et al. 1956; Suwa et al. 1973; Putnam 1986; Chu et al. 1989; Tuminello 1989; Tuminello et al. 1993; Frick et al. 2012). Therefore, PTFE, as a very high molecular weight polymer, cannot cross cell membranes, is not bioavailable, and cannot bioaccumulate or be toxic (see Supplemental Data, p 14). High molecular weight fluoropolymers, such as PTFE, therefore meet the PLC criterion for having MW that prevents them from entering the cells. Polytetrafluoroethylene has negligible (<<1%) oligomeric content (Starkweather and Wu 1989), as does FEP (Figure 2.) In summary, fluoropolymers are high molecular weight polymers with narrow MWD and negligible oligomer content.

Reactive functional groups and RFG ratio to MW

Fluoropolymers satisfy the PLC criterion of RFGs and RFG ratio to MW. Polytetrafluoroethylene most typically has a terminal $–CF_3$ group that is not an RFG. When this is not the case, the most common terminal group is –COOH, which is

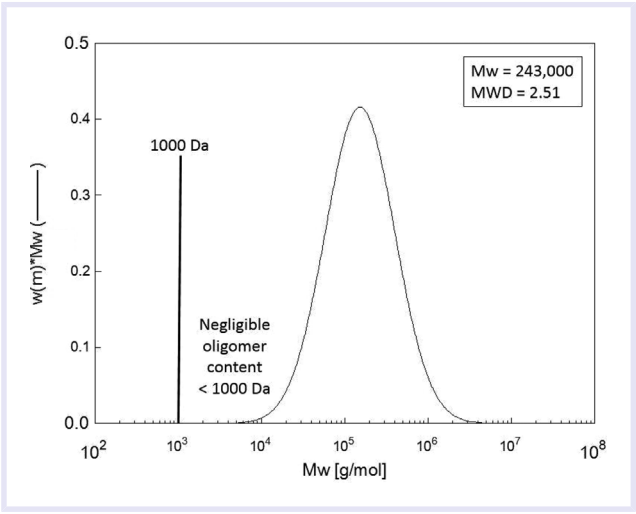


Figure 2. A fluorinated ethylene propylene (FEP) fluoropolymer molecular weight distribution from a rheological study. MW = molecular weight; MWD = molecular weight distribution.

categorized by the USEPA as a low-concern functional group. In unique cases, based on production method and ingredients used, PTFE may have end groups that may contain O, and H, N, or S, depending on the initiator or chain transfer agent used in polymerization. Fluoropolymers have a very high MW, which yields an FGEW on the order of 10^5 or more, well beyond the FGEW threshold of concern.

Low MW leachables

Fluoropolymers satisfy the PLC criterion of low MW leachables. Concentration of leachables from fluoropolymers, particularly PTFE "fine powder" (ASTM [2015] 4895-16 Type I fine powder definition), are typically very low (<1 ppm) (see Supplemental Data). This finding can be explained by the sensitivity of the PTFE polymerization reaction to contamination and is due to the postpolymerization processing steps aggressively exercised to wash out residuals and drive off volatiles. In order to achieve high MW polymerization of TFE, all traces of telogenic H- or Cl-bearing impurities must be removed (Ebnesajjad 2011; Supplemental Data).

In the analysis done on PTFE (see Supplemental Data, p 32), residual TFE monomer was not detected in PTFE resin by headspace GC-MS with a limit of detection of 1 ppm. In addition, publicly available analytical data from independent industry authorities demonstrate that TFE is not detected in finished articles made from fluoropolymers at detection limits down to about 0.01 ppm wt/wt (SPI 2005). Table 3 compares the molecular weight and the 8-h time weighted average (TWA) (American Conference of Governmental Industrial Hygienists [ACGIH], threshold limit value [TLV]), for monomers used to make fluoropolymers (ACGIH 2010). The TWAs are the exposure levels to which a worker could be exposed in an 8-h shift without adverse effects. The monomers have significantly lower MW, have lower TWAs, and are reactive. Note that the fluoropolymers are high MW, have no TWAs, and are inert. Table 3 illustrates that polymers do not have the same health hazards or MWs as their monomers.

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Table 3. Fluoropolymer and monomer molecular weight and TLV data

Substance	CAS Nr	Molecular weight	ACGIH TLV 8-h TWA
Monomer: TFE	116-14-3	100	2 ppm
Monomer: Ethylene	74-85-1	28	200 ppm
Monomer: HFP	116-15-4	150	0.1 ppm
Monomer: PPVE	1623-05-8	266	200 ppm (vendor limit)
Polymer: PTFE	9002-84-0	389 000–45 000 000	None
Polymer: ETFE	25038-71-5, 68258-85-5	530 000–1 200 000	None
Polymer: FEP	25067-11-2	241 000–575 000	None
Polymer: PFA	26655-00-5, 31784-04-0	200 000–450 000	None

ACGIH = American Conference of Governmental Industrial Hygienists (ACGIH 2010); CAS = Chemical Abstracts Service; ETFE = ethylene tetrafluoroethylene; FEP = fluorinated ethylene propylene; HFP = hexafluoropropene; PFA = perfluoroalkoxy polymer; PPVE = perfluoropropylvinyl ether; PTFE = polytetrafluoroethylene; TFE = tetrafluoroethylene; TLV= threshold limit value; TWA = time weighted average.

Elemental composition

Fluoropolymers meet the widely accepted elemental composition criterion (BIO by Deloitte 2015). The USEPA, in updating its Polymer Exemption Rule, which applies to new polymers only, changed some review procedures to address certain side-chain fluorinated polymers that may degrade into small, mobile, and persistent substances (USFR 2010). This has contributed to confusion regarding the assessment of fluoropolymers. The exclusion of polymers under this step is not a conclusion of hazard, but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process.

When USEPA updated the polymer exemption rule in 2010, the agency excluded polymers containing $–CF_3$ or larger chains that are covalently bound to C. The agency's rationale for the change was "...because the Agency has receiving information which suggests that polymers containing PFAS (perfluoroalkyl sulfonates) or PFAC (perfluoroalkyl carboxylates) may degrade and release fluorochemical residual compounds in the environment. Once released, PFAS or PFAC are expected to persist in the environment, may bioaccumulate, and may be highly toxic..." (USFR 2006).

Although USEPA recognized that PFAS and PFAC chemicals with longer C chain lengths (C7 and longer) may be of greater concern, it stated that there is insufficient evidence at this time, however, to definitively establish a lower C chain length limit to meet the "will not present an unreasonable risk" finding, which is the determination necessary to support an exemption under section 5(h)(4) of TSCA. The USEPA believes that it is possible for polymers containing these other types of perfluoroalkyl moieties to also degrade over time in the environment, thereby releasing the perfluoroalkyl moiety (USFR 2006).

The updated USEPA polymer exemption definition in 2010, summarized in the Objective and Rationale section for the Final Rule, may imply that new fluoropolymers with pendant or terminal –CF3 groups, such as FEP, do not meet the polymer exemption eligibility for reduced PMN reporting (USFR 2010). However, the summary definition in USFR (2010) lacks critical context found in the preamble to the Final Rule, which elaborates the conditions that would be necessary to exclude a perfluoro chemical from the polymer exemption:

- The first condition is cited above, "...polymers containing PFAS (perfluoroalkyl sulfonates) or PFAC (perfluoroalkyl carboxylates)..." where the C or S atom is an integral part of the polymer molecule; and
- the second condition notes that, polymers containing fluorotelomers or "...perfluoroalkyl moieties that are covalently bound to either a carbon or sulfur atom where the carbon or sulfur atom is an integral part of the polymer molecule can be attached to the polymers using conventional chemical reactions."

For the PFAS and PFAC as described by USEPA, the agency offers a clarification about the nature of the linkage, stating "How these materials are incorporated into the polymer is immaterial (they may be counter ions, terminal/end capping agents, or part of the polymer backbone)" (USFR 2010). The key characteristic is the presence of a –CF3 group that is attached to, or forms part of, the polymer backbone and "this link (between the polymer backbone and the –CF3 group) is susceptible to degradation and cleavage." (USFR 2010). Thus, in USEPA's review, the presence of –CF3 group is important because it is a structural alert to consider potential degradation products. The USEPA will make a determination whether the potential degradation of the polymer in question presents an unreasonable risk to health and the environment under TSCA. As shown in Table 2, these fluoropolymers are not subject to degradation.

Water and lipid solubility and the octanol–water partition coefficient

Fluoropolymers, such as PTFE, are not soluble in octanol or water. Therefore, it is not possible to measure or calculate a

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K_{OW}. Because solubility in octanol is predictive of lipid solubility, PTFE cannot dissolve in cell membrane lipids to gain access to cellular contents, nor is it small enough to enter the cell due to its very high MW. Because PTFE cannot enter the cells, it is not capable of bioaccumulation or bioconcentration in aquatic life.

Stability

Under normal, foreseeable uses, fluoropolymers are stable. Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. Molecules with M_n <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment. Fluoropolymers, in general, have exceptional chemical and thermal stability; that is why they are so unique and useful. This is due to very strong C–F bonds that are stable under even extreme conditions (Gangal and Brothers 2015). Polytetrafluoroethylene is inert and chemically resistant to all solvents except molten alkali metals, chlorine trifluoride, and oxygen difluoride. Polytetrafluoroethylene, as a representative fluoropolymer, has the best chemical resistance of all currently known polymers and is insoluble in all known solvents, including water (Drobny 2006).

Abiotic stability

Polymers are stable; monomers are not. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Although PTFE will rapidly degrade in ionizing radiation (e.g., gamma radiation or high energy electron-beam radiation), it is resistant to photolysis (Drobny 2006). Photoinduced reactions with fluoropolymers do not occur. In addition, hydrolysis is a reaction involving the breaking of a bond in a molecule using water. The fluorine envelope surrounding the C backbone of PTFE is very hydrophobic. Fluoropolymers, such as PTFE, are hydrolytically stable, water resistant, and are not subject to hydrolysis catalyzed degradation (Arkles 1973). Finally, chemical oxidation is a reaction involving the loss of electrons from one atom to another. Because the C–F bond is one of the strongest known, and F is the most electronegative element, the C–F bond is thermodynamically stable, unfavorable to lose electrons (i.e., to oxidize) (Arkles 1973).

Biotic stability: aerobic, anaerobic and in vivo

Fluoropolymers like PTFE are biologically inert and not degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic conditions); in vitro and in vivo studies demonstrate this. In vivo degradation involves the breaking of the polymer bonds due to bacteria and other enzymes and oxidants. For example, PTFE hernia patches explanted from patients and examined by scanning electron microscopy, attenuated total reflectance Fourier transform infrared spectroscopy, modulated differential scanning calorimetry, and optical microscope showed no degradation in vivo (King et al. 2013).

Thermal stability

Fluoropolymers, when used as intended under normal, foreseeable use conditions as specified in Table 2 (or "continuous processing temperature") are thermally stable (Puts et al. 2014). The fluoropolymer industry has provided significant information on appropriate use of fluoropolymers (SPI 2005). Thermal gravimetric analysis determines mass loss over time and temperature of a test substance. Polytetrafluoroethylene is one of the most thermally stable polymers. Polytetrafluoroethylene's continuous processing temperature is 260 °C (SPI 2005). This means that PTFE could remain for decades at 260 °C and not decompose (SPI 2005 see percent mass lost per hour at maximum continuous processing temperature).

Outside of normal, foreseeable use conditions (also known as "misuse"), when fluoropolymers are held at temperatures above their recommended processing temperatures, they degrade. Upon decomposition, fluoropolymers generate volatile degradation products (SPI 2005). At 450 °C, the decomposition of PTFE "only proceeds at a rate on the order of one percent per hour. It is not until considerably above the polymer first-order transition temperature (329 °C) that substantial decomposition is observed" (Arkles and Bonnett 1974). As the temperatures increase above recommended processing temperatures, the rate of generation rises and may sufficiently degrade the polymer to produce hazardous gaseous byproducts and polymer (particulate) fume fever (SPI 2005). Temperature, availability of O, the physical form of the polymer article, and the residence time at elevated temperature factor into the ultimate nature of the decomposition products (SPI 2005), mainly fluoroalkenes, hydrogen fluoride, oxides of C, and lower molecular weight fluoropolymer particulates. For PTFE, TFE is the principle gaseous product observed at temperatures near 330 °C. See Supplemental Data for additional information regarding overheating PTFE.

PRODUCT-SPECIFIC REGULATORY REQUIREMENTS

Certain product-specific regulations, such as those for medical devices and food contact for the United States and the EU, require the development of additional data beyond what is required to conduct a PLC evaluation. The following text will discuss food contact requirements for the United States and the EU, and medical device requirements.

Data requirements for food, pharmaceutical, and medical device applications

There are country-specific data requirements for fluoropolymer use in food, pharmaceutical, and medical device applications because the intended use of these products has the potential to directly or indirectly introduce the product into the human body. An extensive fluoropolymer data set has been developed by W.L. Gore for these uses. The clinical history of the safe implantation of more than 40 million PTFE medical devices over 40 y, extensive toxicity data, preclinical

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data, and chemical extractables and migration testing confirmed that fluoropolymers are not bioavailable. Although the data requirements have evolved over time for contacting food, pharmaceuticals, or use in medical devices, the data (some of which are provided in the present article, the Supplemental Data for the present paper, regulatory submissions, and product literature) confirm the conclusion that fluoropolymers are safe for these intended uses and support the conclusion that fluoropolymers should be considered PLCs.

Polymer of low concern data and US and European Union food contact requirements

In general, the data required to support a PLC determination are helpful, but insufficient to qualify a material for food contact use. Submissions to the US Food and Drug Administration (USFDA) to support new food contact substances require extensive data submissions, including, for example, the nature and amount of nonvolatile extractives (USFDA 2017). Fluoropolymers, however, are not new substances in applications where they come in contact with food and have longstanding acceptance by regulators. In the United States, the USFDA is responsible for regulation of materials that come in contact with food and are considered "indirect food additives," specifically polymers (USFR 2016a). Food storage or food packaging materials, such as the fluoropolymers PTFE, FEP, and PFA, are "perfluorocarbon resins" acceptable for use by application and material type, provided they meet the extractable limits specified in the regulation (USFR 2016b).

Similarly, the European Food Safety Agency (EFSA) provides recommendations to the European Commission (EC) within the EU for the regulation of food contact materials, requirements for their evaluation, and authorization of acceptable uses (EC 2004). Polymer clearance is based in part upon the fact that polymers will not migrate into food due to their high molecular weight. The EU focuses on potential low molecular weight moieties, such as residual monomers and leachables, rather than on the polymer itself. The EU food contact regulation requires that monomers, other starting substances, and additives used to produce food contact polymers should be risk assessed and authorized (EU 2011). The regulation lists authorized substances that are permitted to have food contact (EU 2011). This regulation also sets the specific migration limit (SML), which is the maximum permitted amount of substance in food that has been determined not to pose a risk to human health, specifically for individual chemicals (e.g., monomer) (EU 2011). Note that these limits exist whether or not the substance is present in the food contact material (FCM). The monomers, other starting substances, and additives used to produce fluoropolymers for food contact (e.g., PTFE, FEP, and PFA) have been authorized for food contact uses. Representative SMLs for these monomers, additives, and starting substances relevant for fluoropolymers are given in the Supplemental Data (p 14).

Polymer of low concern data and medical device regulatory requirements

Satisfaction of the PLC criteria is insufficient to satisfy medical device requirements. Formal biocompatibility evaluations are required by the USFDA and other global regulatory authorities to support submissions for approval of medical devices and pharmaceuticals (e.g., combination products, such as drug-eluting stents or prefilled single-dose syringes). The International Organization for Standardization (ISO) 10993 Biocompatibility of Medical Devices standards describe a broad array of biocompatibility tests that require consideration for each new device or significant changes to existing devices (ISO 2009). Over the years, medical devices containing PTFE (or expanded PTFE) have been evaluated using ISO 10993 and US Pharmacopeia (USP) Class VI standards (USP 2011) and have been determined to be biocompatible in their intended uses.

The ISO 10993 standards provide guidance for evaluation of the biological response to a medical device. The USFDA, as well as most international regulatory agencies, recognizes and uses ISO 10993 standards to guide safety evaluations of medical devices submitted for their approval. Requirements to demonstrate the biocompatibility of medical devices are set forth in ISO 10993-1, and regulatory authority–specific requirements (e.g., PMDA 2003; USFDA 2016). In addition, country pharmacopeial organizations also specify testing required for biological reactivity of drugs (e.g., US Pharmacopiea, EU Pharmacopiea, Japan Pharmacopiea). The ISO requirements are categorized by the nature of body contact (e.g., mucosal membrane, circulating blood, tissue, bone, dentin) and duration of contact ($<$24 h, $\geq$1 d $\leq$30 d, $>$30 d). Depending on the nature and duration of contact, requirements include cytotoxicity, irritation, sensitization, implantation, acute–subchronic–chronic systemic toxicity, material-mediated pyrogenicity, hemocompatibility (e.g., hemolysis, thrombogenicity, and complement activation), genotoxicity (in vitro and in vivo), carcinogenicity, and developmental toxicity. (See Supplemental Data p 15 for a list of ISO 10993 biocompatibility tests.)

MEETING PLC CRITERIA PRECLUDES A FINDING THAT A CHEMICAL IS OF HIGH CONCERN

Just as regulatory frameworks have mechanisms to identify materials of low concern such as PLCs, they also have mechanisms to identify chemicals of high concern. For example, under REACH, a mechanism exists to identify substances of very high concern (SVHCs). Having demonstrated that fluoropolymers like PTFE should be considered PLCs, we will also demonstrate that these fluoropolymers cannot be SVHCs under REACH, do not meet the PM and PMT criteria proposed by UBA, and do not meet the criteria for listing as a POP under the Stockholm Convention.

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Fluoropolymers and EU REACH SVHC, CMR, PBT, vPvB, and endocrine disrupting chemical (EDC) criteria

According to the European Chemicals Agency (ECHA), SVHCs are defined in Article 57 of Regulation (EC) Nr 1907/2006 ("the REACH Regulation") (EC 2006) and include substances that are

- "Carcinogenic, mutagenic or toxic to reproduction (CMR), meeting the criteria for classification in category 1 or 2 in accordance with Directive 67/548/EEC. This directive was replaced in beginning of 2009 by the new EU regulation (EC) No 1272/2008 on classification, labeling and packaging of chemical substances and mixtures, the so-called CLP Regulation. According to the new CLP Regulation these substances shall be classified as 1a or 1b."
- "Persistent, Bioaccumulative and Toxic (PBT) or very Persistent and very Bioaccumulative (vPvB) according to the criteria in Annex XIII of the REACH Regulation."
- "Identified, on a case-by-case basis, from scientific evidence as causing probable serious effects to human health or the environment of an equivalent level of concern as those above (e.g., EDCs)."

Under REACH, polymer substances are not registered, but the monomers they are composed of are registered, and the registration must be supported by data submissions that are tiered on the basis of tonnage (see EC 2006, Annex VII). The REACH definition of polymer includes materials with as few as 3 repeating units. But such a small molecule would not meet common industry standard definitions for fluoropolymers (ASTM 2015). It is highly unlikely that fluoropolymers meeting the PLC criteria would exhibit the criteria of an SVHC under REACH. Fluoropolymer data developed for other regulatory needs support the predictive value of the PLC assessment criteria and demonstrate the low hazard potential of this class of PFAS. Due to their physical–chemical properties, PLCs are not bioavailable to cause toxicity or to bioaccumulate. Toxicity study data on PTFE in the Supplemental Data (p 15–27), for example, demonstrate a lack of toxicity, including genotoxicity. Although fluoropolymers are persistent, they are not bioaccumulative or toxic and therefore do not meet the PBT criteria.

Fluoropolymers and German UBA–proposed PMT criteria

As regulatory frameworks continue to evolve, more work is needed in the area of PFAS classification to ensure that regulations are appropriate in scope and proportionality. Although some well-known PFAS would qualify as PM or PMT substances as proposed by the UBA (2017), fluoropolymers do not possess these characteristics. Although fluoropolymers are highly stable (persistent), they do not meet the criteria to be mobile or toxic. To demonstrate this point, PTFE, a high molecular weight fluoropolymer and a member of the PFAS group, is assessed (in the last 4 paragraphs of this section) according to the proposed UBA criteria (UBA 2017).

Briefly, the changes to PM and/or PMT assessment proposed by UBA address applicability, persistence, mobility, and toxicity. The UBA proposes an initial step involving assessment of the chemical composition of a substance to determine if the substance is within the applicability domain of the proposed new assessment criteria. The UBA notes that currently only identifiable organic and organometallic chemicals are considered, and purely inorganic substances or substances of unknown or variable compositions, complex reaction products, or biological material are excluded (UBA 2017).

With respect to persistence, UBA proposes that the criterion for persistence be the same as in Annex XIII of REACH, which considers degradation half-lives in marine water, fresh- or estuarine water, marine sediment, and soil as part of the PBT/very persistent, very bioaccumulative (vPvB) assessment criteria; these degradation half-life criteria range from 40 to 180 d. The UBA proposes that a substance meets the persistent criterion if the degradation half-life in marine water at pH 6 to 8 and 12 °C is higher than 60 d, the half-life in fresh- or estuarine water at pH 6 to 8 and 12 °C is higher than 40 d, the half-life in marine sediment at pH 6 to 8 and 12 °C is higher than 180 d, the half-life in fresh- or estuarine water sediment at pH 6 to 8 and 12 °C is higher than 120 d, or the half-life in soil at pH 6 to 8 and 12 °C is higher than 120 d.

The UBA proposes that the mobility criterion for a persistent chemical should be determined on the basis of 2 considerations. First, the water solubility of a substance at pH 6 to 8 and 12 °C must be greater than or equal to 150 μg/L, and the log K_{OC} at pH 6 to 8 and 12 °C must be less than or equal to 4.5. The UBA notes that the mobility criterion should be applied only to substances that have fulfilled the criterion for persistence.

Lastly, with respect to toxicity, UBA proposes a 5-part test for involving data to understand if the substance is carcinogenic, germ cell mutagenic, or toxic for reproduction; if there is other evidence of chronic toxicity; and if there is evidence for effects on or via lactation. The derived no adverse effect level (DNEL) must be less than or equal to 9 $\mu g \cdot kg^{-1}d^{-1}$. The UBA notes that the first 2 considerations are the same criteria defined in Annex XIII of REACH as part of the PBT/vPvB assessment criteria regarding human health. The next 2 criteria specifically address concerns for drinking water exposure and are based on Regulation EC No 1272/2008 (EC 2008) and Cramer class II (Cramer et al. 1978) for substances exhibiting moderate or low biological activity, respectively. The DNEL criterion is based on Kalberlah et al. (2014).

Regardless of the arguments concerning the scientific foundation and credibility of the changes proposed by UBA to REACH PM and PMT assessment criteria, the central question with respect to PTFE is whether chemical-specific assessment would lead to an outcome different from that assuming PTFE behaved similarly to other PFAS substances. Polymers, including fluoropolymers, are different from non-polymeric chemicals and may be regulated differently. Because of these differences, it is recognized that some data requirements may not be applicable to polymers (EU 2011) For example, as we have shown, the physical–chemical criteria of PLC are predictive of lack of hazard.

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With respect to applicability, PTFE is not a substance currently registered under REACH because it meets the REACH definition of a polymer substance: "a molecule that contains a sequence of at least 3 monomer units, which are covalently bound to at least one other monomer unit or other reactant" (EC 2006). However, because PTFE is an identifiable organic substance, the proposed UBA framework for assessment using the proposed PMT criteria would be applicable. Further, PTFE is highly stable and persistent in the environment. It is resistant to thermal degradation, being stable for decades at temperatures up to 260 °C (SPI 2005); is stable in terms of hydrolysis, oxidation, and light (Brydson 1999); and is stable in terms of anaerobic and aerobic degradation (King et al. 2013). Therefore, PTFE would fulfill the UBA's proposed persistence criterion.

In contrast, PTFE is practically insoluble in water and, therefore, is not mobile in the environment. Using the descriptive solubility table for the USP (2011), the water solubility of PTFE would be classified as practically insoluble (1×10^{-5} mg/L or 0.01 μg/L) to very slightly soluble (1×10^{-4} mg/L or 0.1 μg/L) (USP 2011). The mobility of PFTE is 1000 to 10 000× lower than UBA's proposed mobility criterion. Therefore, PTFE does not fulfill UBA's proposed mobility criterion and would not be classified as a PM or PMT substance.

A similar negative finding for PTFE pertains to toxicity. The average molecular weight of PTFE is too large for the polymer to cross a cell membrane, which means it is not bioavailable or toxic. Polytetrafluoroethylene has been tested extensively in the United States and European Union to assess commercial applications for food contact and global medical device regulations (see Supplemental Data for additional details). Results demonstrate the absence of toxicity. Therefore, PTFE does not fulfill UBA's proposed toxicity criterion and would not be classified as a PM or PMT substance (Table 4).

Fluoropolymers and the Stockholm Convention POP criteria

In addition to country and regional regulations, there are global legally binding instruments, such as the United Nations Environment Programme–administered conventions on chemicals and waste (UNEP 2001), such as the Stockholm Convention on Persistent Organic Pollutants. The Convention aims to eliminate POPs by eliminating their production, reducing their use, or limiting their use through a cradle-to-grave approach. For the listing of new chemicals into the Convention, numeric or other criteria have been set for the screening of proposed compounds. Stockholm Convention Criteria (annex D) are compared to those of the USEPA, EU REACH, and the UBA-proposed PMT (Table 4). Fluoropolymers meet the persistence criterion only, not the bioaccumulative, toxic, or mobile criteria.

Fluoropolymers satisfy widely accepted criteria to be considered PLCs. Their physical–chemical properties prevent bioavailability, bioaccumulation, toxicity, and degradation. They have negligible monomer, oligomer, and leachable content and no reactive functional groups with high toxicity. These comparisons of PLC and various regulatory assessment criteria demonstrate that, in the realm of PFAS, high molecular weight fluoropolymers like PTFE have vastly different properties than do other PFAS, and therefore, they are truly a separate class of materials that must be assessed on their own merits as has been done here. They also underscore the value of a global regulatory definition of a polymer.

FUTURE WORK

It is important to acknowledge that the manufacture and end-of-life phases of the fluoropolymer life cycle are not the subject of the present paper. The following reflections are provided on how these may be explored in future work. Fluoropolymer manufacture includes fluoromonomers and a wide array of initiators, catalysts, et cetera, including polymer production aids, some of which are fluorosurfactants (non-polymer PFAS) (see Supplemental Data, p 8, for more information about them). Historically, perfluorocarboxylic acids such as PFOA and perfluorononanoic acid (PFNA) were used as polymer production aids in the manufacture of fluoropolymers. They are no longer used by leading global fluoropolymer manufacturers (USEPA 2017a), who are now using alternative substances such as fluorinated polyether carboxylates (see Supplemental Data Table S2). The toxicological and environmental properties (e.g., persistence, bioavailability, and mobility) of these alternatives are very important. Future work should delve into fluoropolymer manufacture and describe the safety, health, and environmental management practices and controls employed; should describe the applicable regulations; and should assess substances used in fluoropolymer manufacture, their human health and environmental attributes, and their mass balance.

At end-of-life when a fluoropolymer has fulfilled its intended use and will be disposed of, the fate of fluoropolymers should be investigated further. Although there are sufficient data to demonstrate that fluoropolymers such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern (Hintzer and Schwertfeger 2014), the downstream, end-of-life process of incineration merits future work. For instance, at temperatures above 450 °C, PTFE begins to degrade, releasing hazardous substances such as hydrofluoric acid. There are published studies on the incineration of fluoropolymers under normal, foreseeable municipal waste incinerator conditions targeting specific analytes (Taylor 2009). Presently, most legislation addresses the release of hydrogen fluoride (HF) as the only critical parameter; limit values are for stack emissions (e.g., EU 2000). Future work should investigate incineration under a range of relevant foreseeable use conditions to determine more comprehensively the substances formed and their amounts. Such an incineration study is underway with results to be published upon completion (W.L. Gore 2017). In addition, the practice of the open burning of fluoropolymers, or for that matter of any polymer, is unacceptable and unsafe. Responsible incineration of fluoropolymers, adhering to regulatory guidelines, at the end of their life cycle is appropriate.

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Table 4. Comparison of United States, Stockholm Convention, EU REACH, and German Criteria

Criterion	United States[a]	Stockholm Convention[b]	REACH[c,d]	Germany[d,e]
Persistence (half-life)				
P	Water, soil, sediment > 60 d	Water >60 d	Marine water > 60 d	Same as REACH
		Soil, sediment >180 d	Estuarine water > 40 d	
			Fresh or estuarine sediment or soil > 120 d	
vP	Water, soil, sediment > 180 d		Marine, fresh, estuarine H_2O > 60 d	
			Marine, fresh, or estuarine sediment > 180 d	
			Soil > 180 d	
Bioaccumulation				
B	Aquatic BCF > 1000	Aquatic BCF or BAF > 5000	BCF > 2000	
		Log K_{OW} > 5		
vB	BCF > 5000		BCF > 5000	
Toxicity				
	Fish	Toxic or ecotoxic	Long-term aquatic NOEC or EC10 < 0.01	1) Carcinogenic, germ cell mutagenic, or toxic for reproduction[d];
	Low > 10 mg/L	(No numeric criteria)	Classified as carcinogen category 1A or 1B; mutagen 1A or 1B; reproductive toxin 1A, 1B, or 2[d]	2) other evidence of chronic toxicity[d]; and
	Moderate 0.1 mg/L–10 mg/L			3) evidence for effects on or via lactation[d].
	High < 0.1 mg/L			4) DNEL[f] ≤ 9 μg · $kg^{-1}d^{-1}$
			Specific target organ toxicity (STOT RE 1 or 2) upon repeated (chronic) exposure)[d]	
Long-range transport (potential for)		Long-range transport (potential for): Presence through monitoring or modeled data; $t_{1/2}$ (air): 2 d		
Mobility				Mobility: water solubility at pH 6–8, 12 °C, must be ≥150 μg/L, and the log K_{OC} at pH 6–8, 12 °C must be ≤4.5.

BAF = bioaccumulation factor; BCF = bioconcentration factor; DNEL = derived no adverse effect level; EU = European Union; M = mobile; P = persistent; REACH = Registration, Evaluation, Authorisation and Restriction of Chemicals; STOT RE = specific target organ of toxicity repeat exposure; T = toxic; v = very.
[a]USEPA 1999.
[b]UNEP 2001
[c]ECHA 2014
[d]EC 2008
[e]UBA 2017
[f]Barlow 2005; Kalberlah et al. 2014.

Recycling, reuse, and closed loop systems are alternative options at the end of life. Recent work has shown, on a small scale, the ability to convert fluoropolymers back to their monomers for capture (Schlipf 2014; Invertec 2017). This approach to a closed loop economy for fluoropolymers merits additional work and discussion, as does the recycling and reuse of melt-processable fluoropolymers, such as FEP.

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CONCLUSIONS

The present review has brought together fluoropolymer toxicity data, human clinical data, and physical–chemical characteristics, using PTFE as an example to show that fluoropolymers satisfy the widely accepted regulatory assessment criteria to be considered as PLCs. Fluoropolymers are high molecular weight, have narrow molecular weight distribution, and have negligible oligomer content and organic and inorganic leachables. Data show that fluoropolymers have thermal, chemical, photochemical, hydrolytic, and biological stability. Polytetrafluoroethylene has been extensively tested to comply with US and EU food contact and global medical device regulations (e.g., USFDA, CFDA, Korea MFDS, Japan PMDA), including ISO 10993 biocompatibility testing and preclinical animal testing. Toxicology studies on PTFE demonstrate the absence of acute or subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, in vitro and in vivo genotoxicity, hemolysis, complement activation, or thrombogenicity. The data presented demonstrate that the fluoropolymer class of PFAS is well defined, meets PLC criteria, and should be considered as distinctly different from other classes of PFAS. The grouping of all PFAS together is not supported by the scientific data.

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Data Accessibility—All data and information used in this manuscript have been made available in tabulated form (Tables 1–4) by the authors and are included in the paper and the Supplemental Data.

SUPPLEMENTAL DATA

The Supplemental Data contains descriptive and more detailed information as highlighted in the paper.

Figure S1. Where does polytetrafluoroethylene (PTFE) come from?

Figure S2. Fluoropolymer primer: polytetrafluoroethylene (PTFE) polymerization scheme.

Figure S3. Fluoropolymer primer: polytetrafluoroethylene (PTFE) finishing scheme.

Figure S2. A fluorinated ethylene propylene (FEP) fluoropolymer molecular weight distribution from a rheological study.

Table S1. Polytetrafluoroethylene (PTFE) polymerization and post polymerization aids

Table S2. Alterative fluoropolymer processing aids: Sources of data

Table S3. Solubility table from USP 34 NF 29 General Notices, Section 5.3.0, p 6

Table S4. European Union (EU) specific migration limits (SMLs) for monomers in representative fluoropolymers

Table S5. Biocompatibility tests, conditions, and acceptance criteria results for expanded polytetrafluoroethylene patch

Table S6. US Environmental Protection Agency's (USEPA's) chemical categories of concern, 2010

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Critical Review

A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers

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Abstract

Fluoropolymers are a distinct class of per- and polyfluoroalkyl substances (PFAS), high molecular weight (MW) polymers with fluorine attached to their carbon-only backbone. Fluoropolymers possess a unique combination of properties and unmatched functional performance critical to the products and manufacturing processes they enable and are irreplaceable in many uses. Fluoropolymers have documented safety profiles; are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic. Although fluoropolymers fit the PFAS structural definition, they have very different physical, chemical, environmental, and toxicological properties when compared with other PFAS. This study describes the composition, uses, performance properties, and functionalities of 14 fluoropolymers, including fluoroplastics and fluoroelastomers, and presents data to demonstrate that they satisfy the widely accepted polymer hazard assessment criteria to be considered polymers of low concern (PLC). The PLC criteria include physicochemical properties, such as molecular weight, which determine bioavailability and warn of potential hazard. Fluoropolymers are insoluble (e.g., water, octanol) solids too large to migrate into the cell membrane making them nonbioavailable, and therefore, of low concern from a human and environmental health standpoint. Further, the study results demonstrate that fluoropolymers are a distinct and different group of PFAS and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with an earlier publication by Henry et al., this study demonstrates that commercial fluoropolymers are available from the seven participating companies that meet the criteria to be considered PLC, which represent approximately 96% of the global commercial fluoropolymer market. *Integr Environ Assess Manag* 2022;00:1–29. © 2022 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Applications, Fluoropolymers, Low concern, PFAS, Property Combinations

This article contains online-only Supporting Information.

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INTRODUCTION

"Fluoropolymers are high MW polymers with fluorine atoms directly attached to their carbon-only backbone" (Ebnesajjad, 2017). The carbon–fluorine (C–F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding, and beneficial properties and extraordinary functional performance to fluoropolymers (Ameduri, 2020; Ameduri & Sawada, 2017a, 2017b; Banks et al., 1994; Fluoropolymer Products Group of Plastics Europe [FPG], 2021a; Scheirs, 2007). These properties

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include chemical, biological, and thermal stability, heat and chemical resistance, unique dielectric properties, and durability. Additional fluoropolymer properties include fire resistance, weather resistance, nonwetting, and nonstick. Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to ensure optimal performance in many applications, cannot be achieved or guaranteed by alternative materials (FPG, 2021a, 2017; Henry et al., 2018; Performance Fluoropolymer Partnership of the American Chemistry Council [PFP], 2020).

Per- and polyfluoroalkyl substances (PFAS), a universe of substances with widely diverse properties that have been used in industrial and consumer applications since the 1950s, include fluoropolymers as a distinct class (Buck et al., 2011; Henry et al., 2018). A single, globally harmonized definition for PFAS has not yet been agreed upon. PFAS have been defined differently based on their structure and atomic composition (Buck et al., 2021; Wallington et al., 2021). For example, the USEPA's working PFAS structure definition is "a structure that contains the unit R-CF_2-CF(R′)(R″), where R, R′, and R″ do not equal "H" and the carbon–carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included" (USEPA, 2021a). The European Chemicals Agency (ECHA) employed a much broader PFAS structural definition (ECHA, 2020). A recent Organisation for Economic Cooperation and Development (OECD) report, which defined PFAS as fluorinated substances that contain in their structure at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), that is, with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF_3) or a perfluorinated methylene group (–CF_2–; OECD, 2021). This report acknowledges that the term "PFAS" is broad, general, and nonspecific, which does not inform whether a compound presents risk or not, but only communicates that the compounds under this term share the same structural trait of having a fully fluorinated methyl or methylene carbon moiety. Further, the report highlights that, among the substances defined as PFAS, there are distinct substances with very different properties: polymers and nonpolymers; solids, liquids and gases; persistent and nonpersistent substances; highly reactive and inert substances; mobile and insoluble (immobile) substances; and (eco) toxic and nontoxic chemicals. In addition, the report recognizes that PFAS have diverse molecular structures (e.g., neutral, anionic, cationic, or zwitterionic; with or without aromatic rings; nonpolymers or polymers; low or high molecular weight (MW), and thus diverse physical, chemical, and biological properties (e.g., involatile or volatile; water soluble or water insoluble; reactive vs. inert; bioaccumulative or nonbioaccumulative) and as such highly recommends that such diversity be properly recognized and communicated in a clear, specific, and descriptive manner when communicating about PFAS.

There is considerable media and public confusion and misunderstanding regarding PFAS, as the many different chemicals and groups are often not clearly differentiated under the broad term PFAS. Per- and polyfluoroalkyl substances, a large, diverse group of substances with vastly different properties, is too broad to allow effective, science-based assessment and regulation of chemical compounds as an entire group. This point has been raised in recent publications that suggest approaches to effectively group PFAS for regulatory assessment (American Chamber of Commerce in Europe [Amcham], 2020a; Buck et al., 2021; Bundesverband der Deutschen Industrie e.V. [BDI], 2021; Fiedler et al., 2020; Miller et al., 2020; Orgalim, 2021; Royal Society of Chemistry [RSC], 2021; Sha et al., 2019; Wallington et al., 2021). A clear understanding of the origin of PFAS found in the environment, the PFAS that are commercially relevant (Buck et al., 2021), and assessment of their properties are needed to be able to determine which classes of PFAS require management action. PFAS must be assessed based on their chemical, physical, thermal, and biological property differences and uses (Amcham, 2020a; BDI, 2021; Buck et al., 2021; RSC, 2021; Wallington et al., 2021). As regulatory frameworks, such as the EU REACH regulation, continue to evolve, more work is needed to distinguish clearly among PFAS based on their properties to assure that regulations are appropriate in scope, proportionate, and are science-based.

Per- and polyfluoroalkyl substances are divided into two primary categories: nonpolymers and polymers (Buck et al., 2011). Polymeric PFAS, generally known as "fluorinated polymers," include fluoropolymers (discussed here), perfluoropolyethers (PFPE), and side-chain fluorinated polymers (SCFP; Buck et al., 2011; Henry et al., 2018 and Supporting Information: Figure 6.1). This article deals strictly with fluoropolymers. Neither PFPE nor SCFP are discussed here.

The nonpolymer category includes perfluoroalkyl substances and polyfluoroalkyl substances. Certain nonpolymer PFAS substances, for example, short- and long-chain per- and polyfluoroalkyl carboxylic acids and sulfonic acids, received regulatory scrutiny recently due to their toxicity, as well as their persistence, potential to bioaccumulate, and/or mobility in the environment. Regulatory processes have been launched worldwide to address these concerns related to specific nonpolymer PFAS. These targeted regulatory measures have evolved increasingly into restrictions on the entire family of PFAS. For example, five Member States of the European Economic Area have initiated a procedure to prepare a joint restriction proposal under the EU REACH Regulation to limit the risks to human health and the environment from the manufacture and use of all substances in the PFAS family based on structure alone (ECHA, 2020). Although fluoropolymers fit the PFAS structural definition, they have vastly different physicochemical, environmental, and toxicological properties than other PFAS in addition to substantial societal benefits and importance (Fluoropolymer Products Group of Plastics Europe [FPG], 2017, 2021a). For

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these reasons, fluoropolymers should be considered separately and not aggregated with all other PFAS for regulatory action. Concurrently, the USEPA prepared a PFAS Strategic Roadmap laying out how it plans to evaluate and potentially regulate PFAS (USEPA, 2021a). Recognizing that there are many PFAS very diverse in their physical form, chemical structure and composition, functional characteristics, and toxicity profiles, USEPA "is conducting new research to better understand the similar and different characteristics of specific PFAS and whether and how to address groups and categories of PFAS."

Fluoropolymers have documented safety profiles, are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic (Henry et al., 2018). Some fluoropolymers have been demonstrated to meet the "polymers of low concern" (PLC) criteria, and as such do not present notable concern for human health or the environment (Henry et al., 2018). PLC criteria were developed over time within regulatory frameworks around the world as an outcome of chemical hazard assessment processes, which identified physical–chemical properties of polymers that determine polymer bioavailability and thereby report a polymer's potential hazard. For example, many of the physicochemical properties, such as MW, limit the ability of a polymer to cross the cell membrane and therefore limit its bioavailability (Kostal, 2016; Lipinski et al., 2001; USEPA, 2012). The USEPA built on this knowledge to adopt a polymer exemption rule to exempt low-hazard polymers from certain regulatory notification requirements under the Toxic Substances Control Act's (TSCA) new chemicals program (United States Federal Register [USFR], 1984). An OECD expert group on polymers reached consensus on these criteria and their respective metrics, documenting the data required for a polymer to qualify as a PLC to human health and the environment (OECD, 1993). Subsequently, an additional OECD work group concurred that PLC have "insignificant environmental health and human health impacts" (OECD, 2009). In addition, the European Commission commissioned a report (BIO by Deloitte, 2015) wherein several member countries agreed on the polymer properties predictive of adverse human health and environmental hazard. The report outlined eligibility criteria for a polymer to be considered a PLC. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a "Conceptual Framework for Polymer Risk Assessment" ("CF4Polymers"; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessments. They specifically support the findings of Henry et al. (2018) and state that they are "…unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS" (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria for the identification of polymers requiring registration (PRR) under REACH (Wood, 2020a). The Wood report states that the authors consider that fluoropolymers meet the criteria to be considered PLC, "following the recommendations of Henry et al." Considerable debate and comment on proposals have been put forward as the process and discussion advances (American Chamber of Commerce in Europe [Amcham], 2020b; FPG, 2021a; Hafer, 2021).

Four major fluoropolymers have previously been demonstrated to meet the criteria as PLC (Henry et al., 2018). This 2018 study raised interest in gathering similar data for additional commercial fluoropolymer products, both in scope and polymer type. In this study, seven global fluoropolymer manufacturers from the USA, Europe, and Asia collaborated to gather and present data for 14 additional fluoropolymers. In addition to information describing chemical composition, uses, performance properties, and functionalities of the 14 fluoropolymers, author company data for each of the PLC criteria are presented and discussed. The results demonstrate that each of the 14 commercially manufactured fluoropolymers in this study satisfy the widely accepted assessment criteria to be considered PLC and merit such designation. The study results add further evidence to demonstrate that fluoropolymers are demonstrably different and should not be grouped with other PFAS for hazard assessment or regulatory purposes.

USES, PERFORMANCE PROPERTIES, AND FUNCTIONALITY OF FLUOROPLASTICS AND FLUOROELASTOMERS IN THIS STUDY

The fluoropolymers described and evaluated in this study are high-performance materials used in commercial and industrial applications. Described herein are the industries and sectors (Table 1) and the performance properties and functionalities (Table 2) of the study fluoropolymers. The unparalleled combination of properties makes fluoropolymers critical materials for a broad range of applications and industrial sectors including automotive, aerospace, energy production and storage, and electronics (Table 1). Fluoropolymers are an important driver of the European Green Deal (FPG, 2021a) and UN Sustainability Development Goals (United Nations [UN], 2021), supporting smart mobility, clean energy, and sustainable industry. They are used in various components of renewable energy installations, such as hydrogen and photovoltaic panels and facilitate advanced energy storage and conversion technologies such as lithium-ion batteries (FPG, 2021a). Fluoropolymers are (i) durable, stable, and mechanically strong in harsh conditions; (ii) chemically inert, meeting the requirements for low levels of contaminants and particulates in manufacturing environments that are critical to the food and beverage, pharmaceutical, medical, and semiconductor industries; and (iii) biocompatible, nonwetting, nonstick, and highly resistant to

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TABLE 1 Fluoropolymer end uses and industries

	Transportation		Health care		Chemical		Consumer			Telecommunications			Infra-structure	Renewable energy		
Industries End uses	Automotive	Aerospace	Pharma-ceuticals	Medical devices	Oil and gas	Chemical process industry (CPI)	Production of goods	Protection and packaging	Filtration	Electronics and semicon-ductors	Internet and wireless communica-tions	Textiles Technical textiles	Construc-tion and archi-tecture	Energy production	Hydrogen production	Energy storage
Fluoroplastics																
PVDF homopolymer	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
PVDF copolymer	•	•	•	•		•	•	•	•	•	•	•	•		•	•
ECTFE copolymer	•	•	•		•	•				•	•		•			
ECTFE terpolymer			•		•	•										
PCTFE		•	•							•						
FEVE	•	•								•			•			
EFEP	•			•		•				•						
CPT	•									•						
THV	•	•	•			•	•	•	•	•			•	•		•
Fluoroelastomers																
FEPM	•	•	•	•	•	•	•			•			•	•		
FKM	•	•	•	•	•	•	•	•		•		•	•	•	•	•
FFKM		•	•	•	•	•	•			•						
Specialty																
Amorphous		•	•	•		•				•	•				•	•
Ionomer	•			•		•			•	•				•	•	•

Note: See also Chapter 5 in the Supporting Information.
Abbreviations: CPT, chlorotrifluoroethylene-tetrafluoroethylene; ECTFE, ethylene-chlorotrifluoroethylene; EFEP, ethylene-tetrafluoroethylene-hexafluoropropylene; FEPM, trifluoroethylene-propylene copolymer; FEVE, fluoroethylene-vinyl ether; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PCTFE, polychlorotrifluoroethylene; PVDF, polyvinylidene fluoride; THV, TFE-HFP-VF2.

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TABLE 2 Fluoropolymer properties and functionality

See Supporting Information: Chapter 2 for property descriptions	Durable				Inert—Stable				
	Mechanical strength	Wear resistance	Flexibility	Low coefficient of friction	Resistance to chemicals	Weatherability	Cryogenic properties (lower than −50 °C)	High operating temperature range	High limiting oxygen index
Fluoroplastics									
PVDF Homopolymer	•	•		•	•	•		•	•
PVDF Copolymer	•	•		•	•	•		•	•
ECTFE Copolymer	•	•		•	•	•	•	•	•
ECTFE Terpolymer		•		•	•	•		•	•
PCTFE	•	•		•	•	•	•	•	•
FEVE	•	•	•	•	•	•		•	•
EFEP	•	•		•	•	•	•	•	•
CPT				•	•	•	•	•	•
THV			•		•	•		•	•
Fluoroelastomers									
FEPM	•	•	•		•	•		•	•
FKM	•	•	•		•	•		•	•
FFKM	•	•	•		•			•	•
Specialty									
Amorphous			•	•	•			•	•
Ionomer			•		•				•

See Supporting Information: Chapter 2 for property descriptions	Functional								
	Electrical insulator—high data transmission rate	Ionic conductivity	Piezo-electrical properties	Barrier properties	Nonstick properties	Ultra high purity grades for clean applications	Optical clarity	Low refractive index—used for optical effects	Polymer processing additive (PPA)[a]
Fluoroplastics									
PVDF Homopolymer			•	•		•		•	•
PVDF Copolymer			•	•				•	•

(*Continued*)

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TABLE 2 (*Continued*)

See Supporting Information: Chapter 2 for property descriptions	Functional								
	Electrical insulator—high data transmission rate	Ionic conductivity	Piezo-electrical properties	Barrier properties	Nonstick properties	Ultra high purity grades for clean applications	Optical clarity	Low refractive index—used for optical effects	Polymer processing additive (PPA)[a]
ECTFE Copolymer	•			•					
ECTFE Terpolymer				•					
PCTFE				•	•	•	•	•	
FEVE				•			•		
EFEP				•	•		•	•	•
CPT				•	•	•	•	•	
THV				•			•	•	•
Fluoroelastomers									
FEPM	•			•					
FKM				•	•				•
FFKM	•			•		•			
Specialty									
Amorphous	•	•		•	•	•	•	•	
Ionomer	•	•		•			•		

Note: See Chapter 5 in the Supporting Information.
Abbreviations: CPT, chlorotrifluoroethylene-tetrafluoroethylene; ECTFE, ethylene-chlorotrifluoroethylene; EFEP, ethylene-tetrafluoroethylene-hexafluoropropylene; FEPM, trifluoroethylene-propylene copolymer; FEVE, fluoroethylene-vinyl ether; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PCTFE, polychlorotrifluoroethylene; PVDF, polyvinylidene fluoride; THV, TFE-HFP-VF2.
[a]Polymer Processing Additives (PPA): also known as Polymer Processing Aid, Extrusion Process Aids or Polymer Processing and Recycling Aids.

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emperature, fire, and weather (Table 2). Fluoropolymers are the preferred choice of material because of their unique combination of properties that are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for our society providing vital, reliable functionality to a broad range of industrial and consumer products.

Three fluoropolymer types are included in this study: fluoroplastics, fluoroelastomers, and specialty fluoroplastics. Here, we describe briefly each included in this study. Additional details about each polymer are provided in the Supporting Information: Chapter 5.

Fluoroplastics

The fluoroplastics included in this study are: polyvinylidene fluoride (PVDF) homopolymer, PVDF copolymer, ethylene-chlorotrifluoroethylene (ECTFE) copolymer, ECTFE terpolymer, polychlorotrifluoroethylene (PCTFE), fluoroethylene-vinyl ether (FEVE), ethylene-tetrafluoroethylene-hexafluoropropylene (EFEP) terpolymer, chlorotrifluoroethylene-tetrafluoroethylene (CPT) terpolymer, and tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride (TFE-HFP-VF2 [THV]) terpolymer as well as the specialty fluoroplastics, amorphous fluoropolymers, and fluorinated ionomers. Typical monomers used in the manufacture of fluoroplastics include tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride (VDF or VF2), chlorotrifluoroethylene (CTFE), vinyl fluoride (VF), trifluoroethylene (TrFE), and perfluoroalkyl vinyl ethers (PAVEs), which include trifluoromethyl trifluorovinyl ether (PMVE), pentafluoroethyl trifluorovinyl ether (PEVE), and heptafluoropropyl trifluorovinyl ether (PPVE). In some copolymers, monomers that do not contain fluorine attached to the olefinic carbons may be used. These include ethylene, propylene, perfluoroalkyl-substituted ethylenes, and others (Ebnesajjad, 2000, 2003; Grot, 2011).

Fluoroelastomers

The fluoroelastomers included in this study are: trifluoroethylene-propylene copolymer (FEPM), HFP-VF2 polymer and HFP-VF2-TFE polymers (FKM), and TFE-PMVE perfluoroelastomer (FFKM). Typical monomers used in the manufacture of fluoroelastomers include VDF, HFP, TFE, CTFE, PAVEs, as well as propylene, 1-hydropentafluoropropene (HPFP), and 2,3,3,3-tetrafluoropropene (HFO-1234yf; FPG, 2021a). Although fluoroelastomers are based on many of the monomers that are also used for the synthesis of fluoroplastics, they are different because of the specific composition, flexibility with subambient glass transition temperatures, as well as their elastomeric properties, resulting from the cross-linking process. Cross-linking, known as curing or vulcanizing, is a hardening process to form chemical bonds between polymer chains that gives polymers their elasticity (Améduri et al., 2001; Drobny, 2016).

PVDF homo- and copolymers

Polyvinylidene fluoride fluoropolymers are specified by end users across the world for their outstanding combination of properties. Because they have high temperature resistance, low permeability, and high mechanical strength, and provide chemical resistance to a wide range of aggressive chemicals, PVDF fluoropolymers are used as a contact surface for the production, storage, and transfer of corrosive fluids (chemically resistant to halogens and acids) in the chemical processing industry, oil and gas transportation, and cables industry (Arkema, 2021a; Gujarat Fluorochemicals Limited, 2018, 2022; Solvay, 2021a). The outstanding resistance to sunlight/UV exposure make PVDF suitable for architectural coatings. The outdoor aging and weathering properties of PVDF resin led to its use in long-lasting paints for coating metal sheet for the past 50 years. PVDF resins can also be used to protect thermoplastics through coextrusion or film lamination techniques to obtain antigrime and antigraffiti surfaces with exceptional weathering properties. PVDF fluoropolymers also exhibit radiation resistance, desirable burn characteristics, flame, and smoke properties, easy processing on industry-standard equipment, and easy postprocessing steps, such as welding and fabrication. PVDF is used as a binder in lithium-ion batteries as well as PVDF film for solar power panels because of its high thermal and electrochemical stability, its stability under harsh environmental conditions, and its strong adhesion properties are critical to achieving environmental goals.

ECTFE (co- and terpolymers)

Ethylene chlorotrifluoroethylene (ECTFE) is a semicrystalline and melt-processable fluoropolymer obtained by the copolymerization of the two monomers, ethylene and chlorotrifluoroethylene, with an essentially 1:1 alternating structure (Ebnesajjad, 2017). Due to its chemical structure, ECTFE offers a unique combination of properties including chemical resistance, high thermal rating, and very good mechanical properties (Solvay, 2021b). ECTFE terpolymer with added hexafluoroisobutylene monomer displays enhanced stress-cracking performances resulting from chain-structure modifications of the polymer. ECTFE is used widely in anticorrosion applications such as coatings or in self-supporting construction (pipes) and architectural films (Solvay, 2021c). One of the principal advantages of ECTFE fluoropolymer is the ease with which it can be processed. It is a true thermoplastic that can be handled by conventional techniques of extrusion as well as by blow, compression, injection, rotational, and transfer molding. Powder coating methods are also applicable. ECTFE embodies an exemplary trade-off among general properties, offering high chemical and mechanical resistance combined with easy processing of the resin.

PCTFE

Polychlorotrifluoroethylene is a homopolymer of chlorotrifluoroethylene. PCTFE is melt processable and can be

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extruded or molded (Satokawa, 1990). PCTFE has outstanding mechanical properties, especially hardness, and chemical resistance compared with PTFE and PFA, although it is slightly inferior to PFA and FEP in heat resistance and chemical resistance (Daikin, 2021a; Satokawa, 1990). PCTFE has been applied widely in the semiconductor industries and aerospace industries (Curbell, 2021; Daikin, 2021a). In addition to distinguished thermal and chemical stability, it has very low moisture absorption and permeation; therefore, PCTFE is used in pharmaceutical packaging (Honeywell, 2021).

FEVE

Fluoroethylene-vinyl ether fluoropolymer resins are manufactured by copolymerization of fluoroethylene monomer and a vinyl ether monomer and consist of alternating fluoroethylene and alkyl vinyl ether segments (AGC Chemicals Company, 2021a; Parker & Blankenship, 2015). They were developed in 1982 as the first solvent-soluble fluoropolymers in the world (Darden & Parker, 2021; Kojima & Yamabe, 1984; Munekata, 1988; Yamabe et al., 1984). The alternating fluorinated segments provide outstanding UV stability, weather resistance, and chemical resistance, while the vinyl ether segments provide solvent compatibility and cross-linking sites (Parker & Blankenship, 2015; Scheirs, 2007). FEVE resins are used to make ultra-weatherable coatings for architectural, aerospace, automotive, bridge, and industrial maintenance markets (Hoshino & Morizawa, 2017).

EFEP

Ethylene-tetrafluoroethylene-hexafluoropropylene is a terpolymer of ethylene, tetrafluoroethylene, and hexafluoropropylene. It was designed to have many of the properties of ETFE. It has a lower processing temperature, which allows it to be coextruded with conventional thermoplastic polymers such as polyamide, ethylene vinyl alcohol (EVOH), and modified polyethylene. EFEP can be extruded, injection molded, and blow molded, and it is used in many applications such as those identified in Supporting Information: Chapter 4.7 (Daikin, 2011a). EFEP is a melt-processable resin with good processability because of its low melting point. It also has excellent mechanical properties, provides chemical resistance, low permeability, exceptional weatherability, and good heat resistance. Other prominent features include inherent flame retardancy as well as good optical properties given that EFEP is highly transparent and has both a low dielectric constant and loss tangent.

CPT

Chlorotrifluoroethylene-tetrafluoroethylene is a terpolymer of chlorotrifluoroethylene, tetrafluoroethylene, and perfluoroalkyl-vinyl-ether. It is a melt-processable polymer and resin, which is readily processed because of its lower melting point. It can be melt-molded as a thermoplastic resin by extrusion, injection, and compression molding. CPT is a modified perfluoroalkoxy fluoropolymer (PFA), which utilizes chlorotrifluoroethylene to provide low permeability to PFA, and it has many outstanding properties as a hybrid polymer of PFA and PCTFE as shown below. It has demonstrated permeation resistance to organic solvent, chemicals, water vapor, and gasoline (Daikin, 2011b). CPT offers superior permeation resistance against gasoline and flexible fuel and can be part of construction meeting the LEV III requirements (US environmental protection regulations in this automotive application). CPT also has notable barrier properties against many kinds of organic solvents and strong acids, especially HF, HCl, and HNO_3. This is very useful for semiconductor applications (Daikin, 2021b). In addition to the features noted above, CPT also provides heat resistance, excellent weatherability, flame retardancy, and good optical properties owing to its high transparency.

THV

THV fluoropolymers are a group of fluorinated thermoplastic polymers composed mainly of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and vinylidene fluoride (VDF; Dominghaus, 1998; Hintzer & Schwertfeger, 2014; Hull et al., 1997). The melting point of the different grades ranges from approximately 100 °C to nearly 250 °C. THV fluoropolymers are easy to process due to their broad processing windows. Different THV grades exhibit high flexibility, high transparency, bondability to fluorinated and nonfluorinated materials, and very good permeation resistance against fuels and other chemicals. The polymers are used as a barrier layer in fuel hoses, for transparent films and tubing, as matrix materials in composites, and the bonding layer in multilayer construction (Dams & Hintzer, 2017; Hull et al., 1997). The high transparency of the special film makes it an ideal adhesive film for laminated glass and the optimal protective film for surfaces. THV grades compete against other fluorothermoplastic materials for applications that require transparency and low refractive index as well as with fuel barrier materials. Commercial nonfluorinated materials cannot be used as substitutes for THV because of the unique combination of properties. Polymethylmethacrylate (PMMA) is used in conjunction with THV to provide differences in refractive index to create the total reflection needed for polymer optical fibers (Park et al., 2008). Transparent polymers, such as PMMA or polycarbonate, do not have the same chemical resistance or UV resistance to compete directly with THV.

FEPM

Trifluoroethylene-propylene copolymer elastomers, ASTM D1418, are high MW fluoropolymers with alternating tetrafluoroethylene and propylene segments (Kojima et al., 1977). They are also known as TFE-P copolymers. Various articles can be produced by means of compression molding, extrusion, injection molding, and calendering. FEPM elastomers are compounded and cured (cross-linked) to deliver unique and valuable properties by providing exceptional heat resistance with a continuous service temperature higher than

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200 °C, outstanding chemical resistance with little or no deterioration even in contact with strong acids, bases, and oxidants at high temperatures, steam resistance, and high electrical resistivity on the order of 10^{15}–10^{16} Ω/cm (bulk resistivity). Formulated FEPM components are now used worldwide in many critical industrial applications where they must function safely in harsh environments, thereby extending the life of critical components and reducing downtime and costly repairs. FEPM elastomers are used in a range of applications including thermal power plants, oil and gas industry, ocean development, chemical and nuclear plants, automotive, aerospace, heavy-duty diesel, electronics, machinery, renewable energy, food processing, and medical. Their noted heat and chemical resistance make them especially valuable in oil and gas extraction (downhole) applications, where reliability is essential to cost effective and environmentally responsible production (Hull, 1983). FEPM elastomers are also used in high-performance wire and cable applications as insulating materials with the highest heat resistance, for example, lightweight, high-voltage automotive cables and motor cables for Japanese high-speed bullet trains (AGC Chemicals Company, 2021b).

Fluoroelastomers (FKM)

FKM are a family of fluoroelastomer materials defined by ASTM international standard D1418 (ASTM, 2021). FKM fluoroelastomers contain vinylidene fluoride (VDF) as a monomer combined with a variety of other fluoromonomers to create a palette of polymers with properties tailored for specific uses (Dams & Hintzer, 2017; Drobny, 2016; Van Cleeff, 1997; Worm & Grootaert, 2001). Cross-linked FKM fluoroelastomers are amorphous polymers designed for demanding service applications in hostile environments characterized by broad operating temperature ranges in contact with industrial chemicals, oils, or fuels (Worm & Grootaert, 2001). FKM fluoroelastomers are used mainly in fabricated parts (e.g., o-rings, gaskets, seals) to provide barriers against a wide range of fluids under severe service conditions (Drobny, 2016). Their design allows stable extrusion and molding processes and fitting in a wide range of processing constraints, reducing the risk of failure and increasing productivity. FKM fluoroelastomers provide high temperature and aggressive fluids resistance and retention of properties over a wide and demanding range of operating use conditions (high and low temperatures) for sealing and fluid transport applications, offering far superior performance than hydrocarbon elastomers. Applications include aerospace, automotive, oil and gas, chemical processing, electrical, office equipment, food, pharmaceuticals, and consumer wearables. Additionally, uncured FKM fluoroelastomers are used as a polymer processing additive (PPA) or polymer extrusion aids in small amounts (50–2000 ppm) dispersed in polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), significantly improving their film extrusion characteristics, reducing melt fracture and die build-up, as well as increasing productivity, minimizing energy and water footprint, and enabling the extrusion of thin films (Lavallée, 2020; Shell, 2020).

FFKM

Perfluoroelastomers, designated by ASTM D1418 as FFKM, are a fully fluorinated class of elastomers that are typically made up of tetrafluoroethylene (TFE), a perfluoro (alkyl vinyl ether; PAVE), and a cure site monomer(s) (Ohkura & Morizawa, 2017). FFKM elastomers offer superior chemical and temperature resistance, excellent resistance to gas and liquid permeation, and resistance to weather and ozone with operating temperatures ranging from −40 °C to 325 °C (Drobny, 2016; Greene-Tweed, 2021a, 2021b). These polymers can also be compounded to meet the special requirements of upstream, midstream, and downstream oil and gas exploration due to their superior properties (Barnwell, 2021; Daemar, 2021). Because of these properties, FFKM elastomers are used in a wide variety of applications such as critical sealing solutions for the aerospace, pharmaceutical, medical, chemical processing, semiconductor, and oilfield industries (Atkinson, 2018; Marshall, 2017).

Amorphous fluoropolymers

Amorphous fluoropolymers are copolymers of TFE and specialty monomers that yield linear, high molar mass noncrystalline polymers (AGC Chemicals Company, 2021c; Gangal & Brothers, 2010; Hintzer et al., 2013; Korinek, 1994; Resnick & Buck, 1997, 1999). Amorphous fluoropolymers have the outstanding chemical and thermal stability and surface properties of semicrystalline perfluoropolymers as well as the unique properties associated with amorphous materials such as optical clarity and high gas permeability. The optical properties are outstanding, with more than 90% transmission, and thereby low dissipation, over a wide range of wavelengths (e.g., 200–2000 nm). TFE/PDD (2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole) copolymers have the lowest refractive index known for a solid organic polymer (Groh & Zimmermann, 1991). This unique combination of properties makes amorphous fluoropolymers unmatched for uses in degassing, fiber optics, photolithography, antireflective coatings, passivation and protective coatings for medical, military, and aerospace devices, as well as electronic applications (Gangal & Brothers, 2010; Hintzer et al., 2013).

Fluorinated ionomers

Fluorinated ionomers are copolymers of TFE and a perfluorovinylether monomer containing an ionic group, typically a sulfonic acid or carboxylic acid (Grot, 2011, 2013). Fluorinated ionomers can be extruded or cast into film and converted into ion exchange materials (IXMs). IXMs come in a variety of useful forms offering a broad range of solutions for different applications (AGC Chemicals Company, 2021d; Asahi-Kasei, 2021; Chemours, 2021a). These forms include ion exchange membranes (IEMs), dispersions, and resins. IEMs must possess the required ion transport properties for the electrochemical cell in which they reside to perform well

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and work effectively. Some of these properties include high ionic conductivity, chemical resistance, high operating temperature range, low permeability, and balanced durability and performance (Chemours, 2021b).

Ion exchange membranes (IEMs) stand to play a noteworthy role in today's modern world (Chemours, 2021b) and as such, are utilized in a wide range of applications and end-use industries including electrochemical processing, energy production, and hydrogen production. IEMs revolutionized the chlor-alkali industry (Grot, 2013), the manufacture of primarily caustic soda and chlorine, by eliminating the use of hazardous materials such as mercury and asbestos (Asahi-Kasei, 2021) and, in doing so, reducing energy consumption. Water electrolysis, the process of converting water into hydrogen and oxygen, relies on IEM technology. Although this process requires electricity, renewable energy sources such as solar or wind power can be utilized, allowing the potential for hydrogen to be a "clean" energy source (Science Center, 2021). Hydrogen fuel cells, some of which use a type of IEM known as a proton exchange membrane, can then convert hydrogen to electricity, a crucial technology to reach the stated target of the EU New Green Deal (EC, 2021).

STUDY METHODOLOGY AND DATA

Seven global fluoropolymer manufacturers (AGC Chemicals Americas, Arkema, The Chemours Company, Daikin Industries, Gujarat Fluorochemicals Limited, Solvay Specialty Polymers, and 3M Company) participated in this study and contributed data, writing, critique, and analysis. The companies noted above are members of the US-based Performance Fluoropolymer Partnership (PFP) and/or EU-based Fluoropolymer Product Group (FPG).

This study provides data on 14 fluoropolymers, building on a prior study (Henry et al., 2018). The study was chartered within two global industry groups. Participants put forward candidate fluoropolymers of notable commercial importance for the study and provided company and published data that address the PLC criteria. Thirteen PLC criteria that relate to the polymer structure and properties, including three to physicochemical properties and five to stability, set forth in BIO by Deloitte (2015) and presented in prior work on four fluoropolymers (Henry et al., 2018), are addressed in this study (Figure 1). These criteria are briefly described in Table 3 with further description provided in Supporting Information: Chapter 3 and in the prior work (Henry et al., 2018). Participants provided company and published data and a description of methods and/or public references to demonstrate the origin of the data provided. These methods and references are provided in detail in Supporting Information: Chapter 4. The PLC criteria data were compiled and are presented in Tables 4 and 5.

The data assessment was done in two ways: Companies could self-assess the PLC data if they had the technical resources to do so or they could submit their PLC data to a third-party contractor for an independent technical review. The third-party consultant hired by PFP was GSI Environmental Inc. The objective was to be able to publish the references and methods behind the PLC data provided for each fluoropolymer in the study. In cases where the data and/or methods contained confidential business information, the third-party consultant independently evaluated the information supplied before it was shared in a blinded, aggregate form with the participating project companies. In several cases—FKM, PVDF, and ionomers—several companies submitted data for the same fluoropolymer. The data were combined and are presented in Tables 4 and 5. There is no intentional company attribution for the data presented.

The following describes further how the study data were generated and compiled.

- A third-party consulting company (GSI) was engaged to comment independently on data, methods, and references initially supplied by study participants for their respective fluoropolymers. Several study participants used this third-party consultant.
- Following the initial third-party assessment and assembly of the master data Tables 4 and 5 as well as the FKM data in Supporting Information: Table 4.11, a series of subsequent assessments were conducted (within PFP)

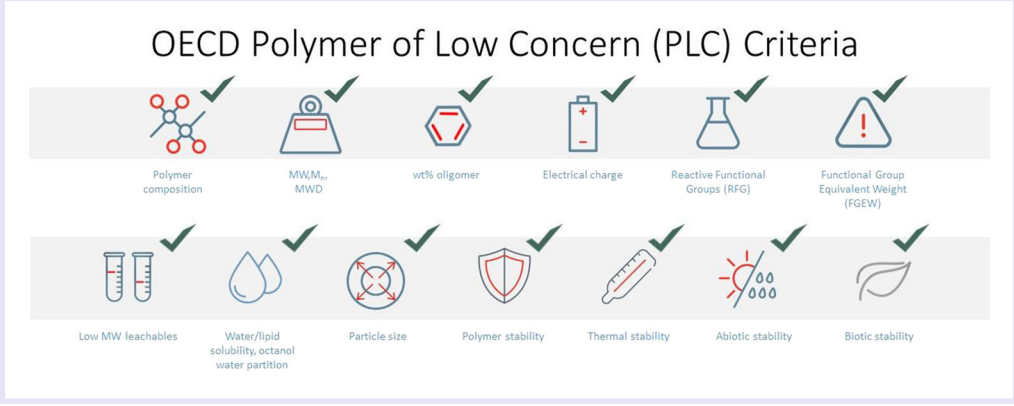


FIGURE 1 OECD polymer of low concern (PLC) criteria add (C) 2021 W.L.Gore & Associates

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TABLE 3 Polymer of low concern (PLC) criteria descriptions

(See Supporting Information: Chapter 3 for additional details) Criterion	Description
Polymer composition	The polymer composition criterion requires structure and elemental composition of the polymer be described and identified (e.g., by Chemical Abstracts Service [CAS] number).
Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da	The number average molecular weight (Mn) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report (BIO by Deloitte, 2015) states that the "most potential health concern polymers have a number average molecular weight, Mn, <1000 Da and oligomer content >1%." The higher the oligomeric content, the more likely a polymer is to be a health or ecotoxicological (OECD, 2009, p. 9).
	Molecular weight (MW) is an important predictor of biological effect because large molecules (>1000–10 000 Da) are too large to penetrate cell membranes (Supporting Information: in Beyer, 1993, p. 14). Because large molecular weight polymers cannot enter the cell, they cannot react with "target organs," such as the reproductive system, and are not bioavailable. "Therefore, as the Mn of a polymer increases, a reduced incidence of potential health concern effects might be expected" (OECD, 2009, p. 20).
	An additional PLC consideration is the weight percentage of oligomers that are <1000 Da. Oligomers may be composed of, for example, dimers, trimers, and tetramers, meaning they have 2- monomer, 3- monomer, and 4-monomer units, respectively. The EU report (BIO by Deloitte, 2015) concluded that most potential health concern polymers have Mn of <1000 Da and oligomer content of >1%: "…the distribution of potential health concern polymers exhibited an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD, 2009, p. 24).
	Molecular weight distribution (MWD), also known as "polydispersity index," measures the heterogeneity of size of polymer molecules in a polymer. The MWD is an important parameter for predicting potential biological effects of polymers because, although Mn may be a large value, low MW oligomers <1000 Da may be present, which could penetrate the cell.
Ionic character	Electrical charge or ionic character can be anionic, cationic, amphoteric, or nonionic. Specifically, cationic polymers have been associated with aquatic toxicity (Auer et al., 1990; USEPA, 1997a).
Reactive functional groups and RFG ratio to MW	A "reactive functional group" (RFG) is defined as an atom or associated group of atoms in a chemical substance that is intended or can be reasonably expected to undergo facile chemical reaction (USFR, 2012). Some highly reactive functional groups (or a high ratio of RFGs per mole) have been associated with adverse human health and ecotoxicology (e.g., acrylates, methacrylates, isocyanates, anhydrides, aziridines; USEPA, 2010).
	The functional group equivalent weight (FGEW) is used to determine if the RFGs in a polymer are substantially diluted by polymeric material to allow the polymer to be a PLC (USEPA, 1997). The FGEW of a polymer is defined as the ratio of the Mn to the number of functional groups in the polymer. The FGEW is used as an indication of the degree of reactivity of the polymer; the lower the FGEW, the more reactive the polymer and the greater the potential for health and environmental impact (OECD, 2009, p. 10).
Low MW leachables	Low MW leachables are chemical molecules, either inorganic or organic, that migrate (i.e., leach) out of the polymer. These could be residual monomers or oligomers resulting from incomplete polymerization processes, surface residues, or other chemicals used in the manufacturing processes (e.g., initiators, catalysts, chain transfer agents, surfactants).
	Low MW leachables are critically important to the potential for a polymer to affect health and the environment, given that they may be able to migrate out of the polymer and cross cell membranes to potentially react with biomolecules. A report to the EU (BIO by Deloitte, 2015) concluded that "Polymers with <1% MW < 1000 Da and low water extractability are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant."
	Monomers, by nature, are reactive. Unreacted monomers left in a polymer may migrate out of the polymer to react with biomolecules to cause potential adverse effects. Regulatory authorities (BIO by Deloitte, 2015) and the OECD Expert Group on Polymers (OECD, 2009) agree that the residual monomer content of a polymer is critical to determining if it qualifies as a PLC.

(*Continued*)

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TABLE 3 (*Continued*)

(See Supporting Information: Chapter 3 for additional details) Criterion	Description
Particle size	Particle size is also a PLC criterion. Particles that are small enough to reach the deep lung upon inhalation are often associated with adverse health effects. Therefore, to qualify as a PLC, median mass aerodynamic diameter (MMAD) of the polymer particle size should be >5 μm.
Structural and elemental composition	In the US, Chemical Categories of Concern are the result of the review of new chemicals by the USEPA under the TSCA (see https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/chemical-categories-used-review-new). The categories describe the molecular structure, boundary conditions such as MW, equivalent weight, the log of the octanol–water partition coefficient, log *P*, or water solubility, and standard hazard (mammalian and ecological) and (environmental) fate tests to address concerns.
Elemental composition	The elemental composition is a factor in the assessment of the eligibility of polymers for reduced notification requirements. The exclusion of polymers under this step is not a conclusion of hazard but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process. These elemental requirements differ across jurisdictions as covered in the report to the EU on global regulatory approaches to polymer assessment (BIO by Deloitte, 2015). For example, in the EU under REACH it is proposed that polymers composed from among these elements, covalently bound to C, have reduced hazard: H, N, O, Si, S, F, Cl, Br, or I (BIO by Deloitte, 2015). In contrast, the USEPA Polymer Exemption Rule states that a polymer is eligible for reduced agency review when it has at least two of the following elements: C, H, O, N, S, or Si (USFR, 1995).
Water and lipid solubility and the octanol–water partition coefficient	Water solubility is the extent to which a compound will dissolve in water. According to the OECD (2009) meeting of the Expert Group on Polymers, polymers with "negligible" water solubility, or those described as "hydrophobic" have been represented with a water solubility of 0.000001 mg/L (1×10^{-6} mg/L; assigned arbitrarily; OECD, 2009). That is equivalent to 1 ppt, a very conservative definition.
	Polymers with water solubility <10 mg/L showed generally low health concerns.
	The octanol–water partition coefficient (K_{ow}) is another criterion to assess chemicals and their environmental and health impact. The K_{ow} is a physical–chemical property at equilibrium to represent the lipophilic or hydrophilic nature of a chemical, the distribution of a compound in octanol, representing the lipophilic nature, to its solubility in water, representing the aqueous nature. The higher the K_{ow}, the more lipophilic the compound. Typically, a K_{ow} >5000 or a log K_{ow} >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. According to the Stockholm Convention, a bioconcentration factor of >5000 and a log K_{ow} >5 is used as a criterion for bioaccumulation.
Stability	Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. As was previously described in the Polymer of Low Concern section under the molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da heading, molecules with Mn <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment.
Abiotic stability	Polymers are stable; monomers are not. Abiotic degradation may involve sunlight, water, or oxygen. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Hydrolytic degradation of polymers is another potential way to break the polymer bonds, creating smaller oligomers that may be bioavailable. Chemical oxidation is a reaction involving the loss of electrons from one atom to another.
Biotic stability: aerobic, anaerobic, and in vivo	Biotic stability is assessed by whether the polymer is degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic) conditions; in vitro and in vivo stability studies demonstrate this. In vivo biodegradation involves the breaking of the polymer bonds by the action of bacteria, enzymes, and oxidants within the organism.
Thermal stability	Thermal stability of a polymer can be assessed when used as intended under normal, foreseeable use conditions or in extreme temperatures during disposal, such as by incineration. Thermal stability testing may involve Thermogravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance.

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TABLE 4 Fluoroplastics and PLC criteria

	Fluoroplastics				
Supporting Information Data: Chapter	**4.1 PVDF**	**4.2 PVDF-HFP copolymer**	**4.3 ECTFE**	**4.4 ECTFE**	**4.5 PCTFE**
	Polyvinylidene fluoride	Vinylidene fluoride, hexafluoropropene copolymer	Ethylene, chlorotrifluoroethylene copolymer	Ethylene, chlorotrifluorethylene, hexafluoroisobutylene terpolymer	Polychlorotrifluoroethylene
PLC assessment criterion[a]	CAS 24937-79-9	CAS 9011-17-0	CAS 25101-45-5	CAS 54302-04-04	CAS 9002-83-9
Structure	$–(CF_2–CH_2)_n–$	$–(CF_2–CH_2)_n–[CF(CF_3)–CF_2]_m–$	$–(CF_2–CFCl–CH_2–CH_2)_n–$	$–(C_4H_2F_6)_n–(C_2H_4)_m–(C_2ClF_3)_i–$	$–(CF_2–CFCl)_n–$
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes	Yes
Molecular weight (Mn)[b] (Mn >1000 Da and oligomer content <1%)	70 000–300 000	80 000–300 000	Mn >50 000	Mn >50 000	70 000–400 000 average based on grade type
Molecular weight distribution Mw[c] ÷ number average M_n	2–3	2–3	1.1	1.7	3
Wt% oligomer (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible	Negligible
Ionic character	Neutral	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs)[d] **and functional group equivalent weight (FGEW)**	None and N/A	None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	Negligible
Residual monomers	<50 ppb	<50 ppb	<50 ppb	<50 ppb	<0.1 wt%
Ratio of residual monomers to molecular weight (typical value)	$\sim10^{-12}$–$\sim10^{-13}$	$\sim10^{-12}$–$\sim10^{-14}$	$\sim10^{-13}$	$\sim10^{-13}$	$<10^{-5}$
Structural similarities to RFG of concern	None	None	None	None	None
Reference standard	ASTM D3222-18a	ASTM D5513-18	ASTM D3275-81	ASTM D3275-81	

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TABLE 4 (*Continued*)

	Fluoroplastics				
Supporting Information Data: Chapter	**4.1 PVDF**	**4.2 PVDF-HFP copolymer**	**4.3 ECTFE**	**4.4 ECTFE**	**4.5 PCTFE**
Physical–chemical properties					
Water solubility and octanol/water partition coefficient, K_{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, MMAD, should be >5 μm)	Powders: 5–300 μm pellets: 2–4 mm	Powders: 5–300 μm pellets: 2–4 mm	D50%: 50–70 μm (typical)	D50%: 50–70 μm (typical)	Pellet: 2-4 μm, flake: 0.54 mm powder: 5–300 micron
Stability					
Hydrolysis, light (hν), Oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp. (°C)	150 °C	150 °C	150 °C	150 °C	120 °C
Meets [a]PLC criteria (Yes or No)	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**
Fluorinated polymerization aid (PA) used? (Yes or No)	No	No	No	No	No
Recommended processing/application (use) temperature (T°C)	Processing: 200 °C–250 °C Use max temp: 150 °C	Processing: 180 °C–250 °C Use max temp: 100 °C–140 °C depending on HFP content	Processing: 250 °C–280 °C Use max. Temp: 150 °C	Processing: 250 °C–280 °C Use max. Temp: 150 °C	Molding: 230 °C –330 °C and Use Max same as above at 120 °C

	Fluoroplastics			
Supporting Information Data: Chapter	**4.6 FEVE**	**4.7 EFEP**	**4.8 CPT**	**4.9 THV**
	Fluoroethylene-vinyl ether copolymer	1-Propene, 1,1,2,3,3,3-hexafluoro-, polymer with ethylene and 1,1,2,2-tetrafluoroethylene	1,1,1,2,2,3,3-Heptafluoro-3-[(trifluoroethenyl)oxy]propane polymer with chlorotrifluoroethylene and tetrafluoroethylene	1-Propene,1,1,2,3,3,3-hexafluoro-polymer with 1,1-difluoroethylene and tetrafluoroethylene
PLC assessment criterion[a]	cbi	35560-16-8	116018-07-6	25190-89-0

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TABLE 4 (*Continued*)

	Fluoroplastics			
Supporting Information Data: Chapter	**4.6 FEVE**	**4.7 EFEP**	**4.8 CPT**	**4.9 THV**
Structure	cbi	$-(CH_2-CH_2)_n-(CF_2-CF_2)_m-[CF_2-CF(CF_3)]_l-$	$-(CF_2-CF_2)_n-(CFCl-CF_2)_m-[CF_2-CF(OR_f)]_l-$	$-(CF_2CH_2)_x-(CF_2-CF-CF_3)_y-(CF_2-CF_2)_z$
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes
Molecular weight (Mn)[b] (Mn >1000 Da and oligomer content <1%)	7000–46 000	130 000	200 000–300 000	131 000
Molecular weight distribution Mw[c] ÷ number average M_n	2.0–4.0	4	2–5	1.8
Wt% oligomer (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Mn <1000 range of <3.5% and Mn <500 is <0.7%	Negligible; <0.1 wt% oligomer content	Negligible; <0.1 wt% oligomer content	wt.% <1000: None
Ionic character	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs)[d] **and functional group equivalent weight (FGEW)**	None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables	Negligible; cross-linked as final product	Negligible	Negligible	No active leachables by USP class VI (121 °C)
Residual monomers	0.12%–1.43% non-fluorinated	Negligible	Negligible	None detected
Ratio of residual monomers to molecular weight (typical value)	10^{-7}–10^{-8}	$<10^{-5}$	$<10^{-5}$	$\sim10^{-13}$
Structural similarities to RFG of concern	None	None	None	None
Reference standard		ASTM D7472	ASTM D7471	

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TABLE 4 (*Continued*)

	Fluoroplastics			
Supporting Information Data: Chapter	**4.6 FEVE**	**4.7 EFEP**	**4.8 CPT**	**4.9 THV**
Physical–chemical properties				
Water solubility and octanol/water partition coefficient, K_{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, MMAD, should be >5 μm)	Solution or flake 150 nm for emulsion	2–4 mm (pellets)	2–4 mm (pellets)	Pellets ~400–750 μm
Stability				
Hydrolysis, light (hν), oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp. (°C)	220 °C	130 °C; low melting point 160 °C–190 °C and high decomposiiton temperature of 357 °C–380 °C	200 °C; low melting point 239 °C–251 °C and high decomposition temperature of >400 °C	Continuous use is expected ~room T. (<100 °C as host resin melts at 120 °C); No expected degradation; fluoropolymer degrades >350 °C by TGA
Meets [a]PLC criteria (Yes or No)	**Yes**	**Yes**	**Yes**	**Yes**
Fluorinated polymerization aid (PA) used? (Yes or No)	No	No	No	Yes and No
Recommended processing/application (use) temperature (T°C)	180 °C–200 °C	Molding temperature: 200 °C–280 °C; Use max as noted above	Molding temperature: 310 °C–330 °C; Use max as noted above	Melt processing: <350 °C Application: <100 °C (in LLDPE)

Abbreviations: ECTFE, ethylene-chlorotrifluoroethylene; HFP, hexafluoropropylene; PCTFE, polychlorotrifluoroethylene; PLC, polymer of low concern; PVDF, polyvinylidene fluoride.
[a]See OECD (2009) and BIO by Deloitte (2015) for details on characteristics of a "Polymer of Low Concern" and Supporting Information: Chapter 3.
[b]Molecular Weight is number average molecular weight which is defined as the total weight of the polymer divided by the total number of molecules. It is the mole fraction of molecules in a polymer sample.
[c]Molecular weight is weight average molecular weight which is determined by summing the weights of all the chians and then dividing by the total number of chains. It is the weight fraction of molecules in a polymer sample.
[d]For definition of reactive functional group, lists of low-, moderate-, and high-concern functional groups and FGEW limits, see USEPA polymer exemption guidance manual, BIO by Deloitte (2015, pp. 191–192), and USEPA (2010). See Supporting Information.

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TABLE 5 Fluoroelastomers and specialty fluoroplastics—PLC criteria

	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	**4.13 Amorphous**	**4.14 Ionomer**	**4.10 FEPM**	**4.11 FKM**	**4.12 FFKM**
	Perfluoro(alkenyl vinyl) ether polymer	Sodium or potassium salts of perfluorosulfonic acid/TFE copolymer or perfluorocarboxylic acid/TFE copolymer	Tetrafluoroethylene-propylene copolymer	1-Propene,1,1,2,3,3,3-hexafluoro-polymer with 1,1-difluoroethylene copolymer and terpolymers	Tetrafluoroethylene-trifluoromethyl trifluorovinyl ether copolymer
PLC assessment criterion[a]	37626-13-4	9002-84-0, 1314-23-4, 409-21-2, 111173-25-2	27029-05-6	9011-17-0, 26425-79-6, 25190-89-0	26425-79-6
Structure	See Supporting Information	See Supporting Information	See Supporting Information	Supporting Information	-(CF2CF2)x -[CF2-CF(OCF3)]y-(Cure Site Monomer)z
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes	Yes
Molecular weight[b] (Mn >1000 Da and oligomer content <1%)	150 000–300 000	>100 000	Various grades vary between 146 000–275 000	30 000–340 000	10 000–1 000 000
Molecular weight distribution Mw[c] ÷ number average M_n	1.4–2.5	1.0–2.4	Various grades give various ratios from 1.4 to 3.3	1.2–2.4	1.2–3.5
Wt% oligomer (Figure MWD) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	<0.01%	Negligible to <1%	Negligible
Ionic character	Neutral	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs)[d]	None and N/A	None and N/A	None and N/A	None and N/A	None and N/A
Functional group equivalent weight (FGEW; typical value)	$>10^5$	$>10^5$	$>10^5$	$>10^4$–10^5	$>10^4$

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TABLE 5 (*Continued*)

	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Low molecular weight leachables	<1 ppm	<1 ppm	No active leachables	<0.4 ppm to <1 ppm	No active leachables
Residual monomers	<1 ppm	<1 ppm	No residual monomers Only cross-linking agent at <1 ppm	<50 ppt to <5 ppm	<50 ppb
Ratio of residual monomers to molecular weight (typical value)	$>10^{-5}$	$>10^{-5}$	10^{-11}–10^{-12}	$>10^{-10}$–10^{-13}	0.25 ppt as Mn = 10^5 (for representative FKM)
Structural similarities to RFG of concern	None	None	None	None	None
Reference standard				ASTM D 1418	
Physical–chemical properties					
Water solubility and octanol/water partition coefficient, K_{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, aerodynamic diameter, MMAD, should be >5μm)	Solution, sheet or pellets	(1) Aqueous dispersion casting (as a film) followed by annealing or (2) Melt extrusion as a membrane (reinforced)	Sheet or crumb	Sheet or block; powders 300–350 μm stability increased/enhanced when cross-linked	Sheet or block; or "crumb"
Stability					
Hydrolysis, light (hν), oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable

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TABLE 5 (*Continued*)

	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Thermal stability at normal foreseeable use maximum continuous Temp (°C)	>250 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C –240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	200 °C	180 °C	200 °C–300 °C
Meets[a] PLC criteria (Yes or No)	Yes	Yes	Yes	Yes	Yes
Fluorinated polymerization aid (PA) used? (Yes or No)	Yes and No	Yes and No	No	Yes and No	Yes and No
Recommended processing/ application (use) temperature (T°C)	<280 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C–240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	–60 °C–204 °C (AFLAS Technical Document)	Melt processing: <300 °C 160 °C–320 °C (cross-linking temperature)	160 °C–320 °C (cross-linking temperature)

Abbreviations: FEPM, trifluoroethylene-propylene copolymer; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PLC, polymer of low concern.
[a]See OECD (2009) and BIO by Deloitte (2015) for details on characteristics of a "Polymer of Low Concern."
[b]Molecular weight is *number* average molecular weight.
[c]Molecular weight is weight average molecular weight.
[d]For definition of reactive functional group, lists of low-, moderate-, and high-concern functional groups and FGEW limits, see USEPA polymer exemption guidance manual, BIO by Deloitte (2015, pp. 191–192), and USEPA (2010). See Supporting Information.

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until all data cells in the tables cited above were backed up with a narrative, a testing method, and/or references where publicly available.
- Where several companies have provided data on the same fluoropolymers, the table data presented provide a multicompany compilation and assessment along with appropriate methods and references.
- Individual companies supplying data are identified as authors, but there is no direct attribution regarding which company supplied which data for this study.

PLC ASSESSMENT RESULTS

This study was conducted on commercial fluoropolymer products using the PLC criteria to characterize their potential hazard. Figure 1 illustrates the PLC criteria used (BIO by Deloitte, 2015; Henry et al., 2018). The pictured criteria encompass structure, physicochemical property, and stability criteria evaluated in the study. Data informing structure criteria, MW, Mn, and MW distribution (MWD), physicochemical property criteria, water and lipid solubility and K_{ow}, and stability criteria are presented in Tables 4 and 5. The study also gathered structural data on (a) residual monomers, (b) ratio of residual monomers to MW, (c) structural similarities to reactive functional groups (RFGs) of concern, and (d) thermal stability at normal foreseeable maximum continuous use temperatures. Brief descriptions of PLC criteria are provided in Table 3 with additional details, including references for each criterion in Supporting Information: Chapter 3. An additional data point gathered was whether the fluoropolymer(s) presented utilized a fluorinated polymerization aid (PA) during manufacture. The study results are presented in Tables 4 and 5 and summarized below.

Polymer composition: Each of the fluoroplastics, specialty fluoroplastics, and fluoroelastomers assessed in this study met the criterion of polymer composition whereby either fluorine (F) and/or chlorine (Cl) must be covalently bound to the carbon-only polymer backbone.

MW and MWD: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the criteria for MW (Mn >1000 Da) and MWD (1–3). The data demonstrate the fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are high-MW solid polymers with fairly narrow MWD and negligible to low wt% oligomer content. The MW for fluoroplastics in Table 4 and specialty fluoroplastics in Table 5 ranged from 50 000 to 300 000, and the MWD ranged from approximately 1.4 to 3. We note that FEVE was measured in its uncured state and that, upon curing, its MW increased significantly. The MW and MWD were determined in a variety of ways depending on the fluoropolymer and its solubility (or insolubility) in various solvents. The MW and MWD data for fluoroelastomers and specialty fluoroplastics in the study are presented in Table 5. The MW and MWD varied because of the various grades of fluoroelastomers ranging from 100 000 to 250 000 with some less than (down to 10 000) and greater than (up to 500 000). MWD was on the order of 1.4 to 3.5. Fluoroelastomer MW is lower for uncured fluoroelastomer versus cured fluoroelastomer. Cured fluoroelastomer is the form used in many formed-use applications (e.g., gaskets and o-rings). The methods and references for MW and MWD data are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Methods included size exclusion chromatography (SEC), gel permeation chromatography (GPC) along with osmotic pressure, and parallel plate rheometry methods.

Weight % oligomer: The criteria for wt% oligomer are less than 5% oligomer content for Mn less than 1000 Da, and less than 2% oligomer content for Mn less than 500 Da (BIO by Deloitte, 2015; Henry et al., 2018; see also the Supporting Information). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the wt% oligomer criteria. Many polymers in the study were reported as "negligible" for oligomers based on analyses conducted. Polymers in the study not cited as negligible have reported numerical data presented in Tables 4 and 5. In addition to SEC and GPC, analytical methods employed included a weight loss upon heating method and the FDA 21 CFR 177.1380 method. The methods and references for wt% oligomer are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

Ionic character: The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are neutral polymers, either containing no ionic groups or may contain anionic at the terminus of their high MW polymer chains as noted in the prior study of fluoropolymers (Henry et al., 2018). Notably different are fluorinated ionomers, which have neutralized (salts) sulfonic acid or carboxylic acid groups pendant to the polymer backbone and as such are neutral and not ionically charged in their polymeric solid form and are low in toxicity and not dermally irritating on skin contact (USEPA, 1997). None of the evaluated polymers in the study have cationic nature. The methods and references for ionic character are presented in the Supporting Information: Chapter 4 with the specific subchapter noted in Tables 4 and 5.

RFG, functional group equivalent weight (FGEW) and structural similarities to RFG of concern: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the RFG and FGEW criteria. The polymers in this study do not contain the reactive functional groups set forth in the PLC criteria (e.g., acrylates, alkoxysilanes, amines, aziridines, carbodiimides, and so forth; see Supporting Information: Chapter 3). Given that the polymers in this study have no RFGs, the FGEW values in Tables 4 and 5 are very large numbers (such as $>10^4$–10^5) or the value given is not applicable due to the lack of RFGs altogether. Even the polymers with some functional groups present (e.g., fluorinated ionomers) are not reactive. For example, the FEVE polymerization process leads by design to a polymer with neutral and/or anionic end groups. FEVE resins do contain a small amount of hydroxyl and carboxyl functional groups. These functional groups are classified as low concern RFG

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by the USEPA (1997) and OECD (2009). There are no RFG structural similarities across the polymers in this study.

Low MW leachables (MW < 1000 Da): All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the low MW leachable PLC criteria, which has been widely discussed (see Supporting Information: Chapter 3 for references). Many of the study polymers report no active leachables, whereas the rest cite values less than 1 ppm (Tables 4 and 5). For FEVE, it is reported that some non-fluorinated polymer PA may well remain in the uncured polymer resin. The methods and references for low MW leachables are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. The data presented in Tables 4 and 5 were determined for each of the respective polymers in this study using techniques such SEC and GPC as the predominant analytical methods along with the use of USP Class VI testing. Additional methods included 21 CFR 177.2600 (USCFR, 2022) and the USEPA's toxicity characteristic leaching procedure (TCLP; SW-846 Test Method 1311; USEPA, 1992).

Residual monomers and ratio of residual monomers to typical MW: PLC criteria of equal interest to the low MW leachables are the residual monomers and the ratio of residual monomers to typical MW (see Supporting Information: Chapter 3 for references). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the residual monomers and ratio of residual monomers to typical MW PLC criteria. The study data presented in Tables 4 and 5 show the polymers in this study have residual monomers ranging from less than 50 ppb for several fluoropolymers and up to less than 0.1% for PCTFE based on the methods utilized. Fluoroelastomers in this study have residual monomers ranging from less than 50 ppb up to less than 5 ppm. Residual monomers were determined in several ways including dynamic and static headspace gas chromatography/mass spectrometry (GC/MS) at 150 °C. The monomers used in most cases have very low boiling points and are thus readily volatilized (and captured or destroyed) during polymer manufacture processing and drying steps. The methods and references for residual monomer determination are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Given the very low residual monomer levels reported, the ratio of residual monomers to polymer MW range from 10^{-11} to 10^{-13} for the study polymers.

Water solubility and octanol/water partition coefficient (K_{ow}): The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in this study are solids that are hydro- and oleophobic, practically insoluble in both water and n-octanol. Therefore, a K_{ow} cannot be computed and is not applicable to these substances. It is worth noting that the practical lack of solubility in water (<10 mg/L) and n-octanol indicate the inability for the study fluoropolymers to actively or passively cross cell membranes. This does mean there is no indication that these polymers can bioaccumulate or bioconcentrate in biota (Henry et al., 2018 and this study). The methods and references for solubility are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

Particle size: To meet the PLC assessment criteria for particle size, a powder must be 5 µm or greater in size (median mass aerodynamic diameter [MMAD]). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the particle size PLC criterion. As shown in Tables 4 and 5, the fluoroelastomers in this study are provided in sheets, blocks, pellets, or "crumb," and the fluoroplastics and specialty fluoropolymers in this study are provided in the form of powders, pellets, sheets, flake, or in dispersions. References and additional information regarding the form of the study polymers is provided in the Supporting Information: Chapter 4.

Stability: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria for hydrolysis, light stability, oxidative stability, and aerobic and anaerobic biodegradability (e.g., breakdown into species with Mn <1000 Da). Public literature has abundant thermal, chemical, and biological stability data for the polymers in this study as stability is a hallmark property for these polymers (Ebnesajjad, 2017). For biodegradation, the assessments were largely made based on property data of the study polymers demonstrating they are insoluble and stable in environmental media and thus are not expected to be bioavailable and therefore not biodegrade.

Additionally, published literature reports (Drobny, 2016; Ebnesajjad, 2017; Grot, 2013; Henry et al., 2018; Polymer Industry Association [PIA], 2019) that the study polymers are stable at foreseeable maximum continuous use temperatures presented in Tables 4 and 5. All polymers, including fluoropolymers can degrade when misused or when heated above their recommended use temperatures (Fluoropolymer Products Group of Plastics Europe [FPG], 2012; PIA, 2019). Of course, users are expected to follow guidance for use provided by manufacturers. Hence, the recommended temperatures for reasonably foreseeable use for the study substances are presented in Tables 4 and 5. References and additional information regarding the stability of the study polymers is provided in the Supporting Information: Chapter 4.

Fluorinated PA: If a fluorinated PA was used in the manufacture of the polymer, it was reported for each fluoropolymer in this study. Nine of the 14 fluoropolymers in the study were reported *not* to have used a fluorinated PA in their manufacture. It is industry practice to use fluorinated PAs when it is necessary to obtain specific end-use property or performance requirements generally related to very high-polymer MWs (see also Supporting Information: Chapter 7). For five study polymers, THV, FKM, FFKM, fluorinated ionomers, and amorphous fluoropolymers, a response of "Yes and No" was provided indicating that for some polymer grades a fluorinated PA is used, but not for others. See Supporting Information: Chapter 4 for additional information.

Results summary: This study examined three fluoroelastomers, nine fluoroplastics, and two specialty fluoroplastics:

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ionomers and amorphous. Data for each were gathered from the author companies and assessed by the PLC criteria applicable to the polymer itself "in use" (BIO by Deloitte, 2015; Henry et al., 2018; OECD, 2009). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria based on the data presented in Tables 4 and 5 with additional details provided describing methods and references in the Supporting Information: Chapter 4.

Including the four fluoroplastics in the prior study (Henry et al., 2018), data for 18 fluoropolymers have been provided for PLC assessment. These polymers have a wide range of compositions and structures and represent most of the global commercial fluoropolymer market (see additional text in the Discussion). These 18 fluoropolymers represent the major fluoropolymers manufactured and are used worldwide in innumerable critical end-use products and applications. Tables 1 and 2 highlight examples of the end-use markets as well as critical functionality and benefits these polymers provide.

Each of the assessed polymers in this study are insoluble in both water and n-octanol, and thus K_{ow} is not applicable. This lack of solubility in water and octanol confirms that fluoropolymers are not mobile in the environment and are not bioaccumulative and not able to bioconcentrate. The stability studies reported here on each of the study fluoropolymers reveal their stability in terms of light, hydrolysis, heat, oxidation, and biodegradation. When coupled with the lack of solubility, these fluoropolymers are most often characterized as relatively inert materials in the environment. Like any other chemical material or product, it is important to follow the fluoropolymer manufacturer's recommended use and temperature conditions. Tables 4 and 5 describe these recommendations for each fluoropolymer. As reported, the physical forms of the fluoropolymers are largely pellets, blocks, crumb, sheets, some powders (all with MMAD >5 μm). The solid fluoropolymers are not nanoparticles, and concerns related to nanoparticles do not apply during normal product use. Due to the properties described above for the assessed fluoropolymers—large molecules with no water solubility—the fluoropolymers are biologically inert without the practical ability to cross cell membranes.

During the evaluation of the study fluoropolymers, there was a conscious focus on several core PLC parameters: MW, low MW leachables, % oligomers, and residual monomers, which are direct outcomes related to fluoropolymer manufacturing. In addition to what is reported here in Tables 4 and 5 for the fluoropolymers themselves, industry efforts to manage emissions during manufacturing are discussed below.

DISCUSSION

Fluoropolymers have substantial, unique societal value: Fluoropolymers possess a remarkable combination of properties and functional characteristics, as shown in Tables 1 and 2, that make them valued materials of choice in a broad range of industries and applications critical to life and a sustainable environment in the 21st century. Their unparalleled combination of properties and performance characteristics deliver functionality to a wide variety of products and systems critical to achieving important societal goals (Amcham, 2020c; FPG, 2021a; Wood, 2020b). They are strategically important to innovation in vital sectors of the global economy requiring high-speed, high-volume data transmission, miniaturization, or operations in extreme temperatures. Moreover, they are crucial to achieving important societal goals such as decarbonization, renewable energies, and/or competitiveness in the digital transition (FPG, 2021a). Fluoropolymers are indispensable for critical applications in the chemical, electronic, semiconductor, healthcare, and transport sectors and the deployment of 5G networks (FPG, 2021a). For many critical applications, fluoropolymers are the material of choice because alternatives are unable to provide the full complement of performance and functionality required. As such, there are currently no viable commercial alternatives to fluoropolymers in virtually every critical application in which they are used (FPG, 2021a, 2017; PFP, 2020).

Commercial fluoropolymers in this study meet the PLC criteria: Widely used by regulators, PLC criteria have been established around the world and documented by OECD expert groups as an appropriate hazard assessment methodology for polymers in-use and can effectively identify low risk fluoropolymers to help prioritize regulatory action (BIO by Deloitte, 2015; OECD, 1993, 2009). Here, we present PLC data, for hazard assessment, that define a group of fluoropolymers' "in-use" properties. PLC is not a comprehensive life-cycle assessment tool. Full life-cycle assessments consider all phases of product "life" including creation (manufacturing) and end-of-life (disposal). Information on manufacture and end-of-life is provided later in this study. Recently, polymers have been under increased regulatory scrutiny. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a Conceptual Framework for Polymer Risk Assessment ("CF4Polymers"; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessment. They specifically support the findings of Henry et al. (2018) and state that they are "unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS" (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria to identify PRR under REACH (Wood, 2020a). The report states that the authors consider fluoropolymers meeting the criteria to be considered PLC, "following the recommendations of Henry et al. (2018)."

The properties and characteristics of fluoropolymers are anchored in the strength of the carbon–fluorine bond, which

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render them highly stable (thermally, chemically, and biologically), inert, and durable—long lasting in use—under exacting and high-performance conditions. Physical, chemical, thermal, and biological stability are important criteria for a polymer to be considered a PLC. The data presented in Tables 4 and 5 demonstrate that commercial fluoropolymers from the author companies meet the criteria to be considered PLC. The PLC criteria for physicochemical properties reflect the state of the polymers in this study, solids, as well as their inertness and stability. None of the fluoropolymers assessed in this study were soluble in water or octanol. They are biologically inert, insoluble in water and octanol, and not expected to move in or between environmental media. Fluoropolymers are also twice as dense as water. These properties and water insolubility mean fluoropolymers are not mobile in the environment and therefore would not be expected to be found in sources of drinking water. Fluoropolymers are neither bioavailable nor bioaccumulative. These solid polymers cannot be absorbed through a cell membrane via passive or active transport and do not bind or interact with the cell surface (see also Supporting Information: Chapter 8). In addition, whereas aquatic and mammalian toxicology studies of fluoropolymers may be desirable for some, they are technically difficult for insoluble, solid, high-MW polymers. The OECD test guidelines reiterate this in many cases. This is confirmed for example in REACH Annex VII guidance, which repeatedly states toxicity is unlikely to occur "if a substance is highly insoluble in water or the substance is unlikely to cross biological membranes" (see Supporting Information: Chapter 9).

Finally, structure criteria including MW, MWD, residual monomer(s), oligomers, and other synthesis by-products, as represented by low MW extractables and leachables have been determined for the fluoropolymers presented and meet values established for the PLC criteria and regulated uses (e.g., USP). The concentrations in the fluoropolymer that have been evaluated are extremely low, reflective of effective manufacturing processes that minimize these compounds complemented by capture and/or destruction systems for such materials. For additional information, see the section below discussing responsible manufacturing. This study and prior work (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on additional commercial fluoropolymers to determine if they too meet the PLC criteria.

Fluoropolymer stability, aka persistence, is not an intrinsic hazard: Fluoropolymers are stable, inert, solid materials. Fluoropolymers resist degradation by acids, bases, oxidants, reductants, photolytic processes, microbes, and metabolic processes; for this reason, they are thermally, chemically, and biologically highly inert. Fluoropolymer stability was presented in the introduction and is further considered in the Supporting Information: Chapters 4 and 5. Fluoropolymers are not expected to degrade under environmental conditions or normal use and processing conditions (Wood, 2020a). They are stable and remarkably durable and are therefore persistent. However, persistence alone does not imply that there is a present or future risk to human health or the environment (Rüdel et al., 2020). Persistence itself is not an intrinsic hazard, as it does not in itself imply or inform the potential for an adverse effect (aka toxicity). There is no language in REACH supporting the notion that persistence alone justifies risk-management measures. REACH has regulated persistence in combination with other properties that do inform potential hazards. In fact, REACH combines persistence with bioaccumulation and toxicity (or "very persistent" with "very bioaccumulative/very mobile" vPvB/vPvM) to justify designation as a substance of very high concern (SVHC) and consideration of potential risk-management measures for uses associated with unacceptable risk. Therefore, persistence on its own does not justify the need for specific risk-management measures. Fluoropolymers themselves are persistent, but they are not bioaccumulative, not mobile, and not toxic and therefore not SVHCs from a regulatory perspective (Ruwona and Henry, 2021).

PFAS grouping and segmentation—Scope of regulatory measures: The OECD definition of PFAS is based only on chemical structure (OECD, 2021). It describes a universe of fluorinated organic substances with vastly different physical, chemical, and biological properties, including polymers and nonpolymers; solids, liquids, and gases; highly reactive and inert substances; soluble and insoluble substances; and volatile and involatile substances and is too broad to allow effective, science-based assessment and regulation of chemical compounds as an entire group (Amcham 2020a; BDI, 2021; Buck et al., 2021; Orgalim, 2021; Wallington et al., 2021). A 2021 OECD report states: "it is highly recommended that such diversity be properly recognized and communicated in a clear, specific and descriptive manner" and "the term 'PFASs' does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene aliphatic carbon moiety" (OECD, 2021).

In this context, the available property data (Tables 4 and 5) reveal that fluoropolymers have distinctly different properties from nonpolymeric PFAS and from SCFPs that have a polymeric backbone that does not contain C–F bonds directly attached to it. The perfluoroalkyl moiety in SCFPs is found in a side-chain connected via a functional group to the polymer backbone and "can potentially lead to the formation of nonpolymer PFAS as a result of degradation" (Fluoropolymer Products Group of Plastics Europe [FPG], 2021b; Wood, 2020a; see Supporting Information: Chapter 6). Segmentation that clearly differentiates the broad PFAS family according to their properties, rather than using a structure-based classification alone (OECD, 2021), is needed for a scientifically sound, risk-based regulatory approach. Regulating all PFAS as one homogenous group (ECHA, 2020) absent consideration of their properties, particularly when the properties are so demonstrably different, neglects basic scientific consideration of these properties,

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which are the foundation of substance differentiation. The USEPA does not consider all PFAS to have similar risk profiles and therefore they are following a categorical grouping approach based on information about similarities in structure, physicochemical properties, and existing test data on the toxicity of PFAS (USEPA, 2021b). Therefore, segmentation based on properties should be conducted before performing any grouping-based risk assessment, placing stable, nonhazardous fluoropolymers that meet the criteria to be considered PLC in a separate category (see also Supporting Information: Chapter 6).

Fluoropolymer market perspective: The commercial fluoropolymer global market sales have been reported to be approximately 230 000 MT (Dams & Hintzer, 2017). Given the expected fluoropolymer market growth, ranging from approximately 4%–5% to 7%–8% (Allied Market Research [AMR], 2022; Future Market Insights [FMI], 2022; FPG, 2021a; Globe Newswire, 2021), a pro forma market table was created for 2021 using a 5% growth rate. Adding ionomers as well as updated amorphous market information (company data) to the above, the total commercial fluoropolymer market sales is estimated to be approximately 330 000 MT in 2021 (see Supporting Information: Chapter 10). Four fluoropolymers: PTFE, FEP, PFA, and ETFE, were the focus of the first fluoropolymer PLC paper (Henry et al., 2018) and account for approximately 64% of fluoropolymers sold globally in 2021 (pro forma basis). The sales volume of these four fluoropolymers is represented by the first four bars in Figure 10.1 in Supporting Information: Chapter 10. This study discusses 14 fluoropolymers representing an additional 32% (pro forma basis) of the global fluoropolymer market. Therefore, this study, in combination with Henry et al. (2018), presents PLC data from the cited manufacturers of commercial fluoropolymers representing approximately 96% of the global commercial fluoropolymer market that meet the criteria to be considered PLC. The projected 2021 sales volume of the major types of commercial fluoropolymers covered in this study (PVDF, FKM, FEPM, amorphous, ionomers, THV, ECTFE, PCTFE, and FFKM, EFEP, CTP, and FEVE) are also represented in Figure 10.1 in Supporting Information: Chapter 10. As noted, estimated market volumes were provided for the sum of FEPM, CPT, EFEP, and FEVE as well as a small "others" category. The fluoropolymer polyvinyl fluoride (PVF) was not covered by these two papers but is also shown in Figure 10.1 in Supporting Information: Chapter 10. Other fluorinated polymers, perfluoropolyethers, and SCFPs are not addressed in this study (see Supporting Information: Chapter 6).

FLUOROPOLYMER LIFE-CYCLE CONSIDERATIONS

This study focuses on the properties of the 14 selected commercial fluoropolymers themselves in-use providing data that demonstrate they meet the criteria to be considered PLC. Additionally, the life-cycle stages of fluoropolymer creation (manufacturing) and disposal at the end of industrial or consumer use (end-of-life) are important to consider. The primary focus in these life-cycle stages is generally nonpolymer PFAS from the manufacturing process or fluoropolymer degradation in end-of-life disposal (ECHA, 2020; FPG, 2021a; Guelfo et al., 2021; Lohmann et al., 2020).

The long-established life-cycle assessment approach to environmental protection and risk management first considers the extent of emissions, their toxicity, and their exposure potential (Guinee et al., 2011). When emissions are sufficiently large in scope, toxicity, and exposure potential, emission-management methods are then considered, including process input changes and emission controls to reduce or eliminate the risk of the emissions. Fluoropolymer manufacturing and disposal life-cycle stages were discussed in the paper that first presented fluoropolymer PLC data (Henry et al., 2018). Here we provide an update and current perspective.

Responsible manufacturing: As corroborated by the data presented here and in prior work (Henry et al., 2018), a large volume percentage and number of commercial fluoropolymers are manufactured that meet the criteria to be considered PLC. Emissions from fluoropolymer manufacture are a key product life-cycle focus. The main focus during the manufacturing phase is not directly related to fluoropolymers but from emissions. Emissions of concern may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended by-products formed during manufacturing. It is important to note that, although some high-MW fluoropolymers require use of a fluorinated PA in manufacturing (see also Supporting Information: Chapter 10), it has been reported that at least 50% of commercial fluoropolymers are made without one (Pro-K Fluoropolymer Group, 2021).

Recently, a group of fluoropolymer member companies of FPG voluntarily committed to responsible manufacturing principles through the commissioning of a Regulatory Management Option Analysis, developed by independent consulting firm Chemservices (FPG, 2021a). Member companies of this group are working on individual projects and joint projects at the trade association level with third-party experts. Specifically, companies have committed to continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of nonpolymer PFAS PAs and/or working with downstream users to increase the recyclability and reuse of its products in line with the objectives of circular economy (FPG, 2021a). Implementation of this voluntary industry initiative to address concerns relating to fluoropolymers will strengthen already ongoing efforts performed by the fluoropolymer industry promoting responsible manufacturing practices. In addition, member companies are committed to working with EU authorities to establish and implement technical actions to guarantee adequate control of the risks derived from the manufacture and use of fluoropolymers to mitigate such risks wherever possible. This will be done following

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transparency principles and agreements to monitor progress. For example, important emission reduction has been demonstrated by major fluoropolymer manufacturers including fluorinated PA recovery for reuse, 99% removal of fluorinated PA in wastewater treatment, and 99.99% capture and destruction efficiency of gaseous emissions routed to a thermal oxidizer (Chemours, 2021c), as well as 99–99.9 plant emission reductions (Daikin, 2021c, 2022). Four other companies have reported replacement of fluorinated PAs with nonfluorinated PAs (Arkema, 2008, 2021b; Chemours, 2022; Gujarat Fluorochemicals Limited, 2022; Solvay, 2022). These are substantial efforts toward mitigating emissions associated with fluoropolymer manufacturing being worked on by fluoropolymer manufacturers. This study and the prior study (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on their commercial fluoropolymers in-use demonstrating that they meet the PLC criteria.

End-of-use: At the end of industrial or consumer use, fluoropolymers may be disposed via the following routes: landfill, incineration (e.g., waste-to-energy [WTE] facilities), or reuse/recycling. There is considerable data demonstrating that fluoropolymers such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern (FPG, 2021a; Hintzer & Schwertfeger, 2014). FPG member companies are working with the industry and end users on this subject and are engaged in a research project aimed at identifying conditions required for proper disposal (incineration) of fluoropolymers (FPG, 2021a).

Fluoropolymers are chemically, thermally, and biologically stable (Henry et al., 2018; this study) and therefore are not expected to transform to dispersive nonpolymeric PFAS when disposed of in a landfill. A recent study presented results from OECD guideline biodegradation studies demonstrating that PTFE is stable and does not degrade under environmentally relevant conditions (Ruwona and Henry, 2021). Further, fluoropolymers that meet the criteria to be considered PLC, such as those in this study and prior work (Henry et al., 2018), have negligible leachables, unreacted monomers, and oligomers most likely destroyed in fluoropolymer use processing and would therefore not be expected to significantly contribute to landfill leachate (Ruwona and Henry, 2021).

Available data reveal that fluoropolymers are mineralized (i.e., all C–F bonds broken, hydrofluoric acid generated, and scrubbed to calcium fluoride) under commercial WTE incineration operating conditions (Aleksandrov et al., 2019; Bakker et al., 2021; DEC, 2021; Giraud et al., 2021a, 2021b). In recent pilot scale studies representative of full-scale WTE facilities, the most common form of end-of-life destruction conducted on PTFE found that combustion converted the fluorine into controllable hydrogen fluoride gas and that, of the 31 PFAS studied, no fluorine-containing products of incomplete combustion were produced above background levels (Aleksandrov et al., 2019). Further, a recent study investigating the presence of PFAS in waste incinerator flue gas stated: "based on a literature review, RIVM expects that most of the PFASs will largely degrade during the incineration process and then be removed when the flue gases are cleaned. The remaining PFASs are expected to be removed during the recovery of the carbon dioxide" (Bakker et al., 2021). The RIVM report affirmed that PTFE is the most stable fluorine-containing polymer. For PTFE, the RIVM report concluded that complete thermal decomposition is achieved at a temperature of approximately 800 °C. It was therefore assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 800 °C. Temperatures at the pyrolysis front and the combustion front in the waste-burning bed range from 900 °C to 1100 °C (Asthana et al., 2006; Ménard et al., 2006), which is well above 800 °C, the temperature at which the complete thermal decomposition of PTFE is achieved (Bakker et al., 2021). Studies for additional fluoropolymers and those with additional pilot and/or full-scale fluoropolymer studies would contribute to this body of data and further affirm their results. The PFP and FPG currently have joint projects working on these potential contributions.

Recycling of fluoropolymer products and articles containing fluoropolymers is difficult because separation of the fluoropolymer from the end products is not always possible (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). This is because fluoropolymers are used predominantly in small components of larger finished articles involving a wide variety of materials. There are several options to recycle fluoropolymer products. In primary recycling, solid fluoropolymer waste is ground and later fed back into the manufacturing cycle of some fluoropolymer products. Recycled fluoropolymers may be used in high-end applications when correctly collected, cleaned, and reprocessed. In secondary recycling, solid fluoropolymer waste is ground, followed by degradation to approximately 1% of the original degree of polymerization by using electron beams, gamma rays, or thermomechanical degradation. The recovered material can be used in the manufacturing of new fluoropolymer products. Lastly, in tertiary recycling or upcycling, solid fluoropolymer is ground, then decomposed into the starting monomers at temperatures higher than 600 °C (pyrolysis) to obtain the same chemical components from which the fluoropolymer was manufactured; monomers, such as tetrafluoroethylene, are purified by distillation, and can then be reused to manufacture new fluoropolymer (3M, 2021; Schlipf & Schwalm, 2014). For the primary and secondary schemes, recycling treatments can be undertaken by the manufacturers of fluoropolymers themselves (onsite), or at a larger scale, mainly by specialist recycling companies. The upcycling needs to be colocated to a fluoropolymer manufacturing plant that can use tetrafluoroethylene.

Primary and secondary recycling is limited because of the presence of fillers, colorants, and other materials in the composition of their final articles. Further, recycling might not work for all end-of-life components, as they are used predominantly in small components of larger

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finished articles involving a wide variety of materials. Therefore, collecting and dismantling for recycling might not be feasible for all products (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). However, it should be noted that upcycling treatment is applicable to some articles containing fluoropolymers, such as pipe liners in chemical plants, as well as other plant components such as pumps, tank liners, seals, hoses, compensators, and many other fluoropolymer components and systems. These are the products for which the high quantities of fluoropolymers are used offering significant recycling potential.

SUMMARY

This study has described the composition, uses, performance properties, and functionalities of 14 commercially available fluoropolymers, including fluoroplastics and fluoroelastomers. Fluoropolymers are the preferred material of choice because of their unique combination of properties, which are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for society and are useful to modern living, as they provide vital, reliable functionality to a broad range of industrial and consumer products. Further, the study has presented data demonstrating the subject fluoropolymers satisfy the widely accepted polymer hazard assessment criteria to be considered PLC. The data presented demonstrate the fluoropolymers in the study are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic, and contain low levels of impurities. These results further demonstrate that the fluoropolymer class should be considered distinctly different and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with earlier work (Henry et al., 2018), the study demonstrates that commercial fluoropolymers are available that meet the criteria to be considered PLC, which represent approximately 96% of the global fluoropolymer market. Lastly, emissions from fluoropolymer manufacture and disposal at end-of-use are a product life-cycle focus. Emissions may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended by-products formed during manufacturing. Fluoropolymer manufacturers recently committed voluntarily to responsible manufacturing principles by continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of fluorinated PAs, and/or increasing recyclability and reusing fluoropolymers in line with the objectives of circular economy.

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CONFLICT OF INTEREST

The authors are employed by companies that commercially manufacture fluoropolymers. SHK is an independent fluorotechnology consultant working on behalf of AGC Chemicals Americas Inc. and principal of BeachEdge Consulting LLC.

DATA AVAILABILITY STATEMENT

Data gathered for this paper is presented in the paper itself and the Supporting Information: Data file provided. Additional data are available upon request from the corresponding author Stephen Korzeniowski ([redacted]@gmail.com).

SUPPORTING INFORMATION

The Supplement contains a glossary of terms as well as additional information on the study of fluoropolymers properties and functionalities, polymer of low concern (PLC) background and criteria, references and methods for the PLC data for the study of fluoropolymers, benefits, features and alternatives assessment for the study of fluoropolymers, the differences between fluoropolymers and side-chain fluorinated polymers, fluoropolymer bioavailability and toxicity studies, fluoropolymer global market information, fluoropolymer socioeconomic analyses and risk-management options analysis (RMOA).

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Critical Use of Fluoropolymers in the Functioning of Modern Society

*Jaime Sales, Michael Schlipf and Deepak Kapoor**

In the context of the upcoming restriction of PFAS, there appears to be significant confusion concerning the most relevant sectors where fluoropolymers are used. This paper intends to clarify that fluoropolymers are used mainly in industrial sectors of high value to society. The outstanding combination of properties that fluoropolymers exhibit makes them extremely valuable materials in a wide variety of applications. While there have been some historic uses in consumer applications, these uses are currently anecdotic, particularly for those linked to very dispersive uses (which excludes use in cookware), and represent a minute proportion of the overall uses when compared to industrial applications, where fluoropolymers' outstanding properties are capitalized on. Fluoropolymers contribute decisively to the progress and well-being of society in five key areas: safety & well-being, environment and circularity, decarbonization, performance and comfort, being the latter the only one that can be attributed to dispersive consumer applications.

I. Introduction

For many years, Per- and polyfluoroalkyl substances (PFAS) have been at the centre of the regulatory debate in many jurisdictions. In Europe, this became even more intense in 2020, after 5 Member States of the European Economic Area expressed an intention to file a restriction proposal under the REACH Regulation on all PFAS.[1] Since then, different debates have taken place involving various stakeholders, trying to clarify which specific chemicals would be impacted by the restriction, and to which extent. The definition[2] used by regulators to define the scope of the proposal leads to approximately 10,000 chemicals potentially under the umbrella of this initiative. The fact that PFAS can be categorised in a significant variety of different sub-groups or sub-families requires certain technical knowledge to fully understand such differences and what is more, the different areas of applications of the components of those sub-groups, which can involve completely opposite fields of application.

Fluoropolymers are a differentiated sub-group in the PFAS universe, pertaining to the group of polymeric PFAS. Even in this group, they can be clearly separated from other polymers due to their composition and structures.[3] These differences apply also to the sectors in which the different materials covered by the PFAS definition can be used. For example, while fluoropolymers are used mainly in industrial applications, other fluorinated polymers (e.g., the so-called Side Chain Fluorinated Polymers) see extensive use in dispersive consumer applications, such as textiles, upholstery, leather, apparel and carpets (TULAC).

Due to their highly valuable properties (e.g., non-stick, temperature resistant, and durability) fluoropolymers have also seen some use in applications with potential consumer contact. The most classical

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1 ECHA, 'Five European states call for evidence on broad PFAS restriction' (2020) ECHA/NR/20/13 <https://echa.europa.eu/-/five-european-states-call-for-evidence-on-broad-pfas-restriction> accesed 1 May 2023.

2 OECD, Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs)' (2020) Series on Risk Management No. 39. Organisation for Economic Co-operation and Development.

3 Jaime Sales, Francisco Hernández, Deepak Kapoor, Marcel van den Noort, 'Fluoropolymers: The Safe Science That Society Needs' (2022) 5 International Chemical Regulatory and Law Review 1, 13-23.

one is the use for coating frying pans to grant anti-adherence properties, or in professional or technical clothing.[4] Direct consumer uses of fluoropolymers are possible, such as in cosmetics,[5] ski waxes [6] or as lubricant for chains in bicycles.[7] However, taking into consideration all the possible applications in which fluoropolymers are used, the contribution of dispersive consumer uses is minimal. Nonetheless, it appears that the relevance of those consumer uses in the regulatory discussion has been disproportionately magnified in comparison with the more critical industrial uses, which are frequently ignored or hidden by certain stakeholders.

Under REACH the correct reporting of the uses of a substance is essential to properly assess the risks associated with its use. Besides manufacture and formulation, the so-called 'end uses' need to be reported. According to ECHA Guidance,[8] 'end-use' means the use of a substance as such or in a mixture, as a last step before the end-of-life of the substance, namely before the substance is consumed in a process by reaction during use (including intermediate use), is emitted to waste streams or the environment or is included into an article. The corresponding definitions of the different end-uses following ECHA Guidance are as follows:

- **Use at industrial site**: All end-uses of the substance (as such or in a mixture) carried out at industrial sites should be reported under this life cycle stage.
- **Widespread use by professional workers**: Widespread uses by professional workers correspond to uses carried out in the context of commercial activities and assumed to take place in most towns of a certain size, by multiple actors each at low scale e.g., local garage, small cleaning businesses.
- **Consumer use:** All end-uses of the substance as such or in a mixture carried out by consumers can be reported under the consumer use life cycle stage.

However, if the substance becomes part of an article, the subsequent life cycle stage (the service life) is to be considered additionally, as follows:

- **Service life**: For a given substance incorporated into an article, the service life is considered to be the period of time an article remains in service (or in use). Articles containing the substance can be used or processed by consumers, by workers at industrial sites and/or by professional workers.

Based on these definitions, the use of frying pans coated with fluoropolymers is not a consumer use; instead, the use of those pans has to be evaluated as a service life. In contrary to the use of a frying pan coated with fluoropolymers uses like cosmetics, ski waxes or bicycle chain lubricants are direct consumer end-uses.

II. Reasons Why Fluoropolymers are Used and Benefits They Provide

The properties that fluoropolymers provide are well known and have been discussed previously by different authors[9] and can be summarised as follows:

- Inertness and non-reactivity; high resistance to corrosion and chemical attack.
- Low and high temperature resistance: with a range as large as -263°C to +260°C for Polytetrafluoroethylene (PTFE).
- Very low coefficient of friction to any solid.
- Low and ultra-low permeation rates.
- Ultraviolet radiation (UV) resistance.
- Excellent electrical insulation, low dielectric constant, low variations of conductivity.
- High level of fire safety; no flame propagation and low smoke generation.

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4 Performance Fluoropolymer Partnership, 'Consumer Products' (2023) <https://fluoropolymerpartnership.com/fluoropolymer-applications-and-uses/consumer-products/> accessed 1 May 2023.

5 US FDA, 'Per and Polyfluoroalkyl Substances (PFAS) in Cosmetics' (2022) <https://www.fda.gov/cosmetics/cosmetic-ingredients/and-polyfluoroalkyl-substances-pfas-cosmetics> accessed 1 May 2023.

6 Wood Group, 'Update of market data for the socio-economic analysis (SEA) of the European fluoropolymer industry' (2022) <https://fluoropolymers.plasticseurope.org/application/files/1216/5485/3500/Fluoropolymers_Market_Data_Update_-_Final_report_-_May_2022.pdf> accessed 1 May 2023.

7 Juliane Glüge, Rachel London, Ian T. Cousins, Jamie DeWitt, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Mark Miller, Carla A. Ng, Sharyle Patton, Xenia Trier, Zhanyun Wang, and Martin Scheringer, 'Information Requirements under the Essential-Use Concept: PFAS Case Studies' (2022) 56 Environ Sci Technol 10, 6232–6242.

8 ECHA, 'Guidance on Information Requirements and Chemical Safety Assessment' (2015) 12.

9 Barbara J Henry, Joseph P Carlin, Jon A Hammerschmidt, Robert C Buck, L William Buxton, Heidelore Fiedler, Jennifer Seed and Oscar Hernandez, 'A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers' (2022) 14 Integrated Environmental Assessment and Management 13, 316–334; Chemservice, 'Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use' (2022).

- High and ultra-high purity with extremely low leach out properties.
- Stress-crack and cut-through resistance.
- Flex fatigue properties enabling thermal expansion/contraction in temperature cycles.
- Biocompatibility.
- High Flex life.
- Durability.
- Hydrophobicity; neither water nor water-containing substances wet fluoropolymers, providing excellent repellent properties to many chemicals.
- Non-stick, and consequently non-fouling properties, along with sufficient bonding in certain multilayer applications.

The benefits that the use of fluoropolymers bring to the different applications in which they are used, based on the combination of the properties described above, can be categorised in mainly 5 groups.

1. Safety

Fluoropolymers are materials known for their outstanding chemical resistance. They can resist attack from virtually any chemical, particularly strong acids, bases and other corrosive substances. In parallel, they are also resistant to high and low temperatures, allowing high reliability in a broad temperature range. This grants fluoropolymers their extreme durability. Due to this combination of properties, fluoropolymers are essential materials in, for example:

- **Chemical processing industry**: whenever harsh chemicals or stringent conditions of use are required (e.g., high temperature operations), fluoropolymers are the material of choice. They ensure reliability of systems which, in case of failure, could result in high-risk situations for workers or the environment, due to potential leakage, spills or releases of highly corrosive substances at very high temperature.
- **Aerospace industry**: fluoropolymers are used for insulation of electrical and data transmission cables. These cables can be subject to extreme conditions where ensuring reliability is critical. As an example, it is estimated that around 300 km cables are needed in regular commercial airplanes, reaching close to 500 km in some of the most modern planes. These cables need to perform in variable conditions, such as high temperatures near the engine and low temperatures in areas close to the external part of the fuselage at high altitudes. On top of this, exposure to aggressive oils is to be expected for these cables. Any malfunction of the electrical system will lead to high-risk situations for passengers and crew. Fluoropolymers provide the best performance, particularly due to their excellent dielectric properties that prevent electric arc fires in cables. As an example, the case of the Swissair 111 flight that crashed near Peggy's Cove, Nova Scotia, on the night of 2 September 1998, resulting in the death of 215 passengers and 14 crew members can be highlighted. The conclusion from the accident investigation report[10] concluded that the accident was caused by a fire generated by electric arc effect, most likely via electrical cable associated with the in-flight entertainment network. It was determined that aircraft certification standards for material flammability were inadequate. It is also worth mentioning that fuel systems in aircrafts are based on fluoropolymer lined equipment, as they are stable in a kerosene environment.

The high chemical resistance of fluoropolymers, combined with smooth surfaces and extremely low amount of leachables, brings about enhanced durability and prevents degradation potential during use. This allows these materials to guarantee high purity of process streams that are handled with the aid of fluoropolymer-based products (e.g., pipes, tubes, pumps, valves, joints, gaskets, seals, o-rings). As previously discussed, this is relevant for the chemical processing industry. But high purity is also critical to ensure safety conditions in other areas, for example:

- **Pharmaceuticals**: the production of medicines and vaccines require highly pure streams avoiding contamination that may come from process equipment, due to degradation from wear or to the effect of aggressive chemicals. Failure to grant this property could result in undesired health effects for the general public via contamination. Furthermore, the fact that articles based on fluoropolymers can be cleaned at high temperatures provides an advantage in front of other materials

10 TSBC, 'Transportation Safety Board of Canada. Swissair 111 Investigation Report - Executive Summary' (2003) <https://www.tsb.gc.ca/eng/medias-media/fiches-facts/a98h0003/sum_a98h0003.html> accessed 1 May 2023.

that may be used in the pharma sector such as glass, which has a tendency to break.
- **Food processing**: a wide variety of food processes must be handled via complex equipment. From conveyor belts to tubes transferring liquids (e.g., coffee machines), fluoropolymer-based equipment guarantees high purity of food avoiding contamination with impurities that could otherwise reach humans. Here, fluoropolymers' outstanding non-stick properties due to their very low coefficient of friction play a key role.
- **Water filtration**: fluoropolymers are necessary elements in membranes used in water filtration systems. The use of lower performing products could reduce the ability of those membranes to ensure clean water that may later be consumed by the general population. Water systems are frequently cleaned with chlorine under pressure. While most materials tend to hold on to bacteria and algae, this is not the case of fluoropolymers.
- **Medical implants**: perhaps the most evident proof that fluoropolymers are intrinsically safe is that they are the material of choice for a variety of medical implants, including cardiovascular stents, patches and other products that are introduced in the human body and intended to remain there for a long time. It therefore becomes evident that fluoropolymers play a vital role in safety of humans.

2. Decarbonization

Fluoropolymers are critical materials that enable the EU Green Deal. Without these materials, key technologies that are expected to help Europe to achieve its ambitious energy transition will not be available, or their efficiency will be seriously compromised. Some examples are the following:
- **Lithium-ion batteries**: fluoropolymers are used as electrode binders and separator coatings in these batteries, providing interconnectivity within each electrode. This facilitates electronic and ionic conductivity, increasing the cell manufacturing productivity and the cell safety. Fluoropolymers offer unparalleled cohesive and adhesive properties under high voltage, allowing for closely packed cathode active materials for high density electrodes. With the use of fluoropolymers, different battery components can be packed more closely together, improving the energy efficiency of a single unit, and helping reduce overall size.
- **Proton exchange membranes in green hydrogen**: electrolysers and fuel cell membranes are used in the production of green hydrogen by an electro-chemical reaction. To enable the movement of protons from the anode to the cathode side of the fuel cell, a proton exchange membrane made of fluoropolymers is used due to the efficiency and unique durability, chemical and temperature resistance properties that fluoropolymers offer for this application.
- **Renewable energies**: fluoropolymers improve the efficiency and durability of photovoltaic panels used in solar energy, as well as for wind turbines.
- **Lambda sensors in automotive**: fluoropolymers are used in lambda sensor cables due to their resistance to high temperatures and chemicals, dielectric strength, flexibility, and electrical insulator properties. In vehicles, lambda sensors adjust the fuel amount that is sent to the engine cylinders by optimizing the air and fuel mixture, which in turn will make the engine work properly and reduce carbon monoxide emissions. Lambda sensors allow for this control system via measurement of oxygen in exhaust fumes. This is a critical element in cars and vehicles to control the rate of gas emissions by ensuring that the catalytic converter works in an efficient way. Lambda sensors ensure that the car complies with the European regulations on pollution and carbon emissions, allowing a better control of environmental emissions.
- **Heat pumps, air conditioning and refrigeration systems**: the contribution of the Heating, Ventilation, Air Conditioning and Refrigeration and hot water heating (HVACR) to the Green Deal and to the REPowerEU plan is acknowledged by the European Commission.[11] Fluoropolymers are fundamental parts in equipment and machinery used in this sector, since they ensure reliable performance. HVACR equipment is subject to continued

11 European Commission, 'Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions. A Green Deal Industrial Plan for the Net-Zero Age' (2023); European Commission, 'REPowerEU: A plan to rapidly reduce dependence on Russian fossil fuels and fast forward the green transition' (2022) <https://ec.europa.eu/commission/presscorner/detail/en/ip_22_3131> accessed 1 May 2023.

changes in temperature and pressure as well as potentially harsh chemicals (refrigerants). Efficient HVACR systems need to rely on materials that will not fail on demand and will last a long time without degradation, including sealings to avoid leakages. Efficient refrigeration also plays a role in safety since it is necessary for preservation of food and medicines.

3. Environment and Circularity

The extreme stability of fluoropolymers makes them long lasting in the applications where they are used. Most of those applications involve the use of equipment based on processed fluoropolymers, in the form of pipes, tubes, or other pieces. Fluoropolymers extend the life of the equipment and devices where they are used. This significantly contributes to the objectives of a circular economy by reducing the amount of waste that society needs to handle. Replacing fluoropolymers by other materials that would be less efficient in providing the required properties would result in reduced life span, increased need for maintenance and increased amount of waste. Since most of the inferior alternatives are also plastic or rubber materials, a ban on the use of fluoropolymers would force society to cope with significantly increased amounts of wastes of those materials. Here it is useful to underline that based on recent studies, fluoropolymer waste is estimated to represent only 0.14% of all plastic waste in Europe, and <0.01% total waste (Conversio, 2022)[12]; removing such an insignificant percentage of waste coming from fluoropolymers would dramatically increase the overall quantity of waste that would have to be managed. According to the World Business Council for Sustainable Development (WBCSD, 2023), the definition of a circular economy model must take into account 'long service life' of resources, products, parts and materials, and also keeping them in use. Under this perspective, it is unquestionable that fluoropolymers are key contributors to expanding the life span of products and to avoiding the increase of waste streams to society would eventually need to handle and manage.

12 Conversio, 'Fluoropolymer waste in Europe 2020 – End-of-life (EOL) analysis of fluoropolymer applications, products and associated waste streams' (2022).

The *construction* sector is of particular relevance when evaluating the contribution of fluoropolymers to circularity. Not only do they improve fire safety and energy efficiency of modern buildings, but they also reduce the need for maintenance, replacement and cleaning of structures built with fluoropolymer-based materials. There are a wide variety of modern buildings such as bridges, stadia and domes that have benefited from the use of modern fluoropolymer architectural and construction solutions.

4. Performance

Fluoropolymers are frequently the high-cost solution when top performance is required. Downstream users through their value chains see fluoropolymers as the only material of choice when highly demanding process conditions are required. This is intimately linked to the fact that such value chains usually lead to top of the range end-products in terms of technology or societal progress.

The *semiconductor industry* is a clear example of this. In the production of modern, high-tech microchips, particularly with extremely reduced size (indispensable in the production of modern gadgets such as small mobile phones, laptops or watches), it is absolutely necessary to ensure ultra-pure process stream – going as far as having to ensure absence of impurities to the levels of part per trillion (ppt). Lithographic processes (which are technically extremely complex) involve the use of extremely pure harsh chemicals (acids) which may easily attack process equipment made of other materials, hence liberating residuals of ancillary equipment, which may be passed to the process and ruining the whole production. Fluoropolymers are the only product class that ensure reliable and economic performance in the production of modern semiconductors.

A similar rationale can be established for *electric cables*. As in the case of aircrafts, fluoropolymers are used for insulation of high-volume data transmission cables. Modern technology (e.g., 5G) relies on top performance of the materials involved in the process. Furthermore, data centres involved in the storage and processing of information operate under extremely stringent specifications in terms of fire safety. With their excellent dielectric properties and fire resistance, fluoropolymers are practically the only reliable option to cover the high demands of this industry.

5. Comfort

Certain products that use fluoropolymers and are in direct contact with consumers are marketed for enhanced performance while this seems a disguise for better comfort. Waterproof apparel, cosmetics, ski waxes, bicycle chain lubricants would fall under that category

Frequently there is a thin line separating 'comfort' and 'safety'; for example, heating systems for seats in vehicles are based on fluoropolymer insulated electric cables. It could be argued if this feature is truly necessary for the functioning of society (a question that would likely need to be answered from the perspective that the feature is already available in most cars – hence population would need to face a downgraded in this option); but if the feature is to be maintained, efficient insulation for such cables is necessary in order to avoid fire and to prevent passengers from electrocuting. Similarly, again referring to the automotive industry, fluoropolymers are used for the manufacture of different parts of car equipment, such as door hinges and seat height adjustment bearings. These parts can be regarded as pivot points which are subject to sporadic demand while cars are running, requiring high reliability and very low friction conditions. Not providing an efficient material for this application would take car technology probably different years back and consumers would need to face squeaking and noisy driving experiences, in addition to increased maintenance, reparations and break-downs. While this property may not be necessarily linked to safety, it could be questioned whether European society is ready to accept reduced functionality in these applications which would lead to significantly reduced comfort when driving or traveling by car – or other means of transport.

Where comfort is truly the only reason for use of fluoropolymers (i.e., a 'nice to have' feature), there could be room for debate if society wishes to maintain those uses or not. The most renowned example is the use of fluoropolymers as anti-stick material in frying pans. Again, for this use it could be argued if 'comfort' alone is truly the only reason for use. Frying pans with highly anti-stick coatings allow for reduced use of oil during cooking (linked to a healthier and safer life-style), reduced use of cleaning agents (less chemicals in the environment) and improved durability of the article (helping circularity objectives). Furthermore, uses of frying pans coated with fluoropolymer are safe, because the temperatures required for decomposition of PTFE will not be reached during normal use, and food will burn before such temperatures are reached. In addition to this, in the event that small particles of PTFE may be released due to excessive use, there is no risk for health because such particles will be eliminated by the human body without any possibility of biological interaction, due to its inertness and the fact that they cannot cross biological membranes.[13] Also, those frying pans will eventually end-up in waste plants where they will be treated as metallic waste, therefore under conditions that should not result in environmental concerns. In summary, this use cannot be considered as very dispersive.

In contrast to designed functional or constructive fluoropolymer parts, dispersive uses of fluoropolymers by consumers (e.g., cosmetics, ski waxes, lubricants for bicycle chains), may eventually result in some releases of fluoropolymers to the environment. Again, the key factor is that those polymers are safe due to their nature and not pose a risk to humans or the environment. Still, if the aspiration of society is to not have these materials in the environment, it should be possible to remove such applications from the market without necessarily placing limits to the relevant industrial applications where fluoropolymers are extremely valuable for society, and where they play a significant role in enhancing safety, decarbonization, circularity, innovation and progress. For example, the already existing microplastics restriction under REACH could be a good instrument to force reduction and eventually elimination of such uses.

III. Key Sectors of Application of Fluoropolymers

The true value of fluoropolymers becomes apparent when they are used in industrial applications. Concerns expressed in the PFAS restriction proposal in relation to fluoropolymers are mainly related to low

13 Barbara J Henry, Joseph P Carlin, Jon A Hammerschmidt, Robert C Buck, L William Buxton, Heidelore Fiedler, Jennifer Seed and Oscar Hernandez, 'A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers' (2022) 14 Integrated Environmental Assessment and Management 13, 316–334

Wood, 2021 - Sector of use	Volume 2020 (MT)	Volume %
Transport	15,500	39.2%
Chemical and Power	11,000	27.8%
Electronics	3,500	8.9%
Food and pharmaceutical industry (F&P)	2,000	5.1%
Cookware	2,000	5.1%
Textiles and architecture	1,500	3.8%
Renewable energy	500	1.3%
Medical applications	500	1.3%
Other sectors, not included above	3,000	7.6%
TOTAL	39,500	

volume consumer applications of which the use is dispersive. Such applications are ultimately of very limited interest to the fluoropolymer industry, and claims are already being made that in most of those applications fluoropolymers could be a 'nice to have', but not truly necessary.[14]

Different initiatives on market research related to fluoropolymers have been performed, with the aim to provide volumes used in the different sectors in which these high value products are used.[15] However, it is difficult to get precise data on some of those consumer uses. In some occasions, such information is flagged as confidential.[16] Nevertheless, it is possible to extract valuable information from such market research activities. The following table shows the data that is available from both initiatives.

Differences in the definition of market segments used in various market research reports result in slightly different numbers. Nevertheless, for the purpose of our analysis, the information displayed on volumes clearly reflects that the major share of fluoropolymer uses is in high value, high technological sectors related exclusively to industrial applications. Putting these figures in context, it appears evident that minor consumer applications, such as uses in cosmetics, ski waxes or bicycle chain lubricants are extremely small and therefore of no interest to the fluoropolymer industry, and no significant impact is to be expected if those uses are discontinued.

IV. Conclusions

Fluoropolymers bring high value to society. This is achieved via the combination of extraordinary properties that they offer. Such value is maximised when fluoropolymers are used in industrial applications in high technology sectors. The use of fluoropolymers

14 C&EN, 'How fluoropolymer makers are trying to hold on to their business' (2023) <https://cen.acs.org/materials/polymers/fluoropolymer-makers-trying-hold-business/101/i8?linkId=100000191672537> accessed 1 May 2023.

15 Astute Analytics (2021). Global Fluoropolymers Market. Industry Dynamics, Market Size, and Opportunity Forecast for 2027. April 2021; Wood (2021). PFAS in the treatment of skis — Use, Emissions and Alternatives. Report for Miljødirektoratet/ Norwegian Environment Agency.

16 Wood Group, 'Update of market data for the socio-economic analysis (SEA) of the European fluoropolymer industry' (2022) <https://fluoropolymers.plasticseurope.org/application/files/1216/5485/3500/Fluoropolymers_Market_Data_Update_-_Final_report_-_May_2022.pdf> accessed 1 May 2023.

Astute Analytical, 2021 - Sector of use	Volume 2020 (MT)	Volume %
Industrial equipment: chemical industry	27,700	37.8%
Electronics W&C	9,450	12.9%
Industrial equipment: other	6,500	8.9%
Transport: automotive	5,280	7.2%
Industrial equipment: Semiconductors	4,515	6.2%
Household	3,840	5.2%
Batteries	3,000	4.1%
Construction	3,000	4.1%
Medical & Pharma	2,800	3.8%
Other	2,500	3.4%
Transport: aerospace	2,035	2.8%
Other electronics	1,425	1.9%
Transport: other	1,265	1.7%
TOTAL	73,310	

allows for very high standards related to protection of workers and the general population, efficient development of green energy systems, improved longevity of equipment and articles thus helping the circular economy, and outstanding performance in vital sectors that are critical to ensure Europe's autonomy and technological superiority in comparison to other global economies. In contrast, the value of fluoropolymer in some consumer applications that have been related to potential concerns is very limited and is only related to relative improvement of comfort features.

In addition to this, it should be noted that fluoropolymers have been traditionally the innovative solution of choice by many industries to improve process conditions, either related to safety, development of options to decarbonize the economy or to improve durability of materials. A ban on critical uses of fluoropolymers, or any regulatory initiative that may place barriers to the use of these low risk, high value materials will limit or slow down the speed of innovation in the EU.

Consumer uses, or uses of fluoropolymer-based products by consumers that may be regarded as dispersive (handling of which is understood to be more difficult to control in comparison with activities in an industrial set-up) are of no paramount interest to society, and while fluoropolymers are acknowledged to pose no risk themselves to human health or the environment, limitations to those uses would not result in major negative impact to the European society. Still, the fact that legislation to control such uses is already in place (e.g., via the EU REACH microplastics restriction) suggests that no further action is required, and that eventually those uses will progressively disappear from the European market. If there are societal preferences to limit such uses, a broad restriction of all uses of fluoropolymers via a REACH restriction does not appear to be neither efficient nor justified.

CHEMSERVICE

TECHNICAL REPORT:

Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use

Version 1

19 July 2022

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Executive Summary

This report describes in detail a selection of specific applications in which different fluoropolymers are used. The objective of the report is twofold; on one side, it intends to highlight the key combination of properties that fluoropolymers provide in a selection of high technology industries. On the other side, a detailed description of possible alternatives to fluoropolymers is given, and expected trade-offs related to a hypothetical substitution of fluoropolymers by such alternatives are described and justified. This aims at explaining what could be the consequences that should be expected (not only for direct industrial users, but for the European society as a whole) if the use of fluoropolymers was to be discontinued due to a potential regulatory ban that could be derived from the inclusion of fluoropolymers in the scope of the upcoming PFAS restriction under REACH.

It is worth highlighting that the scope of this report is limited to fluoropolymers as a clearly separate family of substances within the broad group of PFAS, including other polymeric PFAS such as perfluoropolyethers and side chain fluorinated polymers, which should not be confused with fluoropolymers and are definitely not in the scope of the present report.

The case studies that are described in this report are based on specific applications as reported by a selection of downstream users of fluoropolymers. Those downstream users were requested to provide information via a detailed questionnaire developed specifically for this project. Where relevant, one-to-one conferences with the respondents were set-up in order to expand on the replies provided, in order refine and expand on the information provided. This information has been complemented with publicly available literature or references with the objective to further clarify the application described.

Where available, information on expected socio-economic impacts related to a potential substitution (or lack of availability) of fluoropolymers has been provided. Information in this case has been usually sought from industry associations involved in some of the specific industrial sectors covered.

It should be noted that the applications described in this report should be considered as a reduced sample of the broad industrial sectors that rely on fluoropolymers today. Further work is expected to be developed in order to add further cases, and to expand on the socio-economic impacts of fluoropolymers for critical industrial sectors in Europe.

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List of abbreviations and acronyms

ACEA	European Automobile Manufacturer's Association
ACM	Acrylic Rubber
AEM	Ethylene acrylate copolymer
ASTM	American Society for Testing and Materials
BAT	Best Available Techniques
BPA	Bisphenol A
BPS	Bisphenol S
C/A	Chlor/Alkali
CMR	Carcinogenic, mutagenic, or toxic for reproduction
COM	European Commission
DHBP	4,4'-dihydroxybiphenyl
EEA	European Economic Area
EFPIA	European Federation of Pharmaceutical Industries and Associations
EL	Electrolyser
EPDM	Ethylene propylene diene rubber
EPR	Ethylene propylene rubber
ETFE	Ethylene tetrafluoroethylene
ESIA	European Semiconductor Industry Association
EU	European Union
EV	Electric vehicles
FEP	Fluorinated ethylene propylene
FKM	Vinylidene fluoride-hexafluoropropylene copolymer
FPG	Fluoropolymers Product Group - PlasticsEurope
GDP	Gross domestic product
GHG	Greenhouse Gases
JRC	Joint Research Centre
HFC	Hydrofluorocarbons
HFFR	Halogen free flame retardants

HFO	Hydrofluoro-olefins
HNBR	Hydrogenated nitrile butadiene rubber
HVACR	Heating, Ventilation, Air Conditioning and Refrigeration
ISO	International Organization for Standardization
MBR	Membrane bioreactor
MDI	Methylene diphenyl isocyanate
MLD	Minimal Liquid Discharge
MNB	Mononitrobenzene
MVQ	Methyl Vinyl Silicone Rubber
NBR	Nitrile butadiene rubber
NSF	National Sanitation Foundation (USA)
OECD	Organisation for Economic Co-operation and Development
PAG	Polyalkylene glycol
PAI	Polyamideimide
PBI	Polybenzimidazole
PE	Polyethylene
PEEK	Polyether ether ketone
PEI	Polyetherimide
PEM	Proton Exchange Membrane
PES	Polyether sulfone
PET	Polyethylene Terephthalate
PFA	Perfluoroalkoxy polymer
PFAS	Per- and polyfluoroalkyl substances
PLC	Polymer of Low Concern
POE	Polyester oil
POM	Polyoxymethylene
PP	Polypropylene
PPSU	Polyphenyl sulfone
pro-K	German Association for Semi-Finished Plastics and Consumer Products

PTFE	Polytetrafluoroethylene
PU/TPE-U	Thermoplastic Polyurethane
PVC	Polyvinyl chloride
PVDF	Polyvinilidene fluoride
PVE	Polyvinyl ether oil
RACHP	Refrigeration, Air Conditioning, and Heat Pump
REACH	EU Regulation 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals
RES	Renewable energy sources
R&D	Research and Development
SME	Small and medium enterprise
UHMWPE	Ultra-high molecular weight polyethylene
UV	Ultraviolet radiation
VoP	Velocity of Propagation

1. Introduction

Fluoropolymers are a separate family of fluorinated polymers, which can be clearly differentiated from other substances typically included in the Per-and polyfluoroalkyl substances (PFAS) group of chemicals. In fact, they can also be further differentiated from other polymeric fluorinated substances, such as side-chain fluorinated substances or perfluoropolyethers (FPG, 2022a). Fluoropolymers are structurally characterised by having fluorine atoms directly attached to their carbon-only backbone.

Existing scientific data demonstrates that, because of their unique characteristics such as the negligible solubility in water or the high molecular weight, fluoropolymers cannot enter or accumulate in the human bloodstream, and cannot degrade into other PFAS under intended use conditions, nor under environmental conditions at the end-of-life phase of their applications. Therefore, it is considered that fluoropolymers do not impact water quality, and do not pose a significant risk human health, or the environment (Henry et al., 2018). This allows the conclusion that by far most fluoropolymers meet the Organisation for Economic Co-operation and Development (OECD, 2009) criteria to be identified as Polymers of Low Concern (PLC). While originally the focus was placed on a set of 4 fluoropolymers, more recent research has expanded these conclusions to cover a larger number of substances, reaching an estimate of >96% volume of fluoropolymers in the global market (Korzeniowski et al., 2022).

However, since fluoropolymers match the OECD definition of PFAS, they could be included in the scope of the restriction proposal that five Competent Authorities from Member States of the European Economic Area[1] (EEA) have announced on the broad PFAS group of chemicals under the REACH Regulation[2]. Therefore, fluoropolymers could face market restrictions in the EEA if their differentiated properties are not clearly highlighted in such restriction proposal. This could even lead to a ban on the uses of these high value materials in the different applications in which they are used.

While the uses of fluoropolymers are primarily related to industrial applications, these substances are involved in value chains that have a strong impact in many sectors and articles that will eventually reach end-users. Fluoropolymers also play a key role in enhancing key avenues of progress that have been highlighted as extremely relevant to ensure environmental objectives and industrial autonomy in the EEA, such as transport, semiconductors, telecommunications, renewable energy, or chemical processing industries.

Fluoropolymers have unique physicochemical properties which render them specialty plastics that are virtually chemically inert, non-wetting, non-stick, and highly resistant to temperature variability, fire, and weather and exhibit low flammability. They also display features such as low coefficient of friction, dielectric strength, and flexibility. These properties, and particularly the joint combination of all of them in single products, make them irreplaceable in many

[1] European Union (EU) 27 + Iceland, Norway, and Liechtenstein

[2] Regulation (EC) No 1907/2006

applications, and it is commonly accepted that their unique set of properties cannot be matched by alternative materials, particularly in the wide range of operability they offer. In fact, fluoropolymers are frequently the high-cost option in many industries, being the material of choice only when other products are known to fail to provide the required properties for the desired application.

The objective of this report is to highlight specific examples of uses of fluoropolymers, with details on how the benefits that these materials provide to the use are related to the combination of properties they offer. In addition, an evaluation of potential alternative substances that could be used to replace fluoropolymers in each use has been performed. Potential trade-offs that could be expected due to substitution have been highlighted, not referring to impacts on the direct uses, but on potential consequences that could be expected down the value chain and which could affect the general population, as well as broader environmental and innovation expectations within the EEA.

Information on the case studies that are described in this report has been collected via questionnaires that were delivered to a set of downstream users involved in primary handling of fluoropolymers. The questionnaire was also shared with a number of associations representing different industrial sectors involved in the use of fluoropolymers. Since some of these associations delivered the questionnaire to their members, it is not possible to establish the number of users that received it. A total of 27 responses were collected, which were then filtered in terms of quality of the information provided. Where deemed useful for a better understanding of the case, one-to-one videoconferences were organized with the respondents. It should be noted that due to time constraints and complexity issues, most of the cases described have been built with feedback from only one responding company. Efforts have been made to reassure the reliability of replies received (with cross-checking information from public literature), and final versions of the cases have been double-checked with experts from the German Association for Semi-Finished Plastics and Consumer Products (pro-K) for final validation. A copy of the questionnaire that was delivered to the downstream users can be found in **Annex I**.

Where available, information on the relevance of each sector of use in terms of socio-economic importance for the European society has been highlighted. This information has been provided by the sectorial associations that could be impacted due to a ban on the use of fluoropolymers. However, most of the respondents were primary users of the fluoropolymer substances in very complex value chains. For this reason, the potential impact of a restriction on the use of fluoropolymers in each application may be difficult to quantify. In any case, it is clear that the socio-economic importance of fluoropolymers increases significantly through the different steps in the multiple value chains in which they are involved.

The list of fluoropolymers covered in this report can be found in **Annex II**.

2. Properties of fluoropolymers and socio-economic importance

The key properties that fluoropolymers provide to a wide variety of industrial applications can be summarised as follows (FPG, 2021):

- Inertness and non-reactivity; high resistance to corrosion and chemical attack.
- Low and high temperature resistance: with a range as large as -263°C to +260°C for PTFE.
- Very low coefficient of friction to any solid.
- Low and ultra-low permeation rates.
- Ultraviolet radiation (UV) resistance.
- Excellent electrical insulation, low dielectric constant, low variations of conductivity.
- High level of fire safety; no flame propagation and low smoke generation.
- High and ultra-high purity with extremely low leach out properties.
- Stress-crack and cut-through resistance.
- Flex fatigue properties enabling thermal expansion/contraction in temperature cycles.
- Biocompatibility.
- High Flex life
- Durability.
- Hydrophobicity; neither water nor water-containing substances wet fluoropolymers, providing excellent repellent properties to many chemicals.
- Non-stick, and consequently non-fouling properties, along with sufficient bonding in certain multilayer applications.

In terms of socio-economic value of fluoropolymers, the Fluoropolymer Group of PlasticsEurope (FPG) has currently updated information (FPG, 2022b) from a previous socio-economic analysis that was performed on these substances (FPG, 2017). However, it is worth noting that this information is limited to the production, employment and revenue values of the fluoropolymer manufacturers and importers in the European Union (EU). While relevant, the importance of these figures is clearly minimised in comparison of the value that fluoropolymers enable downstream for end use applications. For example, while total revenue obtained from the whole fluoropolymer industry in the EEA in 2020 was of 740 million EUR (with 70 million EUR directly sold to the electronics industry), the revenue reported by the European Semiconductor Industry Association for the same year was 32.85 billion EUR (ESIA, 2020). As reported by downstream users, modern semiconductors cannot be produced without the use of fluoropolymers in the process, as will be explained in one of the case studies covered in this report. This means that fluoropolymers can multiply their direct value by nearly 500 times in the applications in which they are used, which gives a clear indication of their critical relevance for many important industries in Europe.

3. Case studies evaluated

3.1. Sector of use 1: Industrial uses

3.1.1. Application 1.1: Use of PTFE, PFA and ETFE in the production of lined equipment in the chemical processing industry

Description of the application

Polytetrafluoroethylene (PTFE), Perfluoroalkoxy polymer (PFA), and Ethylene tetrafluoroethylene (ETFE) are used in pipes, expansion joints, vessels, and fittings for the chemical processing industry, with the objective to protect equipment from direct contact at high temperatures (up to 230°C) and very aggressive media, such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4) or hydrofluoric acid (HF). Other highly aggressive substances may be sodium hydroxide (NaOH), potassium hydroxide (KOH), or sour gases.

As an example, desorption columns lined with PTFE are used in the recycling process of hydrochloric acid in the chemical industry. Streams with low acid concentrations are treated in these desorption columns, resulting in more concentrated streams that are then reused in the initial or further processes within chemical plants.

When there is no need to protect equipment or chemical products from the effect of corrosion, black steel piping and fitting systems are currently used by the chemical processing industry. An example of this could be the mineral oil industry. Such unprotected steel constructions are however limited to situations in which:

- Chemicals are not corrosive (or less corrosive) to steel.
- Processes in which short system lifetime (e.g., cycles of 2 years) is acceptable.
- Metallic ion impurities in the streams handled in the relevant processes do not raise situations of concern, neither from a quality nor from a safety perspective.
- Additional cleaning steps are available, that can remove the above-mentioned impurities. However, such systems add costs to the process.

It should be noted that such cases are not frequent in the chemical process industries, and that some sort of corrosion protection on the equipment to be used is typically required.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Flexibility
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation, between (-250°C to + 230°C)
- Barrier properties (low permeation of process media through fluoropolymer liner)

- Non-stick properties
- Flex fatigue properties to enable thermal expansion/contraction during temperature cycles

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are**:**

- Polypropylene (PP) lining systems
- Rubber lining systems
- Tantalum-based piping
- Stainless steel (V2, V4, 316 L, Hasteloy, Inconel) and some precious metals
- Enamel / glass lining systems

PP and rubber lining systems

These alternatives could work only under a narrower range of operating conditions. PP or rubber-based systems would only withstand temperatures up to 100-120°C without degradation, in comparison to higher temperatures (230°C) that are required for some processes, in which fluoropolymers are effective. Furthermore, the lifetime and duration of these lining systems is lower than 5 years.

These alternatives are sufficiently available and at a competitive price in comparison with fluoropolymers. In fact, where the process conditions do not require the use of fluoropolymers, they are already implemented by industry as the material of choice. However, it needs to be considered that due to much shorter lifetimes, PP or rubber lined equipment for the chemical industry would need to be frequently replaced if these systems were to be used under aggressive conditions, and therefore costs would be significantly increased.

Tantalum based piping

In principle, tantalum may offer similar performance as compared to fluoropolymers in the chemical process industry.

However, tantalum is more expensive and not competitive when compared to fluoropolymers. In addition to this, it is highly unlikely that tantalum supply could cover the demand that would be required to completely replace fluoropolymers in this application for the whole European chemical industry. Furthermore, tantalum is ranked as a conflict mineral which is frequently mined under unclear conditions. Therefore, supply (as well as prices) of this metal could be subject to significant constraints and result in business uncertainty in the future.

Stainless steel (V2, V4, 316 L, Hasteloy, Inconel) and some precious metals

Stainless steel offers similar chemical resistance like PTFE or PFA. Harsh, corrosive chemicals may extract metal ions in low concentration from the steel. While this could be acceptable in

some applications, it renders this alternative not feasible for use in cases in which high purity would be required.

This alternative is much more expensive compared to the combination black steel + PTFE/PFA used in current piping systems. The costs of using this alternative may go up to 5 times higher than the use of fluoropolymer lined systems. In special cases, metals like silver or even gold may be considered; in such cases, the cost of the alternative options could be 10 times higher, or more.

Enamel / glass lining systems

Enamel or glass based lined pipes could work under certain conditions, but not reaching the wide range of temperatures and aggressive media that fluoropolymers can withstand. These materials are brittle and could break easily when subject to temperature changes or acid attack. Service life of piping systems would be much shorter than with the use of fluoropolymers (perhaps reaching 5 years, but certainly below 10 years, in comparison to fluoropolymers that can last decades in operation).

Enamel glass linings are also more expensive than fluoropolymers (estimated at twice the price). Again, the need for further maintenance and higher replacement rates of these systems renders them as a non-viable option as an alternative to fluoropolymers in this application.

Potential impacts related to substitution

Use of PP, rubber or enamel/glass lined piping and fitting systems could create high risks situations for workers and the environment. The probability of cracking and integrity failure would be significantly increased in the process industry. This would be particularly critical when strong acids such as hydrochloric acid, sulfuric acid or hydrofluoric acid are used, which are highly corrosive and could generate great damage on workers and the environment.

Related to the hydrochloric acid example, PTFE linings are used to protect steel shell, pipes, and other equipment from direct contact to hot, concentrated hydrochloric acid. PTFE linings are critical for safe operation since they eliminate or minimize corrosion. Corrosion on equipment results in risk of leakage and severe accidents. Depending on process conditions, corrosion can appear within hours of operation and can have sudden, unpredictable effects, potentially leading to serious injuries to workforce, contamination of the environment and operational downtime. Hence, PTFE liners allow for the safe production of high-quality hydrochloric acid.

Many chemical establishments in the EU are multi-purpose plants, which means that they can run different processes at different times. For example, one process may be run for which P systems could be effective, but after a few weeks, a new process could be undertaken in which the combined properties that fluoropolymers provide are required. A scenario in which fluoropolymers would not be available for use in the process industry would create a significant challenge in terms of restructuring and reorganizing chemical establishments and in the end, it is likely that companies would decide to run their processes involving harsh

conditions (e.g., involving strong acids at high temperatures) in other locations outside the EEA where the use of fluoropolymers would still be allowed. This could result in the loss of a significant part of basic chemicals production within the EEA and severely damage the objectives of developing a stronger industry.

The possibility to replace fluoropolymer-based lining systems with stainless steel or other metals, which could work from a technical perspective in certain cases, would likely generate significant market distortions. This is because only the larger chemical companies may afford replacing the piping, vessels and fitting systems lined with fluoropolymers, and still this could also reduce the flexibility of those companies to run certain processes. Small and Medium Enterprises (SMEs) in the EU would be significantly impacted if they were forced to substitute fluoropolymers with metal-based alternatives.

It should also be noted that the use of PP or rubber lined piping systems would lead to the need of more frequent maintenance and replacement. This would significantly increase the amount of these products that would need to be disposed. For PP, recycling options are not identified, therefore the amount of waste of this material would increase dramatically, and therefore objectives related to a circular economy in the EEA would be jeopardized. Moreover, if fluoropolymers were to no longer be used in chemical plants, this could imply the need to take down such installations and subsequently starting them up again, which are two high risk instances that should be avoided

Regarding the hydrochloric acid example, it should be noted that this is a main chemical base material (~20 million tonnes produced per year worldwide) which is used in the production of further essential chemical base materials. For example, hydrochloric acid is used for the production of polysilicon materials (wafer, computer chips and connected markets), in the steel industry (refining ore, pickling and cleaning of metal, etc.), for food production, in the oil industry, for production of pulp and paper, and other industries, all of which would be directly impacted if fluoropolymer lined piping and fitting systems would not be available.

In addition to these end users, a significant number of companies supplying using fluoropolymers for the production of this kind of systems to the general chemical industry would face significant challenges, since they have developed high technical expertise on fluoropolymer-based piping equipment. Continuity of all these business in the EEA would be at risk.

Conclusions on the application

Single alternatives could eventually cope with some of the requirements required in the chemical industries, in terms of equipment protection. However, it is the combination of properties that fluoropolymers provide, particularly high resistance to chemical attack and wide range of temperature of operation, combined with low permeation and non-stick properties for a smooth development of chemical processes, which render them as the material of choice for many chemical industries in the EEA. Substitution by the limited set of

alternative materials would create a wide variety of problems both for the industries directly involved (e.g., suppliers and users of piping and fitting systems), as well as for the European society as a whole. On one hand, high risk situations for workers and the environment may be created, involving processes dealing with strong acids at high temperature. On the other hand, the use of alternatives could lead to situations in which conflict minerals would be required (tantalum), with significant ethical constraints as well as economic ones (related to volatile pricing and supply uncertainty), or to significant increase of waste streams of other plastics or rubber that could pose a challenge to the circular economy objectives. Ultimately, it is reasonable to assume that, should fluoropolymers not be available for this application, significant relocation outside the EEA of a large number of companies (mostly, but not only, SMEs) may occur, not only of direct downstream users of fluoropolymers, but of end-use industries that work with fluoropolymer based piping and fitting systems in the chemical industry.

In conclusion it can be stated that, evaluating jointly the benefits of continued use of fluoropolymers, as well as the negative effects that could be generated for the European society if fluoropolymers were not available for these applications, the continued use of fluoropolymers in in lined piping and fitting systems for the chemical industry should be granted to ensure a safe, sustainable, and competitive chemical industry.

3.1.2. Application 1.2: Use of PFA, PTFE, FKM in the production of lined pumps in the chemical processing industry

Description of the application

PFA and PTFE are used for lining pumps in the chemical processing industry, with the objective to avoid corrosion under specific conditions of chemical attack. In addition, vinylidene fluoride-hexafluoropropylene copolymer (FKM) based seals such as o-rings are used in those processes to avoid releases of hazardous materials.

An example that can be highlighted of this use is related to chemicals involved in the manufacture of polyurethane foams, which are used for example in building insulation. mononitrobenzene (MNB) is used for the production of methylene diphenyl isocyanate (MDI), which is a raw material for the production of polyurethane. In the process, sulfuric acid is diluted with nitric acid (HNO3) to produce MNB. The use of nitrosulfuric acid leads to a highly corrosive environment.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties, e.g., flexibility (ASTM D2176 - Test Method for Folding Endurance of Paper and Plastics Film by the MIT tester, with MIT > 1 million)
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation (between (-60°C to + 200°C)
- Barrier properties (minimum wall thickness 3.5 mm)

General description of alternatives and comparison with fluoropolymers

Chrome/Nickel alloys are usually considered as possible alternatives for this use. While these materials can be used for lining in pumps to operate certain chemical processes, and are still in use today, they are not able to cope with every specific anti-corrosion situation. In fact, those alloys were used for the lining of pumps and seals used for the MNB plants in the 1970s, however this led to frequent failure of the equipment, resulting in significant challenges in terms of maintenance and safety, related to corrosion and leakage from mechanical seals.

The introduction of PFA/PTFE lined pumps in the 1980s solved safety (related to unexpected releases of highly corrosive material that could reach operators) as well as environmental issues (due to release of ecotoxic mixtures). These systems offer a much higher protection against corrosion in this chemical process and minimise the need for replacement of the equipment, resulting in higher efficiency but also in increased worker and environmental protection. Particularly, PTFE-based systems (magnetic coupling pumps with stationary sealing) replaced mechanical sealed (rotating sealing) pumps which are more effective to avoid leakage to the environment.

It should be noted that in the past, other materials such as those described in **Application 1.1** (enamel/glass or rubber-based lined pumps) were used for this application, however corrosion always led to significant difficulties for developing the process in a safe and reliable way.

Potential impacts related to substitution

Returning to the use of chrome/nickel alloys would significantly damage the efficiency of the MNB/MDI process in the production of polyurethane foams. More importantly, it would increase risk of corrosion in processing plants and increase risk of damage to humans and the environment, not to mention the reduction in efficiency of the process and higher costs related to the need for more frequent maintenance and replacement of equipment. It is to be expected that such increases in costs would be transferred through the supply chain, reaching the end users of polyurethane foams. Replacement by other materials such as rubber or enamel is not considered as they are of even inferior performance compared to chrome/nickel alloys for this application.

Conclusions on the application

Industrial equipment based on chrome/nickel alloys is still in place and used nowadays to provide for corrosion protection in certain chemical plants. Corrosion guides are available for critical fluids and conditions which describe the corrosion resistance. The selection of the adequate material for key industrial equipment such as pumps must be done on a case-by-case basis, however frequently mixed fluids (e.g., sulfuric acid and nitric acid) are not always described in those guides, and therefore the company developing specific processes needs to test the specific material of choice on a case-by-case basis.

Removing fluoropolymer lined pumps and seals from the market would push technology back to levels of the 1970s and reduce the choice of materials for extremely corrosive chemical processes, which would result in a decrease of safety and environmental standards, as well as a reduction of the competitiveness of the European industry. Processes that today are run using fluoropolymer- based solutions (which occurs only when other materials that continue to be available on the market, such as chrome/nickel alloys, do not perform properly) would likely be moved to other countries where fluoropolymers are still allowed, and products manufactured in such processes would likely need to be imported rather than manufactured in the EEA.

3.1.3. Application 1.3: Use of PTFE matrix composites in the production of seals and gaskets for industrial machines

Description of the application

PTFE-based materials are essential components of highly reliable sealing mechanisms. These mechanisms are applied in a wide variety of industrial sectors, such as the chemical processing industry, automotive, aviation, food processing, and power generation.

Gaskets are a typical system to keep two pieces of an equipment together. They are defined as a mechanical seal which fills the space between two or more mating surfaces, generally to prevent leakage from or into the joined objects while under compression. It is a deformable material that is used to create a static seal and maintain that seal under various operating conditions in a mechanical assembly.

PTFE based seals and gaskets are used across a broad range of industries that require processing harsh chemicals. They are used in the vast majority of manufacturing plants involving chemical processes. One example is the Chlor/Alkali (C/A) process in which chlorine, sodium hydroxide and hydrogen are produced via electrolysis. These chemicals are then used in a broad range of applications. This process requires highly reliable sealing systems which are based on PTFE to guarantee adequate performance.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (15-40 MPa)
- Flexibility
- Low coefficient of friction (maximum 0.2)
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation (-100°C to + 250°C)
- Weather resistance
- Non-stick properties
- Fire retardancy / smoke suppression
- Low bacterial / algae growth

General description of alternatives and comparison with fluoropolymers

Asbestos fibre gaskets have been highlighted as potential replacements for PTFE-based sealing systems. These systems were used in the past and they could have satisfactory performance but certainly not at the levels that fluoropolymers provide, particularly in extreme conditions of mechanical strength required, variability of temperatures and chemical conditions. Other elastomers such as hydrogenated nitrile butadiene rubber (HNBR) and plastic materials, such

as polyethylene (PE) or PP, could eventually be used but providing limited mechanical strength and chemical resistance.

Potential impacts related to substitution

Ensuring proper sealing systems is a critical feature in the chemical processing industry. Failure in these systems could result in the release of hazardous materials and pose a risk to workers and the environment. Furthermore, the lower performance of alternatives would result in the need for increased maintenance procedures, resulting in additional costs for companies as well as an increase of waste material. Materials such as polyurethane, PP or HNBR, are expected to have a lifetime of 50% compared to PTFE based seals and gaskets. PTFE-based solutions are frequently more expensive and are used only when it is known that other materials will not provide the desired performance, to a point in which the application may result not viable.

Looking at the C/A example, according to the Best Available Techniques (BAT) for this process (JRC, 2014), the development of non-asbestos sealing systems started in the 1970s, taking about 10-15 years until viable alternatives to asbestos were introduced. These alternatives are all based on PTFE-based sealing systems. According to the Joint Research Centre (JRC), "With its superior characteristics regarding stability against chlorine, caustic soda, and other chemicals, as well as its dimensional stability, it was considered an ideal alternative to asbestos. Asbestos swells during operation in a diaphragm cell and this increases the energy demand. PTFE does not show this swelling effect, and therefore the energy demand would be lower. In addition, the high stability against chlorine and caustic soda should result in the diaphragm having a very long lifetime."

In terms of economic relevance, it is estimated that the C/A process covers approximately 25% of the EU specialty chemical industry which has a revenue of roughly 225 million EUR[3]. C/A is a good proxy for harsh chemicals because it tracks with the key processing attributes that rely on PTFE sealing solutions. These processes outstand for their reduced risks of leaks which protect safety of people and the environment. Harsh chemical processing has an essential function for the EU chemical manufacturing industry, and it is interlinked with a large number of downstream industries. Just to name a few, the following very different sectors can be considered:

- Agriculture: 178.4 billion EUR turnover and 9.7 million jobs in 2020[3].
- Chemical manufacture: 588.88 billion EUR turnover and 1.2 million jobs in 2019[3].
- Semiconductors: 40.43 billion EUR turnover and 200,000 jobs in 2021 (ECIA, 2022)

The economic impact of disruption in EU chlorine production would flow from initial production through all end use applications of the material, amplifying the effect. The propagation of the impact would be similar for other harsh chemicals such as sulfuric acid.

[3] Data provided by responses to the questionnaire based on information from Statista and Eurostat.

The use of asbestos fibre gaskets as an alternative to fluoropolymers would result in an increased risk of cancer due to the well-known carcinogenic properties of this material. Because of this, disposal of materials containing asbestos is complex and regarded as a hazardous activity, which needs to be considered as sealing systems using asbestos in the chemical industry would need to be more frequently replaced.

Conclusions on the application

Ensuring adequate sealing of machinery and equipment used by a wide variety of industries is of outmost importance. Materials used for this function need to be reliable and frequently withstand extreme conditions in terms of temperature, mechanical strength, and chemical attack. If those industries are not able to provide the required performance, significant impacts would be expected in terms of malfunctioning of such equipment, which could result in damage to people and releases of chemicals to the environment. Furthermore, inefficient sealing systems would result in sub-optimal operating conditions which could result in increased energy consumption leading to higher emissions of greenhouse gases (GHG), which could have a negative impact on the overall environmental objective established in the Green Deal.

Downgraded performance would imply reduce competitiveness of the European industry in many sectors. Industrial companies based in the EEA would face significant issues to maintain their high levels of performance and efficiency, so it is quite possible that those companies would eventually relocate their production to non-EU countries where the use of fluoropolymer-based seals and gaskets may still be allowed (even more so if the restrictions are expanded to other components that would also require fluoropolymers, see case 1.1). This situation will imply also that the technology will be transferred to the non-EU area so a loss of knowledge will occur.

Removal of PTFE-based seals and gaskets would kick technology backwards by 50 years, since technical solutions to asbestos in sealing systems in, for example, the C/A process were initiated in the 1970s. The use of PTFE for this process is currently considered Best Available Technique and removing it from the market would go against significant achievements made in the field of chemical process innovation, in addition to having replaced a well-known human carcinogen substance, a feature that is not shared by PTFE which is regarded as a Polymer of Low Concern (PLC) due to the lack of hazardous properties for human health and the environment.

3.1.4. Application 1.4: Use of PSEPVE and PTFE matrix composites in the production of membranes for electrochemical processes

Description of the application

Sulfonated tetrafluoroethylene (PSEPVE) is used in the production of membranes used in the C/A process. PTFE matrix is used to reinforce those membranes. In the C/A process, chlorine and its co-products are created by electrolysing a salt solution with a direct electric current that ultimately converts chloride ions into chlorine.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (15-40 MPa)
- Flexibility
- Resistance to harsh chemicals
- Resistance to high temperature
- Wide temperature range of operation (-100°C to + 250°C)

General description of alternatives and comparison with fluoropolymers

The manufacture of chlorine is an industrial process that has been on-going for more than 100 years. Traditionally, the only two alternatives to the use of membrane cells are mercury cells and diaphragm cells. In the mercury cell process, sodium forms an amalgam (a 'mixture' of two metals) with the mercury at the cathode. This amalgam reacts with the water in a separate reactor called a decomposer where hydrogen gas and caustic soda solution at 50% are produced.

The diaphragm cell process works with a combination of water and sodium chloride to create a brine solution, which is processed and filtered to remove impurities. Heat is applied to the solution and more salt is added until the purified brine solution is prepared for the electric current. In this case, an asbestos diaphragm is usually used to separate the cathode and anode, which will create the current (Mesothieloma, 2017).

Potential impacts related to substitution

Both mercury and asbestos are toxic materials and could generate significant issues to human health. In fact, according to Eurochlor (2022), the mercury cell system for the C/A process has been discontinued in Europe since 2017. As per asbestos, indications provided in the application described previously (**Application 1.3** describing gaskets and sealing systems) remain valid. Socio-economic relevance of the C/A process described previously can also be considered relevant for the production of membranes for C/A cells.

Conclusions on the application

In addition to safety considerations, the membrane cell system to produce chlorine via the C/A process is much more effective, and it requires less energy to produce the same quantity of product (at a higher purity), than the two alternatives (mercury and diaphragm cells). There is currently no other alternative known that would work in this process, which would withstand the combination of chemical aggressive environment of operation and very high temperatures that can be achieved in the process. This is a perfect example to demonstrate how the use of fluoropolymers has allowed for innovation and improved safety conditions of operation, removing the use of well-known hazardous materials from a very important industrial use and replacing them by materials that meet the conditions of PLC. For this application, different types of fluoropolymers are relevant, such as sulfonated TFE (for the production of the membrane itself) and PTFE matrix composites (to protect and reinforce durability of the membrane).

3.1.5. Application 1.5: Use of PTFE, PVDF, PFA in the production of filter systems for waste treatment in the chemical processing industry, power plants and other sectors

Description of the application

PTFE, PFA and Polyvinilidene fluoride (PVDF) are used in filter bags and filter systems which are needed to convert predominantly toxic or hazardous components, such as gaseous dioxins and furans or nitrous oxides from highly aggressive and corrosive gas streams, bringing concentrations of those chemicals below established regulatory limits. Furthermore, PTFE is used in large heat exchangers that enable the desulphurisation process at power plants by maintaining required temperature conditions of treated streams.

Typical sectors involved are chemical processing industries, but also waste incineration, metallurgical processes, cement manufacturing and power plant flue gas cleaning, which have stringent environmental requirements in terms of limiting emissions to air.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength
- Wear resistance
- Flexibility
- Low coefficient of friction
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation
- Barrier properties
- Non-stick properties

General description of alternatives and comparison with fluoropolymers

There are potential alternatives materials such as fibre threads available from different suppliers. In the past, some of these contained asbestos, which needs to be taken into account from an overall safety perspective. Currently, these fibres provide lower performance, which results in higher power consumption and shorter lifespan of these materials (resulting in higher replacement rates, adding costs to the process and the value chain).

Such fibres are less resistant to higher temperatures, they have limited ability to incorporate catalysts and other active components which destroy or capture harmful emissions. Lower chemical resistance results in higher filter failures, increased emissions, and more frequent replacement.

Other materials such as PP and polyether sulfones (PES) can also be used for filter systems, but again they are not expected to perform at the same demanding conditions under which fluoropolymer-based filter pieces can provide reliable operation.

Potential impacts related to substitution

Emission control in harsh and aggressive environments is an essential function across many industries (e.g., construction, manufacturing of petroleum products, metallurgy, etc.) and is interlinked with many downstream industries. Filters containing fluoropolymers are used in the most demanding applications such as hazardous waste incinerators, to prevent toxic pollutants from being released to the environment. Products containing fluoropolymers have a common benefit of reducing risk of emissions, which protect health and safety for people and the environment. They are necessary for many industries to meet existing environmental emissions regulations.

Filters made with fluoropolymers also provide necessary cooling and cleaning for advanced electrical products to avoid overheating. It is assumed that nearly all the advanced semiconductor chip sets and memory devices imported into the EU use filters containing fluoropolymers. Semiconductors and memory devices are essential devices for the function of many end-uses across many industries. Likewise, the pharmaceutical industry may also require high levels of performance for filtering systems, which can only be achieved with the use of fluoropolymers.

Furthermore, when alternatives are evaluated, their potential toxicological and ecotoxicological impacts should be taken into consideration. In the case of PES, publications suggest that they may have potential endocrine disrupting properties and may actually be considered of equivalent concern to bisphenol A – BPA (Kang et al., 2014), and based on recent research, they are related to generation of other bisphenols during degradation (Li et al., 2022), therefore this and similar materials may not be considered a suitable alternative from a safety perspective, as this could lead to regrettable substitution.

Conclusions on the application

Fluoropolymers such as PTFE, PFA and PVDF are key components of filtering systems that are required in several industries in which hazardous chemicals are handled. The efficiency of such filtering systems is crucial to ensure adequate environmental protection, and operation within predefined regulatory limits. If fluoropolymers were not available for use in such applications, the possibility to comply with such limits could be impaired and operation in a number of sectors and industries may have to be discontinued due to failure to comply with existing regulatory standards. This would effectively force shutdowns and relocation of industries. In some processes with less demanding conditions, alternative materials may be used but this could imply more frequent demands, higher replacement rates and ultimately increased costs, which could be transferred through the value chains reaching the end users. More important, if substitution is forced with some alternative materials such as PES, there may be a risk of introducing potentially hazardous materials that could be related to endocrine disrupting effects.

3.2. Sector of use 2: Energy production

3.2.1. Application 2.1: Use of PTFE, PVDF and FKM in the production of lithium-ion batteries

Description of the application

PTFE and PVDF are used as electrode binders and separator coatings in lithium-ion (Li-ion) batteries, providing interconnectivity within each electrode. This facilitates electronic and ionic conductivity, increasing the cell manufacturing productivity and the cell safety. PVDF offers unparalleled cohesive and adhesive properties under high voltage, allowing for closely packed cathode active materials for high density electrodes. Thanks to PVDF, different battery components can be packed more closely together, improving the energy efficiency of a single unit, and helping reduce overall size.

In parallel to PVDF, FKM is used for the production of cell gaskets used in Li-ion batteries, improving the electrolyte containment efficiency and safety of each cell.

Fluoropolymers also offer high durability, flexibility and other exceptional mechanical properties when used in separators and gaskets, helping resist the harsh conditions faced within a Li-ion battery. This dramatically improves performance, as well as the lifespan of batteries, which are increasingly used in applications that require a guaranteed and dependable level of output.

In this application, the fire retardancy property offered by fluoropolymers also plays a critical role, as the use of these materials allows for the creation of a non-flammable matrix that prevents batteries to catch fire due to overheating, which is a well-known concern related to these batteries.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength
- Wear resistance
- Flexibility
- Low coefficient of friction
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation
- Barrier properties
- Non-stick properties
- Fire retardancy / smoke suppression

General description of alternatives and comparison with fluoropolymers

Other polymeric materials could be used for the application such as PE or Polyethylene Terephthalate (PET). Alternatives to Li-ion batteries are lead acid batteries, which do not contain fluoropolymers.

Potential impacts related to substitution

The use of PE or PET in Li-ion batteries would not be a sustainable solution, as these materials would not offer the combined set of properties that fluoropolymers provide, particularly in terms of both fire retardancy and battery efficiency.

In the case of replacement of Li-ion batteries with lead-acid batteries, it needs to be noted that these batteries offer reduced performance notably in terms of energy efficiency because a lower proportion of the energy stored in lead acid batteries. In addition, lead-acid batteries are heavier resulting in reduced functionality and increased energy consumption compared to Li-ion batteries. In addition, it needs to be considered that lead acid batteries involve the use of a known carcinogenic, mutagenic, or toxic for reproduction (CMR) substance (lead) which is a known human reprotoxicant, with additional hazards related to neurotoxicity and environmental damage.

Conclusions on the application

In the automotive sector, batteries are being increasingly used to power up electric vehicles (EV). And this number is only set to grow, with predictions that by 2030 EV sales will reach nearly 60% of the total car sales (Bloomberg NEF, 2021). In order to achieve the objectives of the EU Green Deal, the development of Li-ion batteries particularly in the transport sector is expected to play a key role. Those batteries could not perform at optimal level if fluoropolymer-based solutions (including PTFE and PVDF as electrode binder and FKM in sealing gaskets) were not available.

3.2.2. Application 2.2: Use of PSEPVE and PTFE in the production of proton exchange membranes for hydrogen production

Description of the application

Electrolysers (EL) and fuel cell membranes are used in the production of green hydrogen (H_2) by an electro-chemical reaction. To enable the movement of protons from the anode to the cathode side of the fuel cell, a Proton Exchange Membrane (PEM) made of sulfonated TFE and reinforced with PTFE is used due to the efficiency and unique durability, chemical and temperature resistance properties that fluoropolymers offer for this application. The technical principles behind this case are similar to those described in **Application 1.4**.

The membrane is the core component in ELs as well as in fuel cells. In the former, the electric current and the catalyst coated membrane split water into hydrogen and oxygen, hence hydrogen is produced, with oxygen obtained as a by-product. In the latter, the membrane separates protons and electrons by using a catalyst, and it provides proton conductivity (thereby producing electric current) while separating hydrogen and oxygen.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (<12 MPa)
- Mechanical properties (E-Modulus <500 MPa)
- Low coefficient of friction (0.05-0.1)
- Wear resistance (<5E-7 $mm^3/N \cdot m$)
- Resistance to high pressure (250°C)
- Resistance to harsh chemicals
- Resistance to high temperatures
- Resistance to low temperatures (-263°C)
- Wide temperature range of operation (-263°C to +250°C)
- High limiting oxygen index
- Ionic conductivity
- Barrier properties

General description of alternatives and comparison with fluoropolymers

Hydrocarbon-based ionomers / sulfonated polymers

Some existing hydrocarbon-based ionomers and hydrocarbonated sulfonated polymers could be considered as alternatives to sulfonated TFE for the PEM production, however they offer significantly lower ionic conductivity, especially at low humidity and they are not sufficiently stable against chemical and mechanical degradation to be used in reliable and efficient fuel cell applications. The life span of alternatives is significantly shorter than fluoropolymers implying a higher maintenance cost and probability of failure, therefore resulting in an

increase in the risk of accidents. Furthermore, the likelihood of replacement is substantially higher as well, leading to higher waste generation.

Polyether ether ketone (PEEK)

Research work has been ongoing for PEEK membrane development. Usually, the properties and performance of these materials can be reasonably good whereas the durability is often poor, as oxidation by oxygen radicals, which are inevitably generated at the cathode electrode, occurs. Activities to replace the conventional fluorinated ionomers with fluorine-free materials have existed for the last 25 years but so far, no commercial product has been released due to poor stability against oxidation.

Switch to other hydrogen-based energy solutions

Production of grey or blue hydrogen comes with carbon emissions as well, as those forms of hydrogen are based on the reformation of natural gas and release carbon (COx), that either get emitted into the environment or are questionably captured underground.

Potential impacts related to substitution

Alternatives do not meet the performance required for hydrogen-based energy production as they fail to achieve the demanding conditions in terms of flexibility, stability, resistance to chemicals and performance (superior ion conductivity) under the ranges of temperature variability that are required in the process, therefore the durability and reliability is significantly reduced along with an increased rate of potential failure. If such failure occurs during e.g., use of a hydrogen vehicle, this could result in accidents and risk for population.

Fuel cell manufacturers are in close contact with the suppliers of components, establishing collaborations to test new materials at a relatively early stage. They are thus able to identify and qualify promising options, promote their industrialisation, and introduce the use of innovative materials, as early as possible. However, building from past experience, at present time it is not possible to establish when a validated alternative material may be available in sufficient volume and with equivalent performance compared to fluoropolymers.

Conclusions on the application

In the case of a ban on fluoropolymers for this use, ELs and PEM for green hydrogen production may no longer be available, at least not in the parameters that modern technology involving the use of sulfonated TEF and PTFE allows. It is possible to produce hydrogen by using combustion engines, but this option will result in an increase in GHG emissions and carbon footprint, therefore the decarbonization objectives planned in the European Green Deal and sustainability policies would be jeopardized, and the transition to cleaner energies would be significantly delayed, if at all possible.

Hydrogen has seen unprecedented development over the last years. Starting as an innovative niche technology, it is fast becoming a systemic element in the European efforts to transition to a climate-neutral society in 2050. It will become a crucial energy vector and the other leg

of the energy transition, alongside renewable electricity, by replacing coal, oil, and gas across different segments of the economy. The rapid development of hydrogen is not only important for meeting the EU's climate objectives but also for preserving and enhancing the EU's industrial and economic competitiveness.

A very large proportion of planned projects involving ELs and fuel cells (and in some applications 100%) are based on this PEM technology. Amongst tracked water electrolysis projects to be completed by 2030 in EU/EEA/UK for which information is available, PEM electrolysis accounts for 53% of the projects and 13% of the capacity. PEM are a non-replaceable and high-priority component enabling this fuel cell technology. Without these membranes, the roll-out of such high-performance fuel cell and water electrolysis applications would be delayed by 10-15 years, thereby impacting a wide range of industries.

According to the Hydrogen Council (2021), there are 200 hydrogen fuel cell projects currently announced in Europe, with investments focussed across multiple industries, from transport to heavy industry. In fact, according to this source, the majority of global hydrogen-related investments expected for this decade will be made in Europe. If the use of fluoropolymers in this sector was to be banned, companies will relocate such investments to non-EEA countries where these restrictions do not apply. This situation will imply also that the technology will be transferred outside of the EEA so a loss of knowledge and competitiveness will occur.

Hydrogen is essential to the production of green energy and will be critical in the achievement of the EU Green Deal objectives as well as the objectives set out at COP21. It is estimated that by 2030, 110,000 fuel cell trucks and busses could be on the road (Ruf et al., 2020), and fuel cell EVs could account for 1 in 22 passenger vehicles; in the construction sector, hydrogen could replace an estimated 7% of natural gas by volume (Hydrogen Roadmap Europe, 2019).

Moreover, based on input provided by Hydrogen Europe (2022), the following impact assessment on a potential ban that could cover fluoropolymers in the EEA can be anticipated:

a) In 3 years

Banning materials under a restriction would slow down deployment of clean hydrogen technology in several markets, as it will effectively eliminate PEM ELs and PEM fuel cells from the market.

An analysis of the current pipeline of renewable hydrogen production projects shows ca. 25% all ELs capacity in projects under current development in the EU rely on PEM technology. Taking the EU hydrogen strategy targets as a predictor of future investments (EU-wide target of 6 GW of ELs capacity by 2024), a ban on key products would jeopardise investments worth ca. 1.125 billion EUR by 2024 in ELs only.

It is worth stressing that PEM ELs (due to capacity for flexible load operation) are best suited for coupling with variable renewable energy sources (RES) and are therefore an indispensable technology for large scale RES integration with power grid. Hence a ban would not only jeopardize green hydrogen markets, but it could also significantly affect

the EU's ability to deploy needed RES generation and make reaching decarbonisation targets practically impossible for 2030 and 2050.

b) In 10 years

Based on same strategy's 2030 target of 40 GW of EL, a ban would: jeopardise investments worth 7.5 billion EUR in ELs only (and total estimate of EL capacity in the EU project pipeline is even greater than strategy targets: 141 GW with 35 GW in PEM ELs, worth an estimate of 18 billion EUR). In summary, bans on fluoropolymers may put at risk a total investment estimate value in clean hydrogen sector of 26-36 billion EUR. In terms of employment and put between 84,000 and 140,000 direct jobs at risk, with an estimation of potentially 242,000-261,000 indirect jobs impacted, resulting in a total potential negative impact of 326,000-401,000 full time employees.

3.2.3. Application 2.3: Use of PTFE and FEP in the production sealing systems for storage, transport and production of green hydrogen

Description of the application

PTFE and fluorinated ethylene propylene (FEP) are materials of choice for sealing components used in production, transport and storage of green hydrogen. This application is challenging particularly from the temperature perspective. On one hand, cryogenic conditions (e.g., close to -268°C) are involved during storage of hydrogen. On the other hand, hydrogen is one of the few gases (with helium and neon) that actually heat up when expanded. Fluoropolymers are well suited to cope with increased temperatures that may occur during hydrogen production.

Fluoropolymer based sealing systems can be involved in may steps in the hydrogen process involving cryogenic conditions, for example for rotatory swivels for loading arms at transport of liquid hydrogen, during storage for hydrogen liquefaction or at pumps and valves used at fuelling stations.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties (<12 MPa)
- Wear resistance (<5E-7 $mm^3/N \cdot m$)
- Flexibility (E-Modulus <500 MPa)
- Low coefficient of friction (0.05 – 0.1)
- Resistance to harsh chemicals: for example, carbon dioxide (CO_2) acts as a solvent for many polymers in cryogenic stage, also for hydrogen or methane (CH_4).
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation (between (-263°C to + 250°C)
- Barrier properties (No swelling when exposed to carbon dioxide, hydrogen, methane)
- Vibration dampening: >0.9
- Impact resistance (IZOD Shrinkage: >8 kJ/m^2)

General description of alternatives and comparison with fluoropolymers

Steel seals and other rubber materials such as nitrile butadiene rubber (NBR) may be seen as potential alternatives

Potential impacts related to substitution

Steel seals would eventually fail because they could not provide the reliability required during the hydrogen cycle. Flanges and bolts to be used in the process require significantly stronger materials during harsh temperature conditions and steel solutions would eventually break leading to releases and significant risks for the operators and the environment.

Similarly, NBR is a material that cannot resist temperatures below -70°C, which is significantly far from the lowest possible temperature during the hydrogen storage and transport processes, which can go as low as -263°C.

Conclusions on the application

A significantly innovative and modern process to generate clean energy such as hydrogen production could be put at risk if fluoropolymers were to be banned for use in the EEA. Because fluoropolymers existed before this technology was developed, these materials have been essential in facilitating this promising energy source, and therefore it cannot be expected that this may continue without the use of PTFE or FEP sealing systems, even if lower performance with the use of other materials was possible. Put simply, the technology could not exist without the use of fluoropolymers.

There are high hopes placed on hydrogen currently as a key vector to support the achievement of a carbon-free energy mix in Europe, as an essential component of the EU Green Deal objectives. Removing fluoropolymers from the EU market could lead to significant damage to those objectives. References to the impact of such a ban on the EEA society are the same as those described for **Application 2.2**.

Conclusions on this application could be extrapolated to other energy considerations such as offshore windmill shafts (involving complex maintenance operations, therefore requiring maximum reliability of components).

3.3. Sector of use 3: Semiconductors and electronics

3.3.1. Application 3.1: Use of PTFE and PFA in the production of pipes and tubes for ultra-high purity requirements in the semiconductor industry

Description of the application

Similar to **Application 1.1**, PTFE and PFA are used in vessels, pipes, fitting systems (e.g., diaphragms in valves) and related infrastructure for the semiconductor industry, with the objective to protect equipment under very aggressive media while granting an extremely high purity of the materials involved in the process. A relevant example of this application would be the use of PTFE or high purity PFA lined columns and tanks to produce high purity sulfuric acid for etching silicon wafers to manufacture electronic chips. This technology allows for larger wafers and ultimately, a more efficient microchip production process. However, it needs to be stressed that most piping and tubing systems used in the semiconductor industry are not lined systems, but the 100% based on fluoropolymer material, as this is the most effective solution to adequately design piping systems in environments that require very high chemical and temperature resistance with flexibility and other properties.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (<10 MPa)
- Flexibility (E-module <500 MPa)
- Resistance to harsh chemicals
- Resistance to high temperature (250°C)
- Wide temperature range of operation
- Barrier properties (low permeation of process media through fluoropolymer liner)
- Non-stick properties
- Flex fatigue properties to enable thermal expansion/contraction during temperature cycles
- Extremely high product purity

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are**:**

- PP lining systems
- Rubber lining systems
- Tantalum-based piping
- Stainless steel: V2, V4, 316 L, Hasteloy, Inconel
- Enamel / glass lining systems

For the semiconductor industry it is absolutely essential to guarantee that the streams treated within the vessels, piping and fitting systems will stay at the highest possible purity levels. For this industry, levels of purity of part per trillion (and even beyond) are required to ensure the highest possible quality, and to reduce production scrap rates for the user of high purity sulfuric acid. For this reason, any material to be used within this process must ensure an extremely low level of impurities, as well as a low level of leaching of the material used for the piping system into the product. In this particular case, even the use of stainless steel or tantalum would not be viable as these materials would not meet the high demand for product purity. Indeed, no metals are allowed to come into contact with chemicals involved in production of semiconductors, as they would act as ion implants in monocrystalline silicon and change its semiconductor properties in an undesired way. The same would apply to tantalum or enamel-based solutions, which would ultimately not guarantee the need for ultra-high purity values. Likewise, materials like PP or rubber would lead to faster degradation and contamination.

Safety considerations of alternatives would be equivalent those presented for **Application 1.1** since this use would also involve the use of highly corrosive acids like sulfuric acid. The same would apply to economic feasibility of alternatives.

Potential impacts related to substitution

In order to maintain and enhance a competitive semiconductor industry in Europe, there is currently no option to replace the use of fluid systems made from fluoropolymers. Even a slight change in the semiconducting properties, which could be generated due to the use of metal-based materials, would not allow the EU semiconductor manufacturing industry to reach the high standards of efficiency and sophistication that are demanded by the modern downstream user sectors (e.g., telecommunications and electronics).

The semiconductor industry has invested heavily to increase the wafer size during the last 30 years. While foundries used to produce 1-inch wafers in the past, currently common wafer size is 300mm. Larger wafer sizes enable the production of more semiconductors from a single wafer, enhancing productivity and efficiency. By replacing fluoropolymer solutions in this industry, a drastic reduction in product quality would have to be accepted, which would bring the European industry to levels of quality that were acceptable only decades ago (in terms of size, precision and reliability of the articles produced), preventing the possibility to supply to increasingly demanding products such as smartphones, tablets, and personal computers, and thus rendering the European industry as non-competitive in front of companies based in other regions of the world.

According to information from the European Semiconductor Industry Association (ESIA, 2022), in 2021 this industry reached sales for a value of 40.43 billion EUR. Being ranked as the most research and development (R&D) intensive sector by the European Commission (COM), the European semiconductor ecosystem supports approximately 200,000 jobs directly and up to 1,000,000 induced jobs in systems, applications and services in Europe. Overall, micro- and

nano-electronics enable the generation of at least 10% of gross domestic product (GDP) in Europe and the world.

Furthermore, highly efficient semiconductors will play a critical role in the achievement of the objectives of the EU Green Deal, as they are a key enabler of low carbon and energy efficient innovative solutions by optimising energy usage in transportation, manufacturing, consumer products and services. Any negative impact on this industry could seriously hamper the development of such solutions.

Conclusions on the application

For most applications dealing with fluoropolymers, the general principle is that it is the combination of properties they offer that make them highly valued materials. While for semiconductors this principle is still valid, there is one property that clearly stands out, which is the ability of fluoropolymers to grant extremely high level of purity for the aggressive chemicals that are required. Certainly, fluoropolymers add the benefit of also granting high durability and reliability which are critical properties in terms of safety considerations during operations.

Modern (and competitive) microchip technology relies heavily on the possibility to use fluoropolymers in the manufacturing process of semiconductors. Without these materials, the European industry would take a step back of around 30 years, which would leave companies based in the EEA at a clear disadvantage in front of the already dominating industries based in other regions. A ban on the use of fluoropolymers would be in contradiction with the plans expressed by the European Commission to thrive in the global microchip race (European Commission, 2021).

Semiconductors are indispensable in today's modern society, related to consumer electronics and communications. In practice, it is thanks to the availability of microchip miniaturisation that mobile phones have reached the level of (reduced) size and sophistication that enable their functionalities. Removing fluoropolymers from the market would result in loss of these features and make it impossible to maintain the technological levels that have been obtained.

3.3.2. Application 3.2: Use of PTFE, FEP and ETFE in electrical cabling for various industrial sectors

Description of the application

PTFE, FEP and ETFE are used in electrical cabling for various industrial sectors. These fluoropolymers are used because of their exceptional electrical and resistance properties, as well as to provide fire and flame retardancy, which are features required in many industrial applications. In addition, fluoropolymers have a high dielectric strength which means that cables insulated with these materials can be thinner than those manufactured with other materials. On the other hand, due to the dielectric properties, fluoropolymers are widely used for cables and wires for communication facilities as insulators for high-frequency electronics.

LAN cables of category 4 or higher are made with FEP to allow for optimum data transmission properties, which is measured as Velocity of Propagation (VoP).

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Flexibility
- Resistance to high temperature (>200°C)
- Resistance to low temperature
- Resistance to chemicals
- Wide temperature range of operation
- Fire retardancy/smoke suppression
- Electrical insulator (high data transmission range)
- Low arc-tracking
- Barrier properties (low permeation of process media through fluoropolymer liner)

General description of alternatives and comparison with fluoropolymers

Engineering plastics, such as polyvinyl chloride (PVC) or PE combined with halogen free flame retardants (HFFR) could be considered as alternatives, however none of them meet the combination of properties that lead to superior performance of fluoropolymers, such as high flexibility, resistance to harsh chemicals and resistance to high temperatures (>200°C), which are frequently required for many industrial applications.

PEEK and ceramic based cable insulations may also be considered, but again these materials would not bring the combined set of properties that fluoropolymers offer and would not perform under the full set of required situations and process conditions.

A critical property in modern electronics which is required to any material that may be used for data transmission cables is minimum signal disruption. If other plastics such as PE are used in LAN cables, VoP is significantly reduced, resulting in less efficient performance. The use of PE would also result in thicker LAN cables.

Potential impacts related to substitution

While alternative materials could be used in industrial cables under conditions that require minimum performance levels (e.g., moderate temperature ranges, low flexibility needs, absence of harsh chemicals or limited voltage), it is often the case that many industries need to cope with very demanding conditions in relation to those properties. A wide variety of end-sectors depend on availability of cables that are able to perform under harsh conditions of use, from coffee machines to switch pumps placed under water, from data processing cables to control systems in industrial processes.

For example, alternative plastics described earlier will typically have a higher minimum working temperature than fluoropolymers, therefore performance will be significantly reduced particularly in cases where coolants are used to decrease temperature, which is typical in data processing systems. In addition, flame retardants increase dielectric constant and dielectric loss, which reduce data communication rates. The use of alternative plastics combined with other flame retardants will result in weaker data processing and slower signal return, reflecting inferior properties if compared to those obtained with the use of fluoropolymers.

The need to provide additional insulation due to the use of degraded performance by the use of alternatives would result in increased weight and size of cables, which would also be more rigid and brittle. Therefore, electrical installations would become bigger and more complex. Furthermore, performance in high-tech properties such as data transmission via LAN cables would be significantly reduced as well.

Conclusions on the application

Fluoropolymers provide a unique combination of properties that are not met by the alternatives, reaching extreme conditions that cannot be achieved with the use of alternatives. If fluoropolymers are not available in electrical cables, performance of a wide variety of industrial applications would be seriously downgraded, resulting in increased maintenance costs, lower reliability, and eventually higher risks for human health (fires) and the environment (increased replacement of other plastics leading to generation waste).

Ordinary wires are not equipped to handle the high-power consumption and high frequencies of e.g., 5G radios and cells. Fluoropolymers increase 5G reliability by insulating and protecting riser cables from fire and heat and allowing for quick data transmission and flexibility.

Under this situation, many industries based in the EEA would face significant issues to maintain their high levels of performance and efficiency, which could result in a significant decrease of competitiveness of those industries. The example that has been provided on reduced performance of data transfer technologies is illustrative of how European based companies could be challenged by competition in other regions of the world if they were forced to transition to lower performance alternatives.

3.4. Sector of use 4: Automotive and aerospace

3.4.1. Application 4.1: Use of PTFE and FEP in the production of electrical cabling for use in aircrafts

Description of the application

This case is a specific example related to the general case of electrical cables described in **Application 3.2**, describing the use of PTFE, FEP and ETFE in industrial machines.

PTFE and FEP are used in electrical cabling for the aerospace industry (aircrafts, but also outer space vehicles), where there is an essential requirement for high-performance under very demanding conditions. Fluoropolymers offer property retention under a wide range of temperatures and exposure to specialty fuels that may be chemically aggressive.

The aerospace industry also relies on fluoropolymers due to their exceptional electrical properties at high voltage and high signal frequencies and resistance properties, as well as fire and flame retardancy and reduced smoke generation.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength: SPE-J-920-A-0061[4] torsion
- Wear resistance: SPE-J-920-A-0061 wire to wire abrasion
- Mechanical properties: SPE-J-920-A-0061 room temperature bend
- Low coefficient of friction: SPE-J-920-A-0061 Pliability
- Resistance to harsh chemicals: SPE-J-920-A-0061 Resistance to aircraft fluids
- Resistance to high temperature: SPE-J-920-A-0061 accelerated ageing (operating temperature may reach 260°C)
- Resistance to low temperature: SPE-J-920-A-0061 cold bend (operating temperature may reach -70°C)
- Wide temperature range of operation: SPE-J-920-A-0061 Climatic
- Dielectric strength: SPE-J-920-A-0061 High voltage test, spark test, surface resistance, overload resistance, resistance to wet arc tracking, resistance to dry arc tracking
- Fire retardancy/smoke suppression
- Low arc-tracking
- Electrical insulator
- Barrier properties

[4] SPE-J-920-A-0061 refers to specifications for wires to be used in Eurofighter type aircrafts

General description of alternatives and comparison with fluoropolymers

Similar to **Application 3.2**, engineering plastics (such as PVC and PE) combined with HFFR could be considered as alternatives, however as discussed previously these materials will not meet the combination of properties that lead to superior performance of fluoropolymers, which are highly needed in aircrafts. Polymeric materials could give some chemical and electrical protection but would fail to perform under the required set of temperature ranges.

PEEK is able to resist up to 260°C, however this material is significantly rigid which greatly impacts on the design of the electrical systems. On the other hand, chemical resistance and electrical properties are inferior to fluoropolymers.

Ceramics could also be an alternative and provide protection against some (not all) chemicals, but flexibility requirements are again not fulfilled, and they would be significantly heavier.

Potential impacts related to substitution

The aerospace industry requires high insulation performance in aircrafts, this is amplified by the need of higher voltages (>230V) at higher altitudes with partial vacuum conditions and where vibrations can lead to product failure, which is not the case if fluoropolymers are used. Furthermore, cables need to be flexible and resistant to high as well as low temperatures, which can go as low as -70°C; if the flexibility requirements are not met, cables will turn rigid and there could be a breakdown risk that may result in a system failure, thus compromising aircraft safety. In addition, most of the alternatives cannot work at 260°C, this temperature may be reached in aircraft engines where high reliability is critical to guarantee safety during flight. PEEK could be an exception in terms of resistance to higher temperatures but again the lack of other properties like flexibility turns this into a non-viable alternative.

Being fluoropolymers resistant to the action of harsh chemicals, their use in cabling is particularly useful in areas of the aircraft where exposure of the cabling system to specialty fuels that may be chemically aggressive could occur. On the other hand, in the event of a fire incident during flight, fluoropolymers are able to provide fire retardancy and reduced smoke generation suppression properties with better performance compared to alternative materials, which is another critical element to ensure safety of passengers and the crew.

The exceptional dielectric properties provided by fluoropolymers allows for cables insulated with these materials to be thinner than those produced with other materials. Less weight improves the agility and speed of aircrafts and reduces the amount of fuel required.

Conclusions on the application

A typical modern aircraft may contain between 150 and 250 km of cables installed (specific models such as the Airbus 380 have > 500km of installed cables). Aerospace companies use fluoropolymers because they provide outstanding performance under highly demanding environments, which cannot be compromised due to safety issues. High durability and reliability of the materials used in aircrafts are required, this poses significant challenges when

those materials need to withstand temperature variability or chemical attack, while offering sufficient flexibility and other properties such as dielectric strength or flame retardancy. Fluoropolymers are the only materials that offer outstanding properties in relation to those properties, all in one single material type.

If fluoropolymers were to become not available for electrical cables used by the aerospace industry, performance of the aviation in general would be seriously downgraded, resulting in increased maintenance costs, lower reliability, and eventually higher risks for safety of passengers and workers.

In addition to these considerations, it is necessary to highlight that the airspace industry has extremely demanding validation procedures for new materials. The approval could take at least ten years, therefore if changes were to be introduced in the systems used in aircrafts, lengthy and costly procedures for certification would need to be taken into account.

3.4.2. Application 4.2: Use of PTFE in the production of lambda sensor for the automotive industry

Description of the application

PTFE is used in lambda sensor cables due to its resistance to high temperatures and chemicals, dielectric strength, flexibility, and electrical insulator properties. Lambda sensors essentially consist of three parts: wiring, grommet and sleeve. PTFE is used throughout these components with the objective to protect the sensor which is directly exposed to exhaust gases.

In vehicles, lambda sensors adjust the fuel amount that is sent to the engine cylinders by optimizing the air and fuel mixture, which in turn will make the engine work properly. Lambda sensors allow for this control system via measurement of oxygen in exhaust fumes. This is a critical element in cars and vehicles to control the rate of gas emissions by ensuring that the catalytic converter works in an efficient way. Lambda sensors ensure that the car complies with the European regulations on pollution and carbon emissions.

To allow for a better control of emissions, it is common that gasoline injection systems in vehicles feature at least two lambda sensors. The air/fuel mixture is optimized by a control sensor upstream of the catalytic converter. Taking the engine load into consideration, the fuel quantity injected is controlled in a manner that an optimum air/fuel ratio is ensured, thus creating ideal conditions for exhaust-gas treatment at the catalytic converter. In case of rich mixtures, the amount of fuel is reduced. With lean mixtures, it is increased. The second lambda sensor downstream of the catalytic converter (the diagnostic sensor) checks if the control sensor works optimally. If there are any deviations, they can be compensated by the control unit.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties (tensile and elongation)
- Resistance to high temperature: ISO 6722 long term heat ageing (operating temperature 280°C)
- Resistance to chemicals: ISO 6722 fluid compatibility
- Resistance to low temperature: ISO 6722 low temperature winding, cold impact
- Weather resistance: ISO 6722 temperature and humidity cycling
- Electrical insulator: ISO 6722 withstand voltage
- Dielectric strength: ISO 6722 withstand voltage
- Fire retardancy/smoke suppression: ISO 6722 resistance to flame propagation

General description of alternatives and comparison with fluoropolymers

Silicon, ethylene propylene rubber (EPR) and ethylene propylene diene rubber (EPDM) could be considered as alternatives, but they are able to operate at maximum temperatures ranging between 150°C and 180°C (specifically, 150°C EPDM, 160°C EPR, and 180°C rubber), therefore

they are not able to work at the required operating temperature of around 250°C, which is frequently encountered in car engines where lambda sensors are installed. In addition to this, alternatives do not meet the mechanical properties (elongation) required by the automotive sector for these critical components.

In addition, EPR and EPDM are resistance to some acids and alkalis, but they are not recommended for petroleum fluids or diester lubricants, products that may eventually become in contact with lambda sensors at some point while in operation.

Potential impacts related to substitution

As mentioned above, alternative materials do not meet the performance required for the adequate functioning of lambda sensor, mainly related to the maximum operating temperature required, which for alternative materials is lower than the maximum temperature that can be achieved with the use of PTFE. This would result in downgraded performance and reduced efficiency to control gas emissions and fuel consumption. This would not be aligned with the decarbonization and sustainability policies that are being promoted by the European Union through the Green Deal.

Alternative materials such as silicon, EDR and EPDM also offer reduced performance on other relevant parameters such as chemical resistance to lubricants or elongation, which are important to ensure adequate fitting and performance in car engines.

Conclusions on the application

Lambda sensors are an essential component that optimizes the functioning of combustion engines to guarantee that gas emissions from vehicles are kept within adequate parameters and fulfil the limits established in the relevant European regulations. The adequate functioning of these components is an essential element to ensure that the objectives to reach net zero carbon emissions by 2050 will be achieved. In order to ensure such adequate performance, PTFE will be required for the production of lambda sensors. While it is expected that combustion engines will be replaced by EVs in the coming years, vehicles based on combustion engines will still be in operation likely until 2050 and, considering the need to provide spare parts for vehicles that will still be operational within approximately 30 years, it can be concluded that PTFE has a key role to play in ensuring the Green Deal objectives in the described application.

3.4.3. Application 4.3: Use of PTFE in the production of control cable liners for the transport industry

Description of the application

PTFE is used in control cable linings for vehicles and aircrafts due to its low coefficient of friction and durability properties, which in combination with some abrasion resistant fillers enable metal wires to slide through the liner as the inner part of cable construction. Control cable liners ensure the well-functioning and safety of vehicles and aircrafts (including spaceships). They are used in many applications such as speedometer cables, hand brake and accelerator cables, gear shift and clutch cables, parking brake and fluid lid opener cables, etc. Control cables are also applied for outdoor power equipment, such as light duty throttle cables or heavy-duty transmission and brake cables. They are even involved in the adequate function of key components related to safety such as wing flaps required to ensure reliability during take-off and landing of aircrafts. Ultimately, these cables are used in any general systems that may require movements in the order of millions of cycles in a lifetime.

These cables need to perform under very demanding and highly variable conditions, e.g., in terms of temperature changes (from cables close to engines to external equipment at high altitude and therefore very low temperatures), resistance to harsh chemicals (fuels and other liquids in vehicles) with no tolerance to failure, situations under which PTFE provides outstanding properties.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (> 40 MPa)
- Wear resistance (>1 million cycles)
- Mechanical properties (elongation break)
- Low coefficient of friction (max 0.2)
- Resistance to chemicals (hydraulic fluids, oils, acidic aqueous solutions)
- Resistance to high temperature (> 250°C)
- Resistance to low temperature (-70°C)
- Wide temperature range of operation
- Fire retardancy/smoke suppression

General description of alternatives and comparison with fluoropolymers

PEEK could be seen as an alternative to PTFE for cable liners. This material offers stability at higher temperatures and can allow for some protection of cables under certain conditions; however, it is not expected to provide the same combination of properties that PTFE offers in one single product.

Potential impacts related to substitution

PEEK is not expected to match the performance required for the lining of control cables intended to be used in the automotive and aerospace industries. Even if additional additives for lubrication were to be used, the results of the application on demand could not be compared with the low coefficient of friction, resistance to chemicals, lifespan, and wide range of operation that PTFE offers, particularly for critical safety systems that need to perform at extremely high cycles in a lifetime. Again, PEEK may proof to be efficient in some cases (e.g., resistance to only some (not all) foreseeable chemical environments in the application, or adequate performance up to +250°C, but not at low temperatures expected in high altitude during flight operation), but not in the broad range of scenarios that can be expected in the automotive and aerospace industries. For this reason, any initiative that could push for replacement of PTFE in control cable liners could create high risk situations for the population, since safety performance of critical transport systems would be downgraded.

Conclusions on the application

Fluoropolymers and in particular PTFE provide a unique combination of properties and remains the best (if not the only) option to facilitate adequate and reliable performance of control systems in land vehicles and aircrafts. If PTFE were not allowed to be used in control cable lining, the performance of these essential components would be seriously downgraded, resulting in a clear compromise to safety of passengers and the population in general. PTFE can be regarded as the top technology option today for these cable liners and removing it from these applications would bring control systems in vehicles to their technological infancy.

Under this circumstance, the whole transportation sector in the EEA, including vehicle and aircraft manufacture, could face an uncertain future and relocation to other countries, mainly in the Americas and the Asia-Pacific region could benefit from technology transfer to guarantee continued availability of highly reliable land vehicles and aircrafts. In addition to the safety considerations, impacts on standards of living of the general population (not only related to massive employment losses in these sectors, but also to affordability of e.g., cars and airplane travel) would need to be carefully evaluated.

3.4.4. Application 4.4: Use of PTFE and ETFE in the production of different auxiliary components for the automotive industry

Description of the application

PTFE and ETFE are used for the manufacture of different parts of car equipment, such as door hinges and seat height adjustment bearings. These parts can be regarded as pivot points which are subject to sporadic demand while cars are running, requiring high reliability and very low friction conditions.

Technical properties required for the material of choice

For these applications, the following properties are relevant for the material of choice:

- Mechanical strength (<12 MPa)
- Tensile strength (>40 MPa)
- Wear resistance (<5E-7 mm^3/Nm)
- Flexibility (E-Modulus <500 MPa)
- Resistance to high temperatures (>250°C)
- Resistance to low temperatures (-30°C)
- Wide temperature range of operation
- Vibration dampening (>0.9)
- Impact resistance (IZOD impact test >8kJ/m^2)

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are:

- Steel/Steel
- High temperature polymers
- Ultra-high molecular weight polyethylene (UHMWPE)

Steel/steel solutions and high temperature polymers

These alternatives require re-greasing the system in very short time frame (e.g., every two weeks) in order to avoid continued squeaking of the systems. Other high temperature polymers also require additional lubrication either like the steel/steel contact or solid lubricants like PTFE.

High temperature polymers

These polymers are so rigid that a press fit assembly is not possible, which in turn requires additional sealing and causes door drop issues due to wear, because wear particles can easily fall out the contact. Furthermore, in relation to seat-height adjustment bearings, the lack of press fit assembly will make it impossible to remove rattling noises from unoccupied seats, making the car noisier.

UHMWPE

UHMWPE has good mechanical, physical and tribological properties, such as: extreme hardness and durability, good chemical resistance, abrasion resistance, impact resistance, being easy to fabricate, a very low coefficient of friction and being a non-polarity polymer, which would have no additional lubrication requirements. However, UHMWPE causes rigidity issues. In addition, this material has a very low temperature resistance, with a melting point of 125°C -132°C, in contrast with PTFE which has a melting point of 327°C.

Potential impacts related to substitution

For door hinges, good lubrication is essential which can be achieved via the use of fluoropolymer-based systems. Alternatives resulting in higher friction would require significant amount of additional lubrication, this would have to be done via the use of oils which would result in environmental impacts. For example, the use of steel/steel systems in door hinges with frequent re-greasing was a feature of the old (and iconic) Volkswagen Beetle model launched in the 1940s.

From an economic perspective, while the steel-steel contact solution may be cheaper in the creation phase, regreasing efforts should be taken into account when evaluating this possibility. In a broader service life consideration of cars, the final outcome would result in higher costs, particularly if the car owner is not able or willing to take care of the service on his own.

In relation to UHMWPE, it is relevant to note that its low temperature resistance would create significant problems to the car manufacturing industry. This would force the complete redesign of the assembly process of cars (a quite complex one), which involves painting at high temperatures. Doors and hoods would have to be painted separately from the car body and assembled later, in contrast with modern technology (i.e., involving the use of fluoropolymers) which allows for the homogenous painting of the car body together with doors and hoods. This would result in significant impact to the car industry. Indeed, while the UHMWPE solution is also more economic (if focus is placed only on direct comparison one-to-one with the fluoropolymers), the fact that this solution would require major technical changes to the car industry could lead to investments for car manufacturers which could be expected to reach amounts near 100 million EUR.

In addition, alternatives must be tested to check that the performance and safety requirements are fulfilled. The substitution must be also approved by the manufacturers of the different applications. This process takes time, depending on the sector the time frame to consider could be in the range of 5-10 years.

Conclusions on the application

The alternatives previously described will likely result in higher maintenance costs and lower car reliability due to the lower quality of the material replacements. As a result, car production could remain in Europe, but cars produced outside the EEA will be more comfortable, less

noisy and they will require less maintenance. Altogether, the competitiveness of the automotive industry in the EEA will be compromised, as manufacturers based outside the EEA will have opportunities for more cost-effective design solutions.

According to information from the European Automobile Manufacturer's Association (ACEA, 2022), in 2018 the automotive industry was responsible for 12.6 million jobs in the EU, including manufacturing, services and construction. This corresponds to 6.6% of the total EU employment. Direct manufacture of motor vehicles employs 2.6 million people. In terms of trade, a positive balance 76.3 billion EUR was achieved in 2020 in the trade of motor vehicles, with 134.1 billion EUR of exports. The automotive industry contributed to 398.4 million EUR in fiscal income from motor vehicles in 2020 (data from EU14). In the same year, the sector of automobiles and parts invested 58.8 billion EUR in research and innovation related activities.

The use of alternatives would bring certain parts of car technology to systems that were used 50+ years ago. In the event that fluoropolymers may not be available for the application described, it is difficult to assume that consumers would accept a recoil in car quality and comfort, particularly when non-EEA car manufacturers may continue to keep those standards at XXI century levels. Going back to noisy and squeaking car components would be considered a significant disadvantage from a competitive perspective, for a very relevant industry in the EEA.

3.4.5. Application 4.5: Use of FKM for sealing applications in the automotive industry

Description of the application

FKM-based fluoroelastomers are used by the automotive industry in various products such as o-rings, gaskets, shafts, joints, fuel and turbo charger hoses and other connector components that are subject to intense temperature, in order to provide highly reliable sealing systems.

With the development of modern and more fuel-efficient turbochargers involving high pressure direct fuel injection, technical performance required from such sealing systems has reached unprecedented levels. It is imperative that no leakage at high temperatures occurs in vehicles in order to ensure safety for passengers and the surrounding population. Moreover, this energy-efficient, highly powerful and complex engines require durable components that will operate for longer periods without requiring frequent maintenance or replacements.

This case may be expanded to other engine-based means of transport such as aircrafts and ships.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (> 8MPa)
- Wear resistance
- Flexibility
- Low coefficient of friction
- Resistance to harsh chemicals, such as synthetic oils
- Resistance to high temperature (> 200°C)
- Wide range of temperature operation (-40°C to 250°C)
- Barrier properties
- Non-stick properties
- Fire retardancy / smoke suppression

General description of alternatives and comparison with fluoropolymers

Other rubber or elastomeric materials such as acrylic rubber (ACM), ethylene acrylate copolymers (AEM), HNBR, UHMW-PE, Polyoxymethylene (POM), PU, PEEK or EPDM could be suggested as potential alternatives. However, they would fail to provide the same level of efficient performance that FKM-based sealing systems offer. Other elastomeric materials such as ACM, AEM or HNBR have much higher friction coefficients, which is not suited for materials that need to be in constant demand for interacting with other pieces of vehicles while in use. UHMW-PE, POM, PU fail in heat resistance as they cannot withstand the temperature ranges required by car engines. PEEK is too hard to perform adequately in the sealing function of highly demanding engines.

EPDM is a synthetic rubber material that can offer good resistance under certain chemical environments, mainly for outdoor applications. It offers a good range of temperature

resistance (-50°C to 150°C). Although EPDM offers good resistance to diluted acids, ketones and alkalis, it does not perform so well in case of fuels, oils and non-polar solvents. It certainly would not be a suitable choice for the automotive sector, or others in which harsh conditions are expected.

In summary, while there are low-cost alternatives to FKM for certain less demanding (e.g., outdoors) applications, for cases such as car engines where highest standards of chemical and thermal resistance are required, FKM is currently the only reliable option available on the market.

Potential impacts related to substitution

If FKM seals were to be replaced by alternatives from vehicle engines, these systems would become less reliable and subject to increased need for maintenance and replacement, because the alternatives described previously would not perform at an equivalent level. All of them would fail to provide the same technical performance as FKM at least in one key property. FKM is currently the only material available on the market that fulfills all the technical conditions that modern turbocharger engines require to operate vehicles in an efficient way.

Conclusions on the application

FKM seals are a good example of fluoropolymers offering not just one but a combination of different properties that are (all of them required) in high technology applications. While other materials are available on the market, and they could offer equivalent performance under one single property required, they would fail to provide the same performance as FKM sealing systems. This makes those alternatives as not suited to be used for sealing systems in the automotive sector. Beyond increased wear rates, maintenance costs and generation of waste from repairs, the critical trade-off that would be derived from the replacement o fluoropolymers from this application is the fact that safety of passengers and the general population would be compromised due to higher risk of unexpected failure of engine components.

3.5. Sector of use 5: Food and water processing

3.5.1. Application 5.1: Use of modified PTFE, PFA and FEP in the production of systems used for food processing

Description of the application

Modified PTFE is used in membranes and bellows for food and beverage processing systems, but also in many components used by this industry such as baking belts, baking trays, cooking liners etc. In addition, PFA and FEP can also be used for different components in food processing and packaging machines. Because of their superior mechanical and non-stick properties, as well as low coefficient of friction, durability, wide temperature range of operation, and chemical resistance, fluoropolymers are used by the food processing industry when harsh conditions of use are required, or when ultra-high levels of purity and quality are needed. Membranes are used to provide aseptic conditions during handling of food, and bellows are designed to provide a dynamic separation element to protect the product from contamination.

Specific European regulations are in place for materials intended to come into contact with food, with positive lists indicating authorised substances, as well as allowed migration limits.

Fluoropolymers offer the high purity and strictest hygienic requirements that the food industry requires. Those properties are crucial in food processing. Materials must also meet inertness and resistance to high-temperature properties to avoid the migration of hazardous substances into the food that would imply contaminations that could create significant problems related to human health. Furthermore, fluoropolymers allow a unique sealing due to their resistance to chemicals and temperature that provides very precise dosing of the components during the process.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (>30 MPa)
- Wear resistance (min 1E-6 $mm^3/(N{\cdot}m)$
- Mechanical properties (min 3E6 cycles)
- Low coefficient of friction (max 0.2)
- Resistance to chemicals
- Resistance to high temperature (150°C)
- Biocompatibility (food approvals required, e.g., NSF – EU10/2011 and GB4806.1)
- Wide temperature range of operation (0°C to 150°C in several operational conditions)
- Non-stick properties
- Fire retardancy / smoke suppression
- Low bacterial/algae growth

General description of alternatives and comparison with fluoropolymers

Elastomers like EPDM, methyl vinyl silicone rubber (MVQ), or NBR could be considered as alternatives, however they can only be used for a limited life cycle (maximum 20,000 life cycles) so the durability of the application is drastically reduced. On the other hand, the combination of resistance to high temperatures and chemicals are not met at an equivalent level that are achieved with the use of PTFE.

Other materials like PVC, polystyrene or silicon could also be recommended but approval state for food contact, chemical resistance against cleaning agents and performance under changing temperatures are coming as trade-offs.

Potential impacts related to substitution

The substitution of PTFE membranes and bellows with a combination of alternative materials would be expected to result in more frequent replacement of the damaged components. It is estimated that this would be increased by a factor of 150, therefore maintenance costs will be significantly increased as well, in addition this would lead to the generation of more waste since materials would need to be disposed frequently. These repairments also mean production losses, lower reliability, reduced life span and efficiency and a higher risk of food contamination. In contrast, fluoropolymers provide a long-life span to the materials due to their resistance to fatigue.

Membranes and bellows functions to avoid contaminations from the equipment and/or the environment will not be achieved by the alternatives which is a critical point for food safety so human health could be compromised. In addition, it will be quite difficult to obtain the demanding cleaning conditions required by the food industry as the resistance to chemicals of the alternatives are lower than fluoropolymers so again, it would result in health issues. In addition, food and drink streams must not excessively stick to the thermocouples or other food quality sensing devices.

All possible alternatives come with significant shorter lifetime cycles. This requires regular repair cycles for the equipment due to failures, which are costly and produce more waste. For low-cost consumer products this would most likely result in that repair costs are higher than buying new product which results in immense waste and recycling challenges. For higher end products for industrial use, the cost of the final product produced will most likely be higher due to more maintenance and labour cost involved. Even here, the consumer buying the final product (coffee, juice, tomato puree, soups, etc.) will pay the higher price, generating increased inflation in the EU zone in the long term.

Europe would lose competitiveness, especially to Asia-Pacific countries where cost is not high and circular economy is not yet a prioritised topic. More low-cost problems would be imported, and the amount of waste would increase as cheaper products (like household coffee machines) will be disposed instead of putting them into service/repair. Trends will get

removed from circular economy back towards “use and trash – then buy new” as it was the case in the past.

Conclusions on the application

Fluoropolymers provide a unique combination of properties that allow food processing equipment to reach extreme conditions, which is not possible with the use of existing alternatives. If fluoropolymers were not available for use in the food industry, performance of those systems would be seriously downgraded, resulting in increased risk of food contamination or reduced food quality, which could in turn derive into serious health concerns for the general population.

Food and Beverage filling and packing is an extraordinarily relevant industry in EEA, all from dispensing fluids like coffee or juices to breweries or packing equipment. According to FoodDrinkEurope (2022), the EU food and drink industry employs 4.5 million people, generates a turnover of 1.1 trillion EUR and 222 billion EUR in added value, making it one of the largest manufacturing industries in the EU These industries are in need of fluoropolymers as the non-stick properties in combination with chemical resistance makes advanced automation processes (with changing media/fluids and cleaning cycles in between) possible. Reducing these, the EEA will suffer a significant loss in both workforce but even more competitiveness towards other regions like Asia Pacific. Production would most likely be moved out of the EEA if product quality and safety would be downgraded due to the use of alternatives. Standard of living and choice of products would also be reduced, and increased waste generation due to disposal of more frequently replaced elements should also be taken into consideration. While this impact may not be as severe as others related to safety considerations, they should be taken into account as well when evaluating the regulatory future of fluoropolymers.

3.5.2. Application 5.2: Use of PVDF in the production of membranes for water treatment

Description of the application

PVDF is used in the production of hollow fibre membranes used in different subsegments of water ultrafiltration systems. For example, these membranes are relevant at industrial and municipal wastewater treatment plants in which treated water is expected to be returned to waterways (e.g., rivers). They are also used in drinking water at municipal water plants, and also at industrial sites (irrigation in agriculture, cooling towers in process industries, etc.).

Hollow fibre membranes are a class of artificial membranes containing a semi-permeable barrier in the form of a hollow fibre. Originally developed in the 1960s for reverse osmosis applications, hollow fibre membranes have since become prevalent in water treatment, desalination, and other applications[5]. Most commercial hollow fibre membranes are packed into cartridges which can be used for a variety of liquid and gaseous separations.

PVDF filtration membranes are used to filter out contaminants such as pathogens (parasites, bacteria, and viruses), micropollutants (such as pesticides, pharmaceuticals, personal care products, endocrine disruptors and microplastics for drinking water production. A membrane bioreactor (MBR) is a combination of membrane processes like ultrafiltration with a biological wastewater treatment process (activated sludge process).

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength: Tensile strength >45 MPa (ASTM D638).
- Wear resistance: 10 years accelerated test (internal standard test).
- Mechanical properties: Elongation at yield > 25% (ASTM D638); Tensile modulus <2200 MPa (ASTM D638).
- Resistance to harsh chemicals: 1,000,000 ppm·hours to sodium hypochlorite (NaOCl) exposure for membrane cleaning, which is a critical chemical used for removing organic constituents and disinfection.
- Non-stick properties: Resistance to fouling by organic constituents present in surface waters.

PVDF membranes are typically rigorously tested and meet drinking water standards throughout the world. Certifications include: NSF 61 and NSF 419 (USA), KTW (Germany), KIWA (Netherlands), ACS (France), DWI (UK), ICIM (Italy), MOH (China), or KWWA (Korea).

General description of alternatives and comparison with fluoropolymers

PES is the most common material that could be described as a potential replacement for PVDF for the production of membranes intended for water filtration. Other compounds such as PE

[5] https://en.wikipedia.org/wiki/Hollow_fiber_membrane

and PP, or even ceramic based materials may be used in membranes, but PES stands out as the most typical option.

Where one-to-one replacements would not be considered, the only other alternative for water treatment would be to return to clarification methods based on the use of a wide variety of chemicals (e.g., flocculants, coagulants), as well as conventional gravity settling and sand filtration, which is a fairly old technology.

In relation to hollow fibre ultrafiltration membranes, it is critical to distinguish between inside-out type and outside-in type. For inside-out hollow fibre membranes, the feed water is fed to the inside bore of the hollow fibre and the clean water passes through the polymer matrix (the separation barrier) to the outside of the hollow fibre. This type of membrane is used on easier to treat applications (e.g., post treatment of potable water, low turbidity surface water). For inside-out hollow fibre membranes, PES can be used effectively. For outside-in hollow fibre membranes, dirty water is on the outside of the hollow fibre and the clean water is collected from the inside of the hollow fibre. Outside-in hollow fibre membranes are used on higher solids and more fouling feed waters (e.g., industrial applications, wastewater treatment, high turbidity surface water). Due to the challenging applications, outside-in hollow fibre membranes are subjected to more aggressive cleaning, including agitation with air scouring and use of high concentrations of cleaning chemicals (e.g., sodium hypochlorite and acids). For these reasons, outside-in hollow fibre membranes are almost exclusively made from PVDF (The MBR site, 2017).

Potential impacts related to substitution

As previously mentioned in the description of other cases, there are indications that PES may be related to equivalent concern as BPA due to potential endocrine disrupting properties (Kang et al., 2014). In addition to this PES-based membranes are known for exhibiting inferior performance compared to the PVDF equivalent. For example, while PES may provide equal mechanical properties (reaching tensile strength above 45 MPa), its elongation at yield is lower (6% compared to 25%), and the resistance to sodium hypochlorite is limited to 250,000 ppm hour. Their reduced flexibility and chemical resistance will make PES membranes brittle during product life, resulting in broken fibres and reduced life expectancy (5-7 years compared to nearly 20 years duration of PVDF membranes). Furthermore, changing existing PVDF-based systems to PES would require significant engineering studies and equipment changes to make PES membranes work. Because the solutions using PES membranes will be more complex with additional treatment steps, the cost of substitution is expected to be in the range of hundreds of millions EUR for making the necessary retrofits. Additionally, future membrane treatment plants will also be much more expensive to construct if PVDF membranes are no longer available.

The change to filtration systems based on non-membrane solutions would result in the need to use older technologies that imply the use of chemicals and less efficient water treatment processes which could seriously impact the quality of water that could return to humans or the

environment. Indeed, MBR technology using PVDF hollow fibre membranes replaced old conventional gravity settling and sand filtration, and it plays a critical role in providing the advanced wastewater treatment needed to allow municipal wastewater treatment plants to effectively comply with the Urban Wastewater Directive [6] (91/271/EEC), to which the protection of aquatic ecosystems, bathing water, and groundwater are closely related.

Membrane filtration also provides high-quality reclaimed water, helping cities to meet the EU Water Reuse Regulation [7] as well as other legislations fostering the recycling of municipal and/or industrial wastewater. The potential role of treated wastewater reuse as an alternative source of water supply is now well acknowledged and embedded within European and national strategies. Water reuse is a top priority in the Strategic Implementation Plan of the European Innovation Partnership on Water, while maximization of water reuse is a specific objective in the Communication "Blueprint to safeguard Europe's water resources" (COM, 2022).

Many cases exist where membrane filtration was determined to be the best available technology (and in some cases the only viable technology) to protect ecologically sensitive water bodies. Examples include plants in Sweden, with 540 Minimal Liquid Discharge (MLD) and commissioned in 2008, which is the largest MBR in the world, Germany (47 MLD, commissioned in 2003), France (108 MLD, commissioned in 2013) and Belgium (86 MLD, commissioned in 2017).

The annual MBR market is estimated at around 5 billion EUR, solutions costing 50-100% more would result in 2.5-5 billion EUR per year additional investment to meet future wastewater treatment needs. For one single membrane producer in the EU, 1000 jobs would be expected to be lost, including high level manufacturing, engineering, and R&D jobs. Another 500-800 jobs could be lost in other functions within the EEA countries, with revenue losses for one company alone expected in the range of would be 250 - 350 million EUR per year.

Conclusions on the application

Fluoropolymers provide the best solution to allow high quality water ultrafiltration systems. Alternative materials or technologies will either imply the use of potentially hazardous chemicals (PES) or the return to technologies that were used decades ago, involving increased use of chemicals which may remain in water that will later return to the environment. Without this technology, more complex and expensive solutions will have to be employed to provide removal of these contaminants. For many of the more challenging surface water sources impacted by increasing weather events brought on by climate change, good alternative solutions are not feasible in practice.

[6] Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment.
[7] Regulation (EU) 2020/741 of the European Parliament and of the Council of 25 May 2020 on minimum requirements for water reuse

3.6. Sector of use 6: Medical and pharma

3.6.1. Application 6.1: Use of PTFE in the production of equipment to be used in vaccine preparation requiring ultra-high purity media

Description of the application

Similar to **Applications 1.1** and **3.1**, PTFE is used in vessels, pipes, and fitting systems (e.g., diaphragms in valves) for the pharmaceutical industry, with the objective to produce medicines and vaccines, requiring ultra-pure media and sterile conditions. In this industry, most of this equipment is not necessarily based on other materials lined with fluoropolymer, but the fluoropolymers are directly used for tubing and piping systems.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (<10 MPa)
- Flexibility (E-module <500 MPa)
- Resistance to harsh chemicals
- Resistance to high temperature (250°C)
- High flex-life (>5E6 cycles)
- Extremely high product purity

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are**:**

- PP lining systems
- Rubber lining systems
- Tantalum-based piping
- Stainless steel: V2, V4, 316 L, Hasteloy, Inconel
- Enamel / glass lining systems

Similar to the case of the semiconductor industry (**Application 3.1**), the highest levels of purity of chemicals used in the production of vaccines or other medical products must be guaranteed. For this reason, elements of equipment in contact with chemicals used in the manufacture of these products have to ensure that no impurities will be generated during the process, which could alter the final composition of the medicines or vaccines.

Potential impacts related to substitution

The possible alternative materials listed previously have already been discussed in previous sections and will not be commented further. Due to potential degradation from rubber or other plastic solutions, and to the release of metals or migration of components from enamel elements, the use of these materials would not guarantee the highest purity demands that

the pharmaceutical industry requires, therefore those products could not be regarded as a viable alternative to fluoropolymers in this application.

Conclusions on the application

While fluoropolymers provide an outstanding combination of properties that are relevant for this use, the possibility to grant the highest possible purity levels and sterile conditions makes these materials the only real material of choice for production of vaccines and certain medicines, for which this property is absolutely essential. Failure in achieving this requirement may result in contamination of vessels and on the final vaccines delivered to the population, which would generate not only an obvious health concern, but also social distress and significant issues related to quality controls, tracking of contaminated vessels and eventually removal of a high number of vaccines that could have been marketed before identifying purity issues. In a situation that fluoropolymers would not be available for this use, production of vaccines requiring ultra-high purity conditions may become not viable within the EEA.

According to the European Federation of Pharmaceutical Industries and Associations (EFPIA, 2022), in 2016 the market value of the European pharmaceutical industry was 199,234 million EUR, with a production value of 248,053 million EUR. Investment in innovation for the same year was 33,949 million EUR, and total spending (public and private) on healthcare as a percentage of GDP at market prices of 2016 reached 8.8%. In terms of employment, the pharmaceutical industry contributed to 747,607 jobs, with additional 115,000 jobs focused on pharmaceutical R&D.

Other than the numbers displayed above, the recent crisis related to the Covid-19 pandemic has demonstrated that it is critical for the protection of the European population to keep a strong pharmaceutical sector ready to deal with immediate challenges from an ever-increasing complex health situation.

3.6.2. Application 6.2: Use of PTFE and FPE in the production of implants for the medical device sector

Description of the application

PTFE is used in interventional delivery devices (e.g., cardiovascular grafts, arteries, hernia mesh, stents, ligaments, etc.) due mainly to its inertness, non-toxicity, and biocompatibility properties, which allow for tissue attachment and cell adhesion without adverse reactions, infections, and rejection issues. In addition to that, PTFE coatings are used to enhance anti-friction properties and enable a smooth travel through blood vessels or other parts of the body.

Interventional delivery devices are crucial and, in many cases, the only solution to solve the malfunction or non-efficient behaviour of the human organs which can lead to very serious health issues. Medical devices are essential for saving lives and enhancing the life quality for millions of people who are suffering from certain illnesses.

PTFE etched liners are used as base for the implant construction, whereas the inner diameter of the PTFE is in direct contact with the media applied through the tubing (either inside the body or extraction from the body). For this application, a very low coefficient of friction is required to not disturb the flow and to not collect residue in the liner, which may impact the performance of the medical procedure. In addition, PTFE is able to withstand several sterilization methods. The etched outer surface is needed to bond the PTFE liner stable, yet flexible on another layer of the device construction.

Moreover, it is always necessary to hold all components of the device construction in place. For this functionality, an FEP heat shrink is always needed. FEP is here used for the shrink ratios 1.3:1 or 1.6:1 which are unique for fluoropolymers to be able to give the stability needed for the device.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties (moderate stiffness and high ultimate elongation)
- Low coefficient of friction
- Chemical inertness
- Resistance to harsh chemicals (chemical inertness to industrial chemical and solvents)
- Resistance to high temperatures (260°C)
- Resistance to low temperatures (-240°C)
- Weather resistance
- Biocompatibility
- Electrical insulator (high data transmission range)
- Dielectric strength (exceptional, stable with frequency and temperature)
- Barrier properties

- Non-stick/lubricant properties
- Low bacterial/algae growth (negligible moisture absorption)
- Gas exchange properties
- Non-aging characteristics

General description of alternatives and comparison with fluoropolymers

PP is one of the more widely used synthetic plastic materials. It is both strong and flexible, easily cut and can readily be integrated by surrounding tissues. Even though this is the most popular synthetic material on the market, it is associated with many complications, including infection issues.

Other polymers usually used in tubes like PVC, PE, thermoplastic polyurethane (PU/TPE-U), or silicone could be considered as alternatives, but they do not allow for the combination of low friction (without stick-slip), multiple use (cleanability and sterilization), high temperature resistance and dielectric strength (electrical surgery) that the various implant-related applications require.

The life span of alternatives is significantly shorter than that of fluoropolymers, implying a higher probability of failure and as a result a significant risk to human health. Furthermore, the likelihood of replacement is substantially higher as well, resulting in higher levels of waste that will need to be disposed of.

Potential impacts related to substitution

Alternatives do not meet the performance required by interventional delivery devices. The non-use of fluoropolymers would result in a severe decline in the life quality of people, or in the worst-case scenario, an increase in mortality because of the lower efficiency of medical devices and/or the rejection of the implant, therefore human health would be significantly compromised.

European companies manufacturing medical devices would most likely relocate outside of the EEA to other countries where such restrictions do not apply, which could result in an increase in health care tourism. Furthermore, it would have a severe economic impact on the healthcare sector, resulting in increased unemployment and dissatisfaction among the population.

Conclusions on the application

A ban on fluoropolymers for their used in medical devices would be expected to have a great impact on society because the European healthcare sector would be with all likelihood set back more than 50 years in terms of innovation, since the most modern technologies would not be available anymore.

Medical devices are regulated by specific regulations to guarantee human health. Material qualification and registration processes for medical devices are lengthy and costly processes. Depending on the application, approval of medical devices could take up to 12 years. These

procedures often involve significant efforts in terms of testing and changes to existing validated processes. To guarantee the adequate health care, the unique combination of properties offered by fluoropolymers to the interventional delivery devices becomes essential.

For many companies, the procedure to find suitable alternate materials, to re-design the components to accommodate new materials to meet the functional requirements and to change the tools for manufacturability will pose big challenges and make the products economically unviable.

Customers will generally use the most cost-effective solution that meets the needs of the application. It should be considered that the costs and time for research, development, testing, qualifications, and changes to processes would be significant even if suitable alternatives could be identified. Any changes would have to be evaluated, more complex environmental health and safety challenges would be created, and increased costs passed down to customers.

3.7. Sector of use 7: Construction

3.7.1. Application 7.1: Use of PVDF in the production of pipe fittings and manifolds for plumbing in the construction sector

Description of the application

PVDF is used in the production of pipe fittings and manifolds for plumbing systems in buildings, both residential and industrial. PVDF was introduced in the 1990s in this sector, due to its excellent resistance to chemicals and corrosion, resistance to high temperature, high compatibility with many chemical substances, stability, inertness, flame retardant and UV resistance properties. The main applications involve heating systems and sanitary water, related to delivery and transport of both gas and water.

PVDF is non-toxic and its smooth surface does not encourage the growth of microorganisms, therefore this anti-fouling property is helpful to prevent contamination of water or gas.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength
- Wear resistance
- Mechanical properties
- Low coefficient of friction
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- UV resistance
- Wide temperature range of operation
- High limiting oxygen index
- Weather resistance
- Low bacterial / algae growth

General description of alternatives and comparison with fluoropolymers

Brass

Brass was a typical material used for plumbing applications and in fact it can still be found today as a potential alternative. However, PVDF was introduced around 30 years ago to replace brass because it is a lighter material, offers better resistance to attack and is not impacted by corrosion, offering 50+years lifetime for the plumbing installation.

Polypheny lsulfone (PPSU)

PPSU is an alternative material that can be found currently on the market ad may be used for plumbing applications. However, replacement of PVDF with PPSU in plumbing applications

could result in several trade-offs, the most relevant ones being related to compatibility with other materials used in plumbing and reduced lifespan of the materials, along with some foreseeable supply issues.

Potential impacts related to substitution

Even if brass fitting systems are still available for plumbing applications today, it needs to be highlighted that this material is prone to corrosion under certain environments. Because small (yet significant) amounts of lead can be found in certain brass compositions, corrosion of brass-based plumbing materials could lead to release of lead and introduction of this hazardous metal into water systems, which can lead to significant issues from a health and environment perspective. The fact that this material is also heavier than PVDF and would eventually reduce the lifespan of the plumbing installations highlight that it is not a suitable replacement to PVDF fittings and manifold equipment.

In relation to PPSU, it needs to be highlighted that is a polyether composed of bisphenol S (BPS) and 4,4'-dihydroxybiphenyl (DHBP), both of which have been related to potential endocrine disrupting properties (Eckardt et al., 2018). Indeed, PPSU has been associated to generation of BPS during degradation (Li et al., 2022), therefore selection of this material as a component of plumbing installations should be evaluated carefully, particularly as a replacement to PVDF in case of a ban on the use of fluoropolymers, as this could lead to regrettable substitution. PPSU is not resistant to UV radiation and therefore there could be a potential risk of decomposition and release of BPS during normal use of fitting systems produced with PPSU.

PPSU is also considered to be more fragile and not resistant to heat which makes this a less reliable material in comparison to PVDF. More significantly, PPSU is known for not being compatible with the typical glue composition (under a well-known commercial brand) that is frequently used by plumbers in their installations. Introducing PPSU for all plumbing solutions would thus create significant problems down the value chain of plumbing installations, in relation to the need to find alternative materials for sealing fittings and manifolds. In addition, new casts for fitting solutions would have to be developed, brining significant additional costs (approximately 15 million EUR are estimated by one single company) to adapt to new standards having to switch from PVDF to PPSU based fittings.

In addition to this, it needs to be noted that water and gas pipe requirements are regulated by specific regulations, which means that new materials need to be approved for these uses. Such approval procedures may take up to 5 years, with obligations to demonstrate that the alternative is safe for use in water applications. This will involve the need for testing and additional research which can be estimated at about an extra 1 million EUR.

As of today, only two companies are identified as suppliers of PPSU in the EEA. This could point towards a supply issue in the case that replacement of PVDF by PPSU could be imposed due to regulatory restrictions on the use of PVDF, including potential price increases of the

alternative. Currently PVDF is a more expensive product compared to PPSU, but this could change if its use would be imposed in the context of a restriction impact on PVDF.

Companies involved in the production of PVDF based fittings and manifolds may consider taking production of these products outside of the EEA. Individual losses for companies in this sector are estimated at 200 million EUR revenue and 400 jobs terminated.

Conclusions on the application

The consequences of a ban on the use of PVDF in plumbing applications, related to the production of pipe fittings and manifolds for use in sanitary and heating systems (water and gas) could result in significant negative impact for the European society. Looking at alternative materials, the two main options available for substitution currently would entail potential issues human health or the environment, being related to higher corrosion risk from brass (and potential release and uptake of metals like lead in water streams), or to potential degradation of PPSU (e.g., via disposal of systems after end-of-life, or by degradation via exposure to UV radiation) resulting in potential release of hazardous chemicals like BPS. It needs to be noted that PVDF was introduced around 30 years ago as a replacement of brass-based solutions, therefore this change would push the European building sector a few decades backwards in terms of innovation.

Both solutions would bring additional negative situations to the broad value chain related to plumbing, from individual company losses in the range of hundreds of millions of EUR and hundreds of jobs at risk, with relocation of activities outside the EEA, to a need for plumbers to re-evaluate basic materials used in construction, such as typical gluing systems for sealing of fittings and re-shaping of casts for new pieces. This could be related to investments in the range of tens of millions of EUR, which would also include research and testing for verification of materials to be in contact with sanitary water. Relatively long time periods for obtaining approvals to use new materials would have to be foreseen as well.

The lack of availability of fluoropolymers in the plumbing sector will therefore imply a competitiveness decrease of the European companies, due to downgraded performance related to the alternatives not being able to match the combination of properties that PVDF provides. In addition to the negative impact on health and environment, and increased costs related to substitution, more frequent maintenance and increased disposal of materials related to shorter lifespans would need to be considered.

3.7.2. Application 7.2: Use of PVDF in façade and infrastructure protection for the construction sector

Description of the application

PVDF is used in coatings for the construction sector to protect and enhance the durability of critical infrastructure elements, especially for metal-based components. These protective coatings are used in, among others, bridges, pipelines, storage tanks, racks that support solar panels, buildings in housing, heavy industry, and airports.

PVDF is used for this application due to its excellent resistance to chemicals and corrosion, resistance to high temperature, high compatibility with many chemical substances, stability, inertness, durability, flame retardant and UV resistance properties. Its exceptional flexibility allows the use in the complex forming and bending of metal building panels. PVDF is also resistant to high humidity environments, non-toxic, and its smooth surface does not encourage the growth of microorganisms, therefore this anti-fouling property is helpful to prevent stains and dirtiness.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Wear resistance: PVDF meets or exceeds the standards for the building panel industry. AAMA 2605, EU equivalent to ASTM D968).
- Mechanical properties: The superior flexibility of PVDF allows for complex forming and bending of metal building panels AAMA 2605 EU equivalent to ASTM D4145, ASTM D522 and ASTM D2794.
- Resistance to harsh chemicals: EU equivalent to ASTM D1308.
- Weather resistance: Exceptional resistance to UV degradation during exterior exposure AAMA 2605 EU equivalents to ASTM G7, ASTM D2244 colour retention, ASTM D4214 chalk resistance and film erosion.
- Barrier properties: Provides enhanced corrosion and humidity resistance VDA 233-102 EU equivalents to ASTM B117, ASTM D2247 and ASTM D4585.
- Fire retardancy / smoke suppression: Exceptional flame spread resistance and smoke development EU equivalent to ASTM E84.
- Low bacterial / algae growth
- Low refractive index for optical effects: Compared to other coating types, the lower refractive index leads to lower pigment demand for film opacity. The use of less pigment supports sustainability initiatives.
- Other properties: These coatings have less tendency to collect dirt and reduced degradation due to UV exposure. This allows for a graffiti resistant coating. This also allows for the coating to maintain solar reflectance values longer. CRRC-1 Program, ASTM D7897 and ASTM E1918.

General description of alternatives and comparison with fluoropolymers

Silicon-modified polyester, polyurethane or high-performance polyester could be taken into account as alternatives. However, alternatives would potentially reduce the life expectancy of building panels from 40 to 50 years or even more down to 20 to 35 years or less, depending on the alternative technology used and the specific setting.

Potential impacts related to substitution

If alternative materials were to replace PVDF in coating applications for buildings, the reliability of coated surfaces would be expected to decline over time due to the reduced efficiency of such materials. This could lead to compromised safety where the coatings are used to protect elements of the critical infrastructure such as bridges and buildings.

The longer durability of fluoropolymer-based coatings results in a reduced environmental impact and maintenance cost over the lifetime of the building, since maintenance activities will be minimised; less removal and replacement of building panels will be required when PVDF is used in coatings compared to alternatives. The low surface energy and hydrophobicity of PVDF also results in reduced dirt, allowing the structures to remain cleaner for a longer time. Finally, PVDF is also resistant to UV radiation, a property that all the alternatives would not offer. This means that non-fluoropolymer coatings could break down through hydrolysis and photochemical reactions, resulting in increased degradation and reduction of protection objectives.

Conclusions on the application

The architecture and construction industries are not only challenged to build structures that withstand extreme weather conditions, but also maintain the exterior appearance for years to come. Consequently, building design teams are always looking for more durable solutions when envisioning projects that use architectural metal panels. This means they are increasingly turning to architectural metal coatings that offer longevity, lasting colour retention and superior protection from the elements.

It is important to highlight that trade-offs from the use of alternatives to PVDF in this application are not related to appearance or other aesthetics properties, but to safety and integrity of infrastructures, some of which are related to housing (buildings), but also to critical components for mobility (bridges), or even for renewable energy systems (solar panels). The use of high technology fluoropolymer-based coatings allows for enhanced fire protection and longer life of coated surfaces, which in turn reduces the need for material replacement and/or recoating. The reduction in waste and material consumption would be expected to result in lower carbon usage. PVDF is used as the back sheet in most solar panels. Furthermore, the use of painted metal structures is amenable to recycling as many metals such as steel and aluminium are recycled through melting in blast furnaces. In general, it is difficult to reuse or recycle applied organic coatings, but high-temperature incineration would be expected to

result in destruction of the PFAS molecular structure and vapor capture and processing is commonly used during recycling efforts.

The use of high-technology fluoropolymer-based coatings allows for the long life of coated surfaces, which in turn reduces the need for material replacement and/or recoating. The reduction in waste and material consumption would be expected to result in lower carbon usage. The extraordinary resilience of fluoropolymer-based coatings means that relatively little of the material would be expected to be released over the product's lifespan. The erosion of the coated film is minimal. This allows for a life cycle and product warranties of 40 years or more.

It should also be noted that the use of PVDF in the construction sector is limited to industrial applications, and that PVDF-based coatings are generally not available for the general public for use in lower value applications.

The lack of availability of fluoropolymers-based coatings for the construction sector will therefore imply a competitiveness decrease for the European companies, due to downgraded performance related to the alternatives not being able to match the combination of properties that PVDF provides. It would be expected that the sheets for coatings may be produced outside the EEA and/or they will be imported in the case the application would be still needed.

In addition to the negative impact on the environment and increased costs related to substitution, more frequent maintenance and increased disposal of materials related to shorter lifespans would need to be considered.

3.7.3. Application 7.3: Use of PTFE, ETFE, FEP, PFA in the production of sealing systems in compressors used for heating and air conditioning equipment

Description of the application

PTFE, ETFE, FEP and PFA (and their composites) are used in the production of seals, bearings, gaskets, and o-rings. These materials are then used in compressors that are installed mainly in houses for heating and air conditioning purposes. However, there are other applications that could be relevant for this use, for example installations destined for food preservation and maintenance (cooling) of medical products (vaccines, etc.).

The industry referred in this case is typically referred to as Heating, Ventilation, Air Conditioning and Refrigeration industry (HVACR) or Refrigeration, Air Conditioning, and Heat Pump (RACHP) industry.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (Compressive and tensile strength, ductility, and modulus).
- Wear resistance (Wear rate, including no scuffing/galling, and ability to conform for high-speed sleeve bearings).
- Mechanical properties (Flexural strength, ability to deform/yield slightly to produce adequate sealing).
- Low coefficient of friction: 0.05 maximum dynamic friction coefficient.
- Resistance to harsh chemicals: must not excessively harden, soften, or crack in the presence of pressurized F-gases such as hydrofluorocarbons (HFC) or hydrofluoro-olefins (HFO) or hydrocarbon refrigerants and their oils, such as polyester oil (POE), polyalkylene glycol (PAG), or polyvinyl ether oil (PVE).
- Resistance to high temperature: temperatures of operation may reach 175°C.
- Resistance to low temperatures: certain HVACR applications (helium/cryogenic) can expose polymers to very cold temperatures (<-60C) due to the cooling effect of the refrigerant.
- Wide temperature range of operation: Must not excessively harden, soften, or crack in the presence of refrigerants and oils under large temperature swings (-60°C to 175°C). This temperature range may come from the refrigerant effect as well as the winter ambient outside.
- Electrical insulator: The internal motors, wire insulation, relays, electrical protectors, etc., come in contact with refrigerant and oils and must maintain their insulative properties equivalent to current fluoropolymer material.
- Dielectrical strength.
- Explosive decompression: Due to the large cyclic variation in gas pressure and temperature in normal operation, the polymer must not absorb excess refrigerant with a corresponding fast release causing material “explosion”.

General description of alternatives and comparison with fluoropolymers

Materials such as polyetherimide (PEI), polybenzimidazole (PBI), polyamideimide (PAI) or phenolic resins have been proposed as potential alternatives, however it should be highlighted that these materials have not been fully tested as replacements for fluoropolymers in the application.

Potential impacts related to substitution

None of the alternative materials that have been flagged as potential replacements for fluoropolymers in this application offer the same degree of chemical resistance. In addition, they are expected to offer inferior protection against friction in front of increased compressor power usage, leading to less reliability and service life (bearing failure rate increase, scuffing/galling rate increase), efficiency reduction (refrigerant leakage from less effective sealing causing capacity loss). In the case of flammable refrigerants (which are becoming more common as they are low global warming type refrigerants), leakage would be a safety concern.

Due to the previously mentioned inferior chemical resistance, alternative may lead to increased chemical degradation and higher chances of releases. This could be a safety concern, particularly as the use of flammable refrigerants is increasing, which are considered of lower global warming impact.

Other properties that would be downgraded are ductility, sealing effectiveness, yielding/conformability with bearings, or high temperature tolerance. All of this would make compressors less reliable, less energy efficient, not to mention the need to face higher product costs due to design changes which would likely become necessary.

It important to understand that HVACR systems are very aggressive to polymers in the general sense. HVACR systems are hermetically sealed and normally last 15 or more years. Compression of the refrigerant causes high gas pressure and temperature swings. Temperatures can range from -60°C to 175°C. Under these conditions, the refrigerant can penetrate into the polymer components or coatings and cause several destructive events (brittleness, softness, and explosive decompression). Another unfortunate consequence is that the refrigerant acts like a solvent to some extent and dilutes the oil. Dilution of the oil causes the oil's viscosity to diminish which reduces the oil's ability to effectively lubricate. There are many moving parts inside a compressor and valves and fluoropolymers are used to help reduce friction and keep the refrigerant sealed. So, all these constraints and hardships make the conditions inside an HVACR system very unique and demanding. As a result, these hardships make choosing a polymer type very difficult. There are not many polymers that can withstand this environment. Fluoropolymers are one of the few classes of polymers that work well in these environments because of the combination of many beneficial properties as described earlier and certainly the ones that offer best performance and reliability. They have been approved for use in HVACR systems for many years.

Conclusions on the application

The HVACR industry represents over 30 billion EUR in turnover, over 200,000 direct jobs and millions of indirect jobs. Even a small perturbation in this industry due the unavailability of fluoropolymers would be fairly substantial. This industry plays a vital role in the EU society. It provides critical climate control and ventilation in homes, hospitals, schools, elder care facilities, and most buildings. The HVACR industry creates the environmental conditions necessary for the application by controlling and monitoring temperature, humidity, and air quality.

Electric heat pump compressors (for hot water and air heating) are vital to reduce Europe's reliance on oil and gas. These elements are expected to play a key role in the achievement of the Green Deal goals. Less reliable, less efficient, and shorter lasting heat pump compressors would be a detriment and slow down decarbonisation objectives. Finally, it should be considered that the incorporation of low global warming refrigerants is becoming an increasing trend in the sector. The fact that these refrigerants are flammable requires absolutely efficient sealing systems, which may not be possible if fluoropolymers are not available for this application.

The following are other important applications: transportation and storage of food and other perishables, reach-in food store display cases, walk-in coolers, computer rooms, breweries, liquid desiccant dehumidification, cannabis processing, ice machines, ultra-low temperature/cryogenic freezing, warehouse climate controlled storage, process chillers in industrial plants, indoor farming, shop air drying, dental air compression, ocean refrigeration containers, rail and bus air conditioning (and monitoring), truck/trailer refrigeration, controlled storage of medicines such as vaccines and laboratory specimens, industrial and commercial chillers. Reducing or eliminating HVACR products caused by premature elimination of fluoropolymers would likely cause a global societal crisis.

3.8. Sector of use 8: Cookware

3.8.1. Application 8.1: Use of PTFE in cookware

Description of the application

PTFE is used in cookware (e.g., frying pans and in bakery trays) due to its long-lasting non-stick performance. The main positive effects resulting from this use are related to safety (preventing metal migration into food), improved health conditions (less oil being used, less burned food), sustainability (less food waste due to burned food, longer life-time of articles which are as well easier to clean, resulting in lower carbon footprint due to less water and detergent usage for cleaning) and hygiene (articles are easier to clean).

It is relevant to highlight that decomposition of PTFE is expected at a temperature of 350°C. Above 260-270°C, slight degradation of PTFE coatings may begin. However, most food will be burned before reaching any of those temperature levels, in fact decomposition of frying oil starts at 180°C, with the Maillard reaction (browning of food) starting at 140°C. Therefore, it is not expected that any decomposition of PTFE would be involved in the cooking process.

It is the case that in the curing process of cookware (not in the end use by consumers), coatings are heated up to 420°C for a short time. Any release of volatile materials (which would in any case be minimal) will be collected and absorbed by abatement techniques that are currently present at any production facility.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Resistance to harsh chemicals (those that may be used for cooking but also for cleaning purposes)
- Resistance to high temperature
- Barrier properties
- Non-stick properties

General description of alternatives and comparison with fluoropolymers

Ceramic materials can be used as an alternative to coat cookware. The use of non coated stainless-steel articles for coating can also be used but these will obviously not provide the desired non-stick properties.

Potential impacts related to substitution

Non-stick properties of ceramic coated cookware are nowhere near to the levels that PTFE provides. This means that replacement needs to occur more frequently, which will result in higher cost for consumers. Furthermore, this solution is not valid in industrial kitchen appliances (e.g., cooking robots) which require very high performance. For this sector, no viable alternatives are considered to be available.

According to the Federation of European manufacturers of Cookware and cutlery (FEC), there are currently 600 million pieces of coated cookware in EU households. Assuming a replacement of coated cookware every 4 years, this results in 150 million pieces of coated cookware being sold in Europe on a yearly basis.

Conclusions on the application

PTFE shows unique long lasting non-stick performance not met by other metals or coating materials up to now.

It needs to be highlighted that PTFE is known as being a non-toxic material. The main concern related to the use of PTFE in cookware was the use of other PFAS surfactants as polymerisation aids during the manufacturing process, where small concentrations of such surfactants may remain in the final PTFE coat and thus be released during the use phase of cookware. However, industry has taken significant steps over the last years to remove the use of those surfactants. It is expected that in the near future, all PTFE grades may be available on the market without involving PFAS in the manufacture. The result of this will be that cookware will be coated with a non-hazardous material that contains no remaining of any other substance of concern. It would therefore be questionable that a non-hazardous product should be banned from applications in which it provides significant benefits to society, related not only to comfort levels, but also to safety and improved health conditions. Indeed, even before such technical developments occurred, release of such PFAS from coated cookware was nevertheless regarded as being improbable, as stated by the German Institute for Risk Assessment (BfR, 2019), which wrote that “toxicologically relevant migration of PFOA (one of the PFAS of highest concern) from non-stick coated cookware is unlikely to happen if the production is done under ‘Good Manufacturing Practice’”.

in 2017, the Danish Consumer Council THINK Chemistry selected 16 frying pans from the Danish market. These products were tested for the release of unwanted fluorine substances. In the test, the frying pans were first washed. They were then filled with olive oil and put in the oven at 200 degrees for 30 minutes. The olive oil was then tested for the content of 22 specific fluorine substances. It was also tested for so-called total organic fluorine, which is a broad term for fluorine substances. No release of fluorine substances was found in any of the frying pans. However, the test shows that the frying pans tested did not release these substances to food. If frying pan material contains fluorine substances in their non-stick coating, the substances are therefore well-bound in the pan's material (Danish Consumer Council, 2017).

4. Conclusions

The case studies described in this report are just a small sample of the many applications in which fluoropolymers are used. However, they can be considered as a good representation of the many key properties that fluoropolymers offer to a wide number of industrial sectors, and which enable highly valuable benefits that end-users in Europe enjoy.

Fluoropolymers are currently irreplaceable for many critical applications, and existing potential alternatives would be associated with significant trade-offs that could compromise safety of workers, general population, or the environment, either due to direct hazardous properties of the alternative, or by downgrading performance of key applications. As of today, it is not anticipated that viable alternatives offering equivalent performance could be developed in the near future.

Fluoropolymers were first discovered and developed in the late 1930s. Since then, many innovative processes have been developed which involve the use of these high-value materials. This has enabled sophisticated and high-performance technological systems that have resulted in the quality standards that the modern society has achieved. Fluoropolymers were frequently introduced in existing industrial sectors to improve safety and reliability conditions, replacing less efficient materials. Under a situation in which fluoropolymers may no longer be available and downstream users would be forced to switch to alternatives, a relevant number of applications could be pushed backwards 50 years or more, in terms of technologies that would have to be used. Clear examples of this would be the manufacture of semiconductors at modern technical standards, or the development of innovative green energy techniques.

On top of this, some of those applications are key enablers of strategic objectives that the European Union has established, in terms of energy and decarbonization (as indispensable components in lithium batteries or green hydrogen production), or related to innovative technology, such as data processing systems. Ultimately, the contribution of fluoropolymers to safety in many systems related to the chemicals industry, vehicles such as cars or airplanes, processing of water and food, or production of vaccines and medicines highlight the important contribution of these materials to the European society. While human safety and environmental protection, as well as contribution to development of clean energy sources have been highlighted as key benefits derived from the use of fluoropolymers, their contribution to the competitiveness of the European industry should also be taken into account. In fact, all the respondents to the questionnaire expressed concerns that a situation in which fluoropolymers may no longer be available for the specific application described could result in strong negative impact to many sectors and eventually relocation of a large number of stakeholders involved in the value chain of fluoropolymers. 100% of the replies obtained in the survey underlined the possibility that Europe would become a net importer of articles and goods manufactured with the aid of fluoropolymers in other regions of the world

that may continue to allow the use of these substances, in an ever increasingly competitive environment.

The vast majority of fluoropolymers have been proven to be polymers of low concern. Furthermore, industry continues to make progress to remove the use of other (small molecule-) PFAS as processing aids in their manufacture of fluoropolymers. In parallel, increasingly effective abatement techniques are able to adequately control industrial emissions. All of these initiatives, coupled to the high value that fluoropolymers bring to the progress, competitiveness, safety, protection, and well-being of the modern European society, suggest that the benefits of the continued use of fluoropolymers would largely outweigh potential risks (if any), related to the manufacture, use and disposal of fluoropolymers. In summary, it appears evident that any regulatory initiative that could impact fluoropolymers should look at establishing mechanisms that would ensure that these materials will continue to be available for the many critical industrial sectors in which they are currently used.

The case studies described have been grouped depending on the sector of use involved, with a description of the specific application in which the fluoropolymers are handled. It should be noted that frequently, the combination of properties offered by fluoropolymers could make the description of one case expandable others. For example, the combination of high range of operating temperature with resistance to harsh chemical environments is relevant for sectors such as the chemical processing industry, food and water treatment, semiconductors, or pharmaceuticals. Therefore, specific cases for those sectors have been described, which are equivalent between each other in terms of describing the benefits that fluoropolymers offer for the application, as well as in relation to the potential alternatives. While this can be clearly seen in some of the cases described in this report, in other situations only one specific example has been provided, however this does not preclude that the application may be relevant for other industrial sectors. For example, the use of fluoropolymers in seals and gaskets has only been described for the chemical process industries, however fluoropolymer-based seals and gaskets are also critical for sectors such as transport of dangerous goods, automotive or aerospace industry (e.g., in safety components such as wing flaps in aircrafts). In any case, the specific cases described should be taken as a small representation of the vast spectrum of applications in which fluoropolymers can be used in the modern society.

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Annex I: Questionnaire for downstream users of fluoropolymers

1. **Please provide identification information of your company in the EEA[1] and the relevant contact person.**

Company Name	
Country	
Contact person name	
Role	
Telephone number	
e-mail address	

2. **Please indicate at least 3 examples of major applications using fluoropolymers that are relevant to your business, and the industries in which they are used.**

   For an overview of possible industry & sector of use, please refer to Annex I. If the application of interest is not found in the Annex, please describe it.

Case #	**Description of application**	**Fluoropolymers used (see list below)**	**Industries involved**
Case 1			
Case 2			
Case 3			

List of (major) fluoropolymers that will be covered in this questionnaire.

Abbreviation	**Name**	**CAS #**
PTFE	Polytetrafluoroethylene	9002-84-0
PFA	Perfluoroalkoxy polymer	26655-00-5 / 31784-04-0
FEP	Fluorinated ethylene propylene	25067-11-2
FKM	Vinylidene fluoride-hexafluoropropylene copolymer	9011-17-0
ETFE	Ethylene tetrafluoroethylene	25038-71-5 / 68258-85-5
PVDF	Polyvinilidene fluoride	24937-79-9

[1] EEA: European Economic Area = EU + Iceland, Liechtenstein, and Norway. It is expected that all the replies to the following questions refer to this economic area.

3. **Please indicate which of the following technical properties are relevant for the applications listed in question 2 (more than one selection is possible).**

   If possible, please indicate any technical requirements that may be relevant to justify the importance of the use of fluoropolymers, including units of properties. For example, "a minimum value of xx Pa for mechanical strength is required for the product to perform in Case 1".

Case 1

Category	Technical property	Relevant to application	Specification & Measurement standard
Durability	Mechanical strength		
	Wear resistance		
	Mechanical properties (e.g., flexibility)		
	Low coefficient of friction		
Inertness – stability	Resistance to harsh chemicals		
	Resistance to high temperatures		
	Resistance to low temperatures (e.g., cryogenic properties < 50°C)		
	Wide temperature range of operation		
	Weather resistance		
	Biocompatibility		
	High limiting oxygen index		
Functionality	Electrical insulator (high data transmission range)		
	Ionic conductivity		
	Piezoelectric properties		
	Dielectric strength		
	Barrier properties		
	Non-stick properties		
	Optical clarity		
	Fire retardancy / smoke suppression		
	Low bacterial / algae growth		
	Low refractive index for optical effects		
	Other (please specify):		

Case 2

Category	Technical property	Relevant to application	Specification & Measurement standard
Durability	Mechanical strength		
	Wear resistance		
	Mechanical properties (e.g., flexibility)		
	Low coefficient of friction		
Inertness – stability	Resistance to harsh chemicals		
	Resistance to high temperatures		
	Resistance to low temperatures (e.g., cryogenic properties < 50°C)		
	Wide temperature range of operation		
	Weather resistance		
	Biocompatibility		
	High limiting oxygen index		
Functionality	Electrical insulator (high data transmission range)		
	Ionic conductivity		
	Piezoelectric properties		
	Dielectric strength		
	Barrier properties		
	Non-stick properties		
	Optical clarity		
	Fire retardancy / smoke suppression		
	Low bacterial / algae growth		
	Low refractive index for optical effects		
	Other (please specify):		

Case 3

Category	Technical property	Relevant to application	Specification & Measurement standard
Durability	Mechanical strength		
	Wear resistance		
	Mechanical properties (e.g., flexibility)		
	Low coefficient of friction		
Inertness – stability	Resistance to harsh chemicals		
	Resistance to high temperatures		
	Resistance to low temperatures (e.g., cryogenic properties < 50°C)		
	Wide temperature range of operation		
	Weather resistance		
	Biocompatibility		
	High limiting oxygen index		
Functionality	Electrical insulator (high data transmission range)		
	Ionic conductivity		
	Piezoelectric properties		
	Dielectric strength		
	Barrier properties		
	Non-stick properties		
	Optical clarity		
	Fire retardancy / smoke suppression		
	Low bacterial / algae growth		
	Low refractive index for optical effects		
	Other (please specify):		

4. **Please indicate a list of potential non-fluoropolymer alternatives [2] (second best alternatives) for the applications listed in question 2.**

Case #	Potential alternatives to fluoropolymers that could be considered as alternatives
Case 1	
Case 2	
Case 3	

5. **Please explain possible trade-offs that could be expected when alternatives to fluoropolymers are used in these applications. Use the following guidance for completion.**

- Amount of product used: how much fluoropolymer is used per year, and how much alternative would be required? If total volumes cannot be reported, please state ratio (e.g., if double amount of alternative would be required, please state 1/2 in the non-fluorinated alternative column.
- Property comparison: how will the main technical function of the manufactured products be impacted if alternatives are used instead of fluoropolymers?
- Combination of functionalities: how will the use of an alternative compare in relation to the combination of technical functions that fluoropolymers bring to manufactured products?
- Overall performance: what will be the ultimate impact on the manufactured products if fluoropolymers were to be replaced with the alternatives?
- Safety & reliability: will there be any impact to the overall safety of the manufactured products (and those further down in the value chain)? If yes, please describe.
- Application life: will the service life of the manufactured products be different if alternatives are to be used in the relevant application? If yes, please describe.
- Circularity: would there be any impact in the contributions of the sector to the circular economy if alternatives to fluoropolymers were used? If yes, please describe.
- Decarbonisation: would there be any impact in the contributions of the sector to a green energy transition? If yes, please describe.
- (Eco)toxicity comparison: how would the alternatives compare to fluoropolymers from a hazard perspective?
- Other: if you can identify additional relevant criteria, please specify, and describe expected impact.

[2] The principle to follow is that there is always a possibility to substitute, therefore indicating that there are no alternatives for a specific application is not a valid reply; there will be opportunities in following questions to describe why an alternative is not considered to be ideal. Alternatives cannot be other fluoropolymers or fluorinated products (e.g., PFAS).

Case 1		
Criteria	**With Fluoropolymer**	**With non-fluorinated alternatives**
Amount of product used:		
Property comparison:		
Combination of functionalities		
Overall performance		
Safety & Reliability		
Application life		
Circularity		
Decarbonisation		
(Eco)toxicity comparison		
Other (please describe):		

Case 2		
Criteria	**With Fluoropolymer**	**With non-fluorinated alternatives**
Amount of product used:		
Property comparison:		
Combination of functionalities		
Overall performance		
Safety & Reliability		
Application life		
Circularity		
Decarbonisation		
(Eco)toxicity comparison		
Other (please describe):		

Case 3		
Criteria	**With Fluoropolymer**	**With non-fluorinated alternatives**
Amount of product used:		
Property comparison:		
Combination of functionalities		
Overall performance		
Safety & Reliability		
Application life		
Circularity		
Decarbonisation		
(Eco)toxicity comparison		
Other (please describe):		

6. **In a hypothetical case that fluoropolymers were not available for use in the EEA, and you were forced to use alternative products, do you think that the application would continue? Or could it be expected that technology would be transferred outside the EEA? Please justify your answer, including potential impacts down in the value chain.**

Case 1	
Case 2	
Case 3	

7. **Please indicate the expected socio-economic impact that should be expected if fluoropolymers were no longer available for these applications, and industry was forced to use alternative products.**
   When providing your replies, please consider the impact (if relevant for each case) of potential technological downgrades resulting from the use of alternatives, particularly since the EEA's economic strength is based on developing and supplying high technology across the globe.

   - Economic impacts: based on your knowledge of the value chain, what could be the consequences to be expected for end-use applications in the EEA if fluoropolymers were to be replaced by non-fluorinated alternatives? If available, quantitative data (real or estimated) would be highly valuable, particularly related to impacts on revenue, GDP and/or jobs that could be lost (direct and indirect); if this is not available, a qualitative estimate based on your experience could also be valuable.
   - Societal impacts: in which way would society be affected, e.g., which products or services would be impacted, and how, if fluoropolymers were no longer available for the specific application under discussion? What would be the consequences for the EEA's position in terms of technological competitiveness compared to other regions globally?

Case 1	
Economic impacts:	
Societal impacts:	

Case 2	
Economic impacts:	
Societal impacts:	

Case 3	
Economic impacts:	
Societal impacts:	

8. **Please provide any additional information that you believe could be relevant to defend the continued use of fluoropolymers in the EEA.**

Annex II: Main fluoropolymers covered in this report

Abbreviation	Name	CAS #
PTFE	Polytetrafluoroethylene	9002-84-0
PFA	Perfluoroalkoxy polymer	26655-00-5 / 31784-04-0
FEP	Fluorinated ethylene propylene	25067-11-2
FKM	Vinylidene fluoride-hexafluoropropylene copolymer	9011-17-0
ETFE	Ethylene tetrafluoroethylene	25038-71-5 / 68258-85-5
PSEPVE	Sulfonated tetrafluoroethylene	31175-20-9
PVDF	Polyvinilidene fluoride	24937-79-9

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Sources must be acknowledged.

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Preface

Background and objectives
The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of specific concern due to the actual consumption in Denmark and for which the use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (DEPA, 2011) includes 40 chemical substances and groups of substances which have either been classified as dangerous or identified as problematic due to other concerns. The criteria employed by the Danish EPA for inclusion of substances on the list include:

- Properties of concern according to the EU 'List of hazardous substances';
- Properties of concern identified using computer-based model calculations outlined in the Danish EPA's 'Advisory list for self-classification of dangerous substances' (the Self-classification list);
- PBT/vPvB substances as identified by the EU;
- Substances on the EU 'Priority list of substances for further evaluation of their role in endocrine disruption'.

Furthermore a tonnage threshold has been used. Substances used in quantities exceeding 100 tons per year in Denmark and fulfilling any of the abovementioned criteria have been included in LOUS 2009. For substances which are the subject of special focus in Denmark, the tonnage threshold can however be different.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure and information regarding ongoing activities under REACH among others.

The Danish EPA will on the basis of the surveys assess the need for any further regulation, substitution/phase out, classification and labelling, improved waste management, development of new knowledge or increased dissemination of information.

This survey concerns PFOA and PFOS-related compounds which constitute one of the 40 substances/substance groups, introduced on the List of Undesirable Substances (LOUS) of the Danish EPA in 2004. The entry in LOUS for these substances is "PFOA and PFOS compounds" and the group of substances is indicated to include at least 175 substances listed in a 2008 survey fluorinated substances in impregnated consumer products and impregnating agents (Jensen *et al.,* 2008). The 175 substances referred to in this report are in the substances group "Perfluorooctane sulfonate (PFOS) and related compounds" from the 2006 OECD list (OECD, 2006). The reason for including the PFOA and PFOS compounds is that they are all potentially degradable to substances which have proven to be persistent and which have been measured in human and animal blood. Furthermore, the substances are indicated to be included in the lists because they are toxic to animals.

As mentioned above, the main objective of this study is to provide background for the Danish EPA's consideration regarding the need for further management measures. The survey includes substances which may not be considered "PFOA and PFOS compounds"; one of the objectives is also to pro-

vide a background for a more specific description of the substance group with a clear definition of which substances are included in the group.

Organisation of the survey
The survey has been undertaken by COWI A/S in cooperation with NIPSECT and BIPRO from June to November 2012. The work has been followed by an advisory group consisting of:

- Louise Grave-Larsen, Lea Stine Tobiassen and Mikkel Aaman Sørensen, Danish EPA
- Ulla Hansen Telcs, Confederation of Danish Industry
- Nanna Rosted Vind, Danish Working Environment Authority
- Saoirse Eriksen, Danish Veterinary and Food Administration
- Allan Astrup Jensen, NIPSECT
- Carsten Lassen, COWI A/S

Data collection
The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

During summer 2012 available literature, relevant legislation and regulatory activities in the pipeline, and statistics was searched using search strings or CAS numbers covering the different groups of perfluorinated and polyfluorinated substances. Data was mainly searched via the Internet on websites of relevant organisations and databases. The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower) and the German Angel.
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Date on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet)
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA) and the INIRIS database.
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;

  - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature.
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
- PubMed and Toxnet databases for identification of relevant scientific literature.

Besides, direct enquiries were sent to Danish and European trade organisations and a few key market actors in Denmark.

Summary and conclusion

Over the period 2012-2015, all 40 substances and substance groups on The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) will be surveyed and reviewed and the Danish EPA will assess the need for any further regulation on the basis of the results, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and related compounds, which were introduced in LOUS in 2004. The entry in LOUS for these substances is "PFOA and PFOS compounds" and the group of substances is indicated to include at least 175 substances listed as "perfluorooctane sulfonate (PFOS) and related compounds" in the first list of perfluorinated and polyfluorinated compounds published by the OECD. This survey addresses all perfluoroalkylated substances and substances that may degrade into perfluoroalkylated substances i.e. substances beyond what is considered "PFOA and PFOS compounds".

The survey addresses three groups of substances:

- perfluoroalkyl substances with a chain of fully fluorinated carbon atoms (= perfluorinated);
- fluorotelomers and other polyfluoroalkyl substances where the carbon chain is not fully fluorinated, but the substances still contain a perfluorinated moiety (part of the molecule), and
- side-chain-fluorinated polymers with side-chains that contain a perfluorinated moiety.

The substances will collectively be referred to as PFCs, but should not be confused with the fluorocarbon greenhouse gases with the same abbreviation. The side-chain-fluorinated polymers differ from fluoropolymers such as polytetrafluoroethylene (e.g. Teflon®) which have fluorine directly attached to the carbon backbone and are beyond the scope of this survey.

The substance group is highly diverse; more than 600 substances from this group are pre-registered under REACH. Many side-chain-fluorinated polymers are not pre-registered because they are exempt from registration under REACH. The substances differ as to the length of the perfluorinated moiety and the functional groups attached to the carbon chain having influence on the fate of the substances in the environment and the potential health and environmental effects of the substances and their degradation products. The substances are partly degraded into the basic perfluoroalkyl acids in the environment, and the substances have been grouped by the OECD into categories based on the substances that they can degrade into; e.g. one group consists of substances that may degrade into perfluorooctane sulfonic acid (PFOS).

A distinction is made between long-chain perfluorinated compounds and short-chain perfluorinated compounds, based on the toxicity and bioaccumulation differences between the two groups. According to the OECD "Long-chain perfluorinated compounds" refers to:

- perfluorocarboxylic acids with carbon chain lengths C8 (with eight carbons in the chain) and higher, including PFOA;
- perfluoroalkyl sulfonates with carbon chain lengths C6 and higher, including PFOS and perfluorohexane sulfonic acid (PFHxS), and
- precursors of these substances that may be produced intentionally or are present as impurities in products.

PFOS and other long-chain perfluoroalkyl sulfonates

PFOS and substances that can degrade into PFOS have traditionally been the substances of most concern. Until 2000, PFOS and derivatives were the main PFCs produced, but from 2000 to 2003 the production of these substances dropped dramatically; currently, global production stands at a fraction of the peak production in 2000. PFOS is, however, still the PFC found in the highest concentration in municipal waste water, in environmental samples of surface water, sediments and biota, in food, and in human blood and breast milk. The concentration in blood and milk has decreased significantly since 2000. The fact that PFOS is still present in high concentrations in the environment reflects partly that the substance is persistent, partly that significant quantities are still accumulated in articles in use in society.

The main dietary intake of PFOS is in fish whereas it for other PFC is more even distributed among food groups. The European Food Safety Authority (EFSA) concluded in 2012 that the intake with food is well below the tolerable daily intake (TDI). EFSA notes that the uncertainty on the assessment is particular high for children younger than 1 year, due to a lack of dietary surveys reporting consumption data for this age group. Sources other than food may contribute significantly to the total human exposure, but reviews of total intake indicate that for adult in the general population the total intake is still well below the TDI. The same is indicated for children, but in this case there are some reservations because the exposure situation of children is not well understood. The TDI is based on animal studies and is under debate.

Population studies have discovered positive associations between serum levels of perfluoroalkylated acids (PFAA) and uric acid levels, thyroid disease, overweight, insulin- and leptin levels, and Chronic Kidney Disease (CKD), which is a major public health problem with increased prevalence. An investigation of children from Faroe Island in the Atlantic showed that commonly prevalent exposures to PFAAs were associated with lower antibody responses to childhood immunizations (vaccinations). The immune system seems to be highly sensitive to PFAAs, and various immune parameters were affected at levels which are found in exposed human populations.

PFOS and four derivatives have a harmonised classification as carcinogenic, toxic to reproduction and acutely toxic.

PFOS and derivatives are included in the list of restricted substances under the Stockholm Convention on persistent organic pollutants with some specific exemptions and acceptable purposes and are in the EU restricted via Annex XVII of REACH with a few specifik exemptions. As part of their revised implementation plans for the Stockholm Convention from 2012, both Denmark and the European Commission have prepared an action plan for reduction of the remaining uses and emissions of PFOS.

The current uses of PFOS and derivatives for exempt application in the EU and Denmark are well described. Data from the Danish Product Register show that six of the registered substances are included in the OECD category of substances that may degrade to PFOS. The total registered production and import was 0.52 t/y. The known consumption for exempt applications, process chemical in hard chromium plating, is only about 0.02 t/y. The data from the Product Register indicates significant consumption of PFOS for applications which are most likely restricted, but it is unclear to what extent it is due to inadequate update of the notifications to the register.

One of the main issues regarding PFOS in Denmark is the presence of PFOS in articles still in use in society. The waste situation for PFOS is well described both at EU-level and in Denmark. The majority of the solid waste containing PFOS and other PFCs in Denmark is disposed of to municipal solid waste incinerators, but it is not known to what extent the substances are destroyed at the temperatures used these waste incinerators. Limited data are available on the destruction efficiency

under the actual conditions in the incinerators. More studies are needed to clarify whether it would be necessary to dispose of PFOS-containing waste to hazardous waste incinerators in order to comply with the requirements of the Stockholm Convention.

PFOS derivatives were used in fire-fighting foam before restrictions were put in place, and cases have been observed of soil, surface water and groundwater having been contaminated with PFOS, PFOA and other PFCs at fire drill sites. The extent of the soil contamination with PFOS and PFOA in Denmark is not known; it is planned that an investigation will be launched under the Danish technology programme to examine soil and groundwater contamination. A study of releases of PFOS and PFOA to the Baltic Sea estimated that the majority of the PFOS releases were a consequence of the former use of fire-fighting foam.

A recent Danish risk evaluation of perfluorinated compounds in sewage sludge concludes that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems where the sludge is applied and that more information on the fate and effects of PFCs in soil is needed.

Perfluorohexane sulfonate (PFHxS) is the PFOS homologue with a 6-carbon chain. Due to its toxicological profile it is considered among the long-chain perfluoroalkane sulfonates. The substance has been detected in waste water, environmental samples, food, human blood and breast milk, but in lower concentrations than PFOS. No information on its use in the EU has been identified, and the substance is not registered in the Danish Product Register. The sources and pathways of PFHxS in the environment are not known. The substance is not regulated or addressed in the registry of intentions under REACH.

PFOA and other long-chain perfluoroalkyl carboxylic acids

The uses of PFOA and other long-chain perfluoroalkyl carboxylates and their precursors, fluorotelomers, are not restricted in the EU. These substances do not have a harmonised classification in the EU. A proposal for identifying PFOA and its salt APFO as Substances of Very High Concern (SVHC) under REACH due to CMR[1] properties is under way and a harmonised classification of two other substances have been proposed. Furthermore, Annex XV dossiers proposing four other long-chain perfluoroalkyl carboxylic acids as SVHCs due to PBT properties have been submitted, and for two other long-chain perfluoroalkyl carboxylic acids, a harmonised classification as toxic to reproduction is in the pipeline. PFOA and other long-chain perfluorinated carboxylic acids and their salts are all extremely persistent in the environment and they bioaccumulate in particular in mammals and birds.

PFOA, like PFOS, is found in measureable concentrations in municipal waste water, in environmental samples of sediments and biota, in food and in human blood and human milk. The concentrations are in general lower than the concentrations of PFOS (typically 2-5 times lower). According to a HELCOM assessment, the risks of PFOA on the Baltic marine environment are currently difficult to assess due to the lack of ecotoxicological information; and consequantly the predicted no effect concentration (PNEC) has not been comprehensively assessed.

EFSA concludes in the 2012 assessment that the total intake of PFOA with food for all age classes and for both average- and high-intake consumers is far below the tolerable daily intake (TDI). Reviews of total exposure from all sources indicate that intake with house dust may be of the same magnitude as the intake with food, but the total intake is still well below the TDI. Studies from several countries have demonstrated a decrease in the concentrations of both PFOS and PFOA in blood and breast milk for the period 2000-2010 while some studies have demonstated a concurrent increase in the levels of other perfluoroalkyl substances such as PFBS, PFHxS, PFNA and PFDA.

[1] CMR: Carcinogenic, mutagenic or toxic to reproduction (human health effects). PBT: Persistent, bioaccumulative and toxic to organisms in the environment (environmental effects)

PFOA and PFNA (with one carbon more than PFOA) are mainly used as polymerisation aids in the manufacture of fluoropolymers such as polytetrafluoroethylene . Concerns is related to emissions from production processes and residual content of PFOA in the final articles. In the USA, the US EPA has initiated the PFOA Stewardship Program with the eight major companies in the industry (including some European companies) which target PFOA, precursor chemicals and higher homologue chemicals. The industry has committed voluntarily to reduce global facility emissions and product content on a global basis by 95 percent no later than 2010, and to work toward eliminating emissions and product content of these chemicals by 2015. The main alternatives are C6-fluorotelomers.

The use of PFOA in the EU and the emissions from its use are well described. The substance is mainly used in the EU for manufacture of fluoropolymers. In the Danish Product Register the total registered consumption of PFOA and substances that may degrade to PFOA was 1 kg/y. Virtually no information is available on the use of other long-chain perfluoroalkyl carboxylic acids at EU level. The Annex XV dossiers for long-chain PFCAs recently submitted concludes that the substances may be used to some extent on the basis of data demonstrating that the substances can be found in the environment. The current registrations under REACH provides very limited information on the actual consumed volumes of the PFCs as most substances are manufactured or imported in tonnages below 1,000 tonnes an consequantly not registered yet.

A number of substances may serve as precursors for PFOA in the environment and for human exposure to PFOA by transformation, degradation or metabolism. Examples of those precursors are long-chain fluorotelomer alcohols (e.g. 8:2 FTOH), perfluorinated phosphonic acids and fluorotelomer-based side-chain fluorinated polymers (further described in the following). These precursors may be present in a wide range of consumer products, such as impregnated clothing and carpets. On the basis of reviews of the literature it has been concluded that FTOHs represented only a negligible contribution (<1%) to the PFOA exposure of adults. An assessment of sources of PFOA to the Baltic Sea estimated with high uncertainty that 30% of the releases were due to transformation of fluorotelomers. If this estimate is correct, the precursors may contribute significantly to the intake of PFOA with food. None of the fluorotelomers or side-chained fluorinated polymers has been proposed as Substances of Very High Concern under REACH. However, a proposal for a harmonised classification of 8:2 FTOH as toxic to reproduction has been submitted.

The French Food Safety Agency and the Norwegian Institute of Public Health have evaluated the potential human health risks related to the residual presence of PFOA in non-stick coatings for cookware and concluded that the consumer health risk is negligible. According to the German Federal Institute for Risk Assessment, it has not been shown that consumers are significantly exposed to PFOA and FTOH from clothing fabrics. However, some authors conclude that given the present state of knowledge, it is not possible to say whether the use of nonstick-coated cooking utensils or packaging materials with PFC-based coating lead to a significant increase in dietary PFC intake.

The pathways and substance flows that lead to the presence of PFOA in the environment and human exposure is still not fully understood. The missing information on the actual consumption with consumer products and the fate of the precursors through use and disposal of the articles hinder more certain modelling of the flows.

Short-chain perfluoroalkyl acids

According to the industry, the short-chain perfluoroalkyl acids and short-chain fluorotelomers are gradually substituting for the long-chain homologues because the short-chain substances are considered to have a better environmental and health profile.

The PFOS and PFHxS have to some extent been replaced by PFBS (with 4 carbon chain) and the long-chain perfluoroalkyl carboxylic acids and telomers are replaced by short-chain fluorochemicals. No data on actual consumption volumes have been available demonstrating to what extent this

shift has taken place, but data on the concentration of different PFCs in human blood and breast milk indicate a change in the exposure from the long-chain to the short-chain homologues.

The main question is how much better the short-chain substances are as compared to the long-chain substances and to what extent they still may be of concern even if they are better than the long-chain homologues.

The short-chain alternatives are as persistent in the environment as the long-chain homologues, but do not bioaccumulate to the same extent as the long-chain substances, as they are excreted more rapidly from the organisms studied. No data on the ecotoxicity of the shorter chain fluoroalkyl carboxylic and sulfonic acids have been obtained.

Concerning human health the short chain PFASs as compared to the long-chain homologues have significantly shorter half-life in human blood, do not appear to cause developmental toxicity, and have less genotoxicological potential.

Fluorotelomers and side-chain-fluorinated polymers

Fluorotelomers and side-chain-fluorinated polymers account for the major part of the present use of PFCs. The fluorotelomers do not have fully fluorinated carbon chains but a part of the chain is perfluorinated and may be degraded to a perfluorinated compound. As an example the fluorotelomer alcohol 8:2 FTOH have a perfluorinated part with 8 carbons (and 2 carbons without fluorine) and may degrade to PFOA and PFNA. The formation of more hazardous transformation products has traditionally been a major concern related to these substances. The substances themselves may, however, also have some environmental and health effects, and a proposal for a harmonised classification of 8:2 FTOH as toxic to reproduction has been submitted.

The world-wide production of fluorotelomers is estimated at 11,000-14,000 t/y. The largets amount is used as intermediates in the production of side-chain-fluorinated polymers but exactly how much is not reported. No exact data on the use in the EU is available, but the side-chain-fluorinated polymers accounted for 77% of the 3.2 t/y PFCs registered in the Danish Product Register. The polymers are used as surfactants for a wide range of applications and the major uses are all-weather clothing and other impregnated textiles, carpets and various coatings on other materials.

As side-chain-fluorinated polymers are polymers, they are exempt from registration under REACH and do in general not appear to have been pre-registered. The status of these polymers under REACH, and particularly side-chain-fluorinated polymers imported from countries outside the EU is not clear. More information on how the use of these substances can be assessed and regulated under REACH is needed.

It has been demonstrated in many studies that a wide range of perfluorinated substances at low concentrations can be extracted from e.g. textiles and packaging treated with side-chain-fluorinated polymers. The releases of substances from the different parts of the life cycle of the substances and the significance of the exposure of humans and the environment is still not fully understood and more information is needed.

Alternatives

Alternatives to PFOS for the remaining uses in Denmark were investigated in 2010/2011 and technically feasible alternatives were identified. The environmental properties of these are currently being evaluated by the Danish EPA.

Alternatives to PFOS for the remaining uses world-wide have been assessed in two studies for UNEP Chemicals in the context of the Stockholm Convention.

Alternatives to long-chain PFCs exist for most applications. The technologically best alternatives to long-chain fluorinated chemicals are short-chain chemicals with a carbon chain length of ≤C8 for perfluoralkyl carboxylates and ≤C6 for perfluoroalkyl sulfonates. The short-chain fluorinated alternatives are as mentioned still rather persistent but much less bioaccumulative and toxic than the long-chain homologues.

In addition some non-fluorinated alternatives, such as siloxanes, propylated aromatics and sulfosuccinates, can be used for specific applications. The non-fluorinated alternatives are in general less persistent and bioaccumulative, but some are toxic.

In general, there is a lack of public data on the properties of the alternatives, partly because the data are protected by commercial secrecy, partly because most scientific research has focused on the polyfluorinated substances.

Sammenfatning og konklusioner

I perioden 2012-2015 vil alle 40 stoffer og stofgrupper på Miljøstyrelsens liste over uønskede stoffer (LOUS) blive kortlagt, og Miljøstyrelsen vil på grundlag af resultaterne vurdere behovet for yderligere regulering, substitution/udfasning, klassificering og mærkning, forbedret affaldshåndtering eller øget udbredelse af information.

Denne undersøgelse vedrører perfluoroctansulfonsyre (PFOS), perfluoroctansyre (PFOA) og beslægtede forbindelser, som blev opført på LOUS i 2004. Betegnelsen i LOUS for disse stoffer er "PFOA og PFOS forbindelser" og gruppen af stoffer er angivet at omfatte mindst 175 stoffer, der er indeholdt i gruppen "perfluoroctansulfonat (PFOS) og beslægtede forbindelser" i den første liste over perfluorerede og polyfluorerede forbindelse, som blev udgivet af OECD. Denne undersøgelse omfatter alle perfluoralkylstoffer og stoffer, der kan nedbrydes til perfluoralkylstoffer dvs. også stoffer, som ikke vil være omfattet af betegnelsen "PFOA og PFOS forbindelser".

Undersøgelsen vedrører tre grupper af stoffer:

- perfluoralkylstoffer med en kæde af kulstofatomer, hvor alle brintatomer er erstattet af fluor (= perfluorerede stoffer);
- fluortelomerer og andre polyfluoralkylstoffer, hvor der ikke sidder fluoratomer på alle kulstofatomer, men hvor stofferne stadig indeholder en del hvor kulstofkæden er perfluoreret, og
- sidekæde-fluorerede polymerer, som er polymerer der er forsynet med sidekæder, der indeholder en perfluoreret del.

Stofferne vil samlet blive refereret til som PFC, men skal ikke forveksles med de fluorerede drivhusgasser som tit omtales med samme forkortelse. Sidekæde-fluorerede polymerer adskiller sig fra fluorpolymerer så som polytetrafluorethylen (f.eks. Teflon®), som har fluoratomer direkte hæftet til kulstofkæden, og som er uden for rammerne af denne undersøgelse. Det er for at understrege denne forskel, at den noget tunge betegnelse ”sidekæde-fluorerede polymerer” anvendes her.

Stofgruppen er meget varieret; der er mere end 600 stoffer fra denne gruppe, som er præregistrerede under REACH. Der er mange sidekæde-fluorerede polymerer, der ikke er ikke præregistrerede, fordi de er fritaget for registrering under REACH. Stofferne er forskellige med hensyn til længden af den perfluorerede del, og de funktionelle grupper bundet til kulstofkæden og dette har indflydelse på skæbnen af stofferne i miljøet og de potentielle sundheds- og miljømæssige effekter af stofferne og deres nedbrydningsprodukter. Stofferne bliver i miljøet delvist nedbrudt til de basale perfluoroalkylsyrer, og stofferne er af OECD inddelt i kategorier baseret på deres potentielle nedbrydningsprodukter; eksempelvis er der en kategori, der består af stoffer, der kan nedbrydes til perfluoroctansulfonsyre (PFOS).

Der skelnes mellem langkædede perfluorerede forbindelser og kortkædede perfluorerede forbindelser, baseret på forskelle i toksicitet og bioakkumulering mellem de to grupper. Ifølge OECD henviser betegnelsen "langkædede perfluorerede forbindelser" til:

- perfluorcarboxylsyrer med C8 kulstofkædelængder (med otte kulstofatomer i kæden) og højere, herunder PFOA;
- perfluoralkylsulfonater med kulstofkædelængder C6 og højere, herunder PFOS og perfluorohexansulfonsyre (PFHxS), og
- forstadier (precursere) af disse stoffer, der enten fremstilles tilsigtet, eller er til stede som urenheder i produkterne.

PFOS og andre langkædede perfluoralkylsulfonater
PFOS og stoffer, som kan nedbrydes til PFOS, har traditionelt været de stoffer, som har givet anledning til størst bekymring. Indtil 2000 udgjorde PFOS og derivater en stor del af den samlede produktion af PFC, men fra 2000 til 2003 faldt produktionen af disse stoffer drastisk, og i dag udgør den globale produktion kun en brøkdel af mængderne da produktion i 2000 var på sit højeste. PFOS er dog stadig det af PFC'erne, der findes i den højeste koncentration i kommunalt spildevand, i prøver af overfladevand, sedimenter og organismer i miljøet, i fødevarer, og i humant blod og modermælk. Koncentrationen i blod og mælk er faldet markant siden 2000. Det faktum, at PFOS stadig er til stede i høje koncentrationer i miljøet afspejler, dels at stoffet er persistent, dels at der stadig er ophobet væsentlige mængder i artikler i brug i samfundet.

Fisk udgør det vigtigste bidrag til PFOS i kosten, mens indtaget af andre PFC'er er mere jævnt fordelt på fødevaregrupper. Den Europæiske Fødevaresikkerhedsautoritet (EFSA) konkluderede i 2012, at indtaget med fødevarer er et godt stykke under det tolerable daglige indtag (TDI). EFSA bemærker dog, at usikkerheden på denne vurdering er særlig høj for børn under 1 år, på grund af manglende kostundersøgelser for denne aldersgruppe. Andre kilder end fødevarer kan bidrage væsentligt til den samlede eksponering af mennesker, men opgørelser af det samlede indtag viser, at for voksne i den almindelige befolkning er det samlede indtag stadig et godt stykke under TDI. Det samme viser beregninger i relation til børn, men i dette tilfælde er der nogle forbehold, fordi eksponeringssituationen for børn ikke er velbeskrevet.

PFOS og fire derivater har en harmoniseret klassificering som kræftfremkaldende, reproduktionstoksiske og akut giftige.

TDI'en er baseret på dyreforsøg og er under debat. Befolkningsundersøgelser har vist positive sammenhænge mellem niveauer af perfluoralkylsyrer (herunder PFOS og PFOA) i blodserum og urinsyre i blodet, sygdomme i skjoldbruskkirtlen, overvægt, insulin- og leptin-niveauer samt kronisk nyresygdom (CKD), som er et stort problem for folkesundheden og med en øget udbredelse. En undersøgelse af børn fra Færøerne viste, at almindeligt forekommende eksponeringer for perfluoralkylsyrer var forbundet med lavere antistofrespons over for vaccinationer mod børnesygdomme. Immunsystemet synes at være meget følsomt over for perfluoralkylsyrer, og forskellige immunparametre blev påvirket ved niveauer, som findes i udsatte befolkningsgrupper.

PFOS og derivater er medtaget på listen over stoffer underlagt begrænsninger i henhold til Stockholm-konventionen om persistente organiske miljøgifte med nogle specifikke undtagelser og acceptable formål. Stofferne er desuden i EU begrænset via bilag XVII til REACH med nogle få specifikke undtagelser. Som en del af deres reviderede implementeringsplaner for Stockholmkonventionen fra 2012, har både Danmark og EU-Kommissionen udarbejdet en handlingsplan for reduktion af de resterende anvendelser og emissioner af PFOS.

De nuværende anvendelser af PFOS og derivater til anvendelser undtaget i EU og Danmark er velbeskrevne. Data fra det danske Produktregister viser, at seks af de registrerede stoffer indgår i OECD kategorien af stoffer, der kan nedbrydes til PFOS. Den samlede registrerede produktion og import var 0,52 t/år. Det kendte forbrug fra anvendelser undtaget fra begrænsning, - som proceskemikalie i hårdforkromning - er kun omkring 0,02 t/år. Data fra Produktregistret viser et betydeligt forbrug af PFOS til anvendelser, der mest sandsynligt er omfattet af anvendelsesbegrænsningen,

men det er uklart, i hvilket omfang det skyldes utilstrækkelig opdatering af indberetningerne til registret.

Et af de vigtigste spørgsmål vedrørende PFOS i Danmark er tilstedeværelsen af PFOS i artikler, som stadig er i brug i samfundet. Affaldssituationen for PFOS er velbeskrevet både på EU-plan og i Danmark. Hovedparten af det faste affald, der indeholder PFOS og andre PFC'er, bliver i Danmark bortskaffet til kommunale affaldsforbrændingsanlæg, men det vides ikke, i hvilken grad stofferne destrueres ved de temperaturer, der anvendes i de disse affaldsforbrændingsanlæg. Begrænsede data er tilgængelige vedrørende destruktionseffektiviteten under de faktiske forhold i forbrændingsanlæggene. Flere undersøgelser er nødvendige for at afklare, om det ville være nødvendigt, at bortskaffe PFOS-holdigt affald til forbrændingsanlæg for farligt affald for at kunne opfylde kravene i Stockholmkonventionen.

PFOS-derivater blev anvendt i brandslukningsskum før restriktionen blev indført, og der er fundet tilfælde, hvor overfladevand og grundvand er blevet forurenet med PFOS, PFOA og andre PFC'er på brandøvelsespladser. Omfanget af jordforureningen med PFOS og PFOA i Danmark er ikke kendt, og det er planlagt, at igangsætte et udredningsprojekt under teknologipuljen for jord- og grundvandsforurening. En undersøgelse af udledninger af PFOS og PFOA til Østersøen har anslået, at hovedparten af udledningerne af PFOS var en konsekvens af den tidligere anvendelse af brandslukningsskum.

En nyere dansk risikovurdering af perfluorerede forbindelser i spildevandsslam konkluderer, at de aktuelle niveauer af PFOS i dansk slam kan udgøre en langsigtet risiko for økosystemerne i den jord hvor slammet anvendes, og at yderligere oplysninger om skæbne og effekter af PFC'er i jord er nødvendig.

Perfluorhexansulfonat (PFHxS) er en PFOS homolog med en kulstofkæde på 6 kulstofatomer. På grund af sin toksikologiske profil anses stoffet at være blandt de langkædede perfluoralkansulfonater. Stoffet er fundet i spildevand, miljøprøver, mad, humant blod og modermælk, men i lavere koncentrationer end PFOS. Der er ikke fundet oplysninger om anvendelsen af stoffet i EU og stoffet ikke er registreret i det danske Produktregister. Kilderne til PFHxS i miljøet og spredningsvejene er ikke kendt. Stoffet er ikke reguleret og der er ikke registreret intentioner om yderligere tiltag under REACH.

PFOA og andre langkædede perfluoralkylcarboxylsyrer

Anvendelser af PFOA og andre langkædede perfluoroalkylcarboxylater og deres forstadier, fluortelomerer, er ikke begrænsede i EU. Disse stoffer har ikke en harmoniseret klassificering i EU. Et forslag om at betragte PFOA og dets salt APFO som særligt problematisk stof (SVHC) under REACH på grundlag af deres CMR-egenskaber[2] er på vej, og en harmoniseret klassificering af de to stoffer er blevet foreslået. Desuden er der udarbejdet bilag XV dossier, som foreslår fire andre langkædede perfluoralkylcarboxylsyrer som særligt problematiske stoffer på grund af PBT[3]-egenskaber, og for to andre langkædede perfluoralkylcarboxylsyrer, er et forslag om harmoniseret klassificering som reproduktionstoksisk i støbeskeen. PFOA og andre langkædede perfluoralkylcarboxylsyrer og deres salte er alle meget persistente i miljøet og de bioakkumulerer især hos pattedyr og fugle.

PFOA, kan ligesom PFOS, findes i målbare koncentrationer i kommunalt spildevand, i prøver af sedimenter og organismer i miljøet, i fødevarer og i humant blod og mælk. Koncentrationerne er generelt lavere end koncentrationerne af PFOS (typisk 2-5 gange lavere). Ifølge en HELCOM vurdering er risici af PFOA for havmiljøet i Østersøen i øjeblikket vanskelige at vurdere på grund af mangel på data om stoffernes økotoksikologi, og nul-effekt koncentrationen (PNEC) er ikke blevet grundigt vurderet.

[2] CMR: kræftfemkaldende, mutagent eller reproduktionstoksisk
[3] PBT: Persistent, bioakkumulerbart og toksisk i vandmiljøet

EFSA konkluderer i en vurdering fra 2012, at det samlede indtag af PFOA med fødevarer hos alle aldersklasser og for mennesker med både gennemsnitligt og højt indtag er langt under det tolerable daglige indtag (TDI). Opgørelser af den samlede eksponering fra alle kilder indikerer, at indtagelse med husstøv kan være af samme størrelsesorden som indtagelse med fødevarer, men det samlede indtag er stadig et godt stykke under TDI. Undersøgelser fra flere lande har vist et fald i koncentrationen af både PFOS of PFOA i blod og modermælk for perioden 2000-2010, mens nogle undersøgelser har vist en samtidig stigning i koncentrationen af andre perfluoralkylstoffer som eksempelvis PFBS, PFHxS, PFNA og PFDA.

PFOA og PFNA (med et kulstof mere end PFOA) anvendes hovedsagelig som hjælpestoffer ved fremstilling af fluorpolymerer, såsom polytetrafluorethylen (PTFE). Emissioner fra produktionsprocesser og restindhold af PFOA i de færdige artikler har vakt bekymring. I USA har den amerikanske miljøstyrelse indledt et samarbejde (PFOA Stewardship Program) med de otte største virksomheder i industrien (herunder nogle europæiske virksomheder) vedrørende PFOA, stoffer der nedbrydes til PFOA og perfluoralkylcarboxylsyrer med længere kædelængder. Virksomhederne har forpligtet sig til på frivillig basis at reducere de globale emissioner fra produktionsenheder og reducere indholdet af stofferne i produkter med 95 % senest i 2010, og at arbejde hen imod helt at fjerne emissioner og indhold af disse kemikalier i 2015. De vigtigste alternativer er C6-fluortelomerer.

Brugen af PFOA i EU og emissionerne fra dets anvendelse er velbeskrevet. Stoffet anvendes i EU hovedsageligt til fremstilling af fluorpolymerer. I Produktregistret er det samlede registrerede forbrug af PFOA og stoffer, der kan nedbrydes til PFOA på 1 kg/år. Der er stort set ingen oplysninger om brugen af andre langkædede perfluoralkylcarboxylsyrer på EU-plan. De bilag XV dossier for langkædede PFCA'er, der for nylig er blevet udarbejdet, konkluderer på grundlag af data, der viser, at stofferne kan findes i miljøet, at stofferne må blive anvendt i en vis udstrækning. De nuværende registreringer under REACH indeholder meget få oplysninger om de faktiske forbrugte mængder af PFC'er, da de fleste stoffer fremstilles eller importeres i mængder under 1.000 tons og derfor ikke er registrerede endnu.

En række stoffer kan være forstadier til PFOA i miljøet og give anledning til eksponering af mennesker via transformation, nedbrydning eller metabolisme. Eksempler på disse forstadier er langkædede fluortelomeralkoholer (f.eks. 8:2 FTOH), perfluorerede phosphonsyrer og fluortelomerbaserede sidekæde-fluorerede polymerer (yderligere beskrevet i det følgende). Disse forstadier kan findes i en lang række forbrugerprodukter, såsom imprægneret tøj og tæpper. På grundlag af en gennemgang af litteraturen er det konkluderet, at FTOH'er kun gav ubetydeligt bidrag (<1%) til den samlede PFOA eksponering af voksne. En vurdering af kilder til PFOA i Østersøen anslår med stor usikkerhed, at 30% af udslippene skyldtes transformation af fluortelomerer. Hvis dette skøn er korrekt, kan forstadierne bidrage signifikant til indtagelse af PFOA med fødevarer. Der er ingen fluortelomerer eller sidekæde-fluorerede polymerer, der er foreslået som om særligt problematiske stoffer (SVHC) under REACH. Der er imidlertid udarbejdet et forslag til en harmoniseret klassificering af 8:2 FTOH som reproduktionstoksisk.

Det franske agentur for fødevaresikkerhed og det norske Institut for Folkesundhed har vurderet den potentielle helbredsrisiko i forbindelse med tilbageværende mængder af PFOA i slip-let belægninger på kogeredskaber og har konkluderet, at den sundhedsmæssige risiko for forbrugeren er ubetydelig. Ifølge det tyske Institut for Risikovurdering (BfR), er det ikke blevet påvist, at forbrugerne i betydelig grad udsættes for PFOA og FTOH fra tekstiler. Nogle forfattere konkluderer dog, at det på grundlag af den aktuelle viden, ikke er muligt at sige, hvorvidt brugen af kogegrej med slip-let belægninger eller emballagematerialer med PFC-baseret belægning kan føre til en væsentlig stigning i indtag af PFC'er med kosten.

Spredningsveje og stofstrømme, der giver anledning til PFOA i miljøet og eksponering af menneskers er stadig ikke fuldt forstået. Den manglende viden om det faktiske forbrug forbundet med forbrugerprodukter og om skæbnen af de stoffer, der kan nedbrydes til PFOA ved anvendelse og bortskaffelse af artikler, begrænser en mere sikker modellering af stofstrømmene.

Kortkædede perfluoroalkylsyrer
Ifølge industrien er de kortkædede perfluoroalkylsyrer og kortkædede fluortelomerer gradvist ved at erstatte de langkædede homologer, fordi de kortkædede stoffer anses for at have en bedre miljø- og sundhedsprofil.

PFOS og PFHxS er til en vis grad blevet erstattet af PFBS (med en kæde på 4 kulstofatomer) og de langkædede perfluoralkylcarboxylsyrer og fluortelomerer er erstattet af kort-kædede fluorkemikalier. Data om de faktiske forbrugsmængder, som kunne vise i hvilken grad dette skift har fundet sted, har ikke været tilgængelige, men data om koncentrationen af forskellige PFC i humant blod og modermælk indikerer en ændring i eksponering fra langkædede til kortkædede homologer.

Det vigtigste spørgsmål er, hvor meget bedre de kortkædede stoffer er sammenlignet med de langkædede stoffer, og i hvilket omfang de stadig kan give anledning til bekymring, selv om de er bedre end de langkædede homologer.

De kortkædede alternativer er ligeså persistente i miljøet som de langkædede homologer, men de bioakkumuleres ikke i samme omfang som de langkædede stoffer, idet de udskilles hurtigere fra de undersøgte organismer. Der er ikke fundet data om økotoksicitet af de kortkædede perfluoralkylcarboxylsyrer og -sulfonsyrer.

Med hensyn til menneskers sundhed har de kortkædede PFASs sammenlignet med de langkædede homologer betydeligt kortere halveringstid i humant blod, de synes ikke at forårsage skader på afkommet og har mindre genotoksikologisk potentiale.

Fluortelomerer og sidekæde-fluorerede polymerer
Fluortelomerer og sidekæde-fluorerede polymerer udgør størstedelen af den nuværende anvendelse af PFC'er. Fluortelomerer har ikke en fuldt fluoreret kulstofkæde, men en del af kæden er perfluoreret og kan nedbrydes til en perfluoreret forbindelse. Som eksempel har fluortelomeralkoholen 8:2 FTOH en perfluoreret del med 8 kulstofatomer (og 2 kulstofatomer uden fluor) og kan nedbrydes til PFOA og PFNA. Dannelsen af nedbrydningsprodukter, som er farligere en stoffet selv, har traditionelt været en stor bekymring i forbindelse med disse stoffer. Selve stofferne kan dog også have nogle miljø- og sundhedsmæssige effekter, og der er udarbejdet et forslag til en harmoniseret klassificering af 8:2 FTOH som reproduktionstoksisk.

Den globale produktion af fluortelomerer er anslået til 11,000-14,000 t/år. Den største del anvendes som mellemprodukter ved fremstilling af sidekæde-fluorerede polymerer, men præcis hvor meget er ikke rapporteret. Der er ingen præcise oplysninger om brugen i EU, men sidekæde-fluorerede polymerer tegnede sig for 77% af de 3,2 t/år PFC'er, som er registreret i Produktregistret. Polymererne bruges som overfladeaktive stoffer til en bred vifte af anvendelser og de store anvendelsesområder er all-weather tøj og andre imprægnerede tekstiler, tæpper og forskellige belægninger på andre materialer.

Da sidekæde-fluorerede polymerer er polymerer, er de fritaget for registrering i henhold til REACH, og de synes i almindelighed ikke at have været præ-registrerede. Status for disse polymerer under REACH, og især for sidekæde-fluorerede polymerer importeret fra lande uden for EU er ikke klar. Der er behov for yderligere viden om, hvordan anvendelsen af disse stoffer kan vurderes og reguleres i henhold til REACH.

Det er i mange undersøgelser blevet påvist, at en lang række perfluorerede stoffer ved lave koncentrationer kan ekstraheres fra f.eks. tekstiler og emballage, som er behandlet med sidekædefluorerede polymerer. Afgivelse og udledninger af stoffer fra de forskellige dele af stoffernes livscyklus og betydningen heraf for eksponering af mennesker og miljø er stadig ikke fuldt forstået, og der er behov for mere viden.

Alternativer
Alternativer til PFOS for de resterende anvendelser i Danmark blev undersøgt i 2010/2011 og teknisk mulige alternativer blev fundet. De miljømæssige egenskaber af disse er i øjeblikket ved at blive evalueret af Miljøstyrelsen.

Alternativer til PFOS for de resterende anvendelser på verdensplan er blevet vurderet i to studier for UNEP Chemicals som en del af arbejdet under Stockholmkonventionen.

Der findes alternativer til de langkædede PFC'er for de fleste anvendelser. De teknisk set bedste alternativer til langkædede fluorerede kemikalier er kortkædede kemikalier med en kulstofkædelængde på ≤ C8 for perfluoralkylcarboxylater og ≤ C6 for perfluoralkylsulfonater. De kortkædede fluorerede alternativer er som nævnt stadig temmelig persistente, men meget mindre bioakkumulerbare og giftige end de langkædede homologer.

Desuden kan nogle ikke-fluorerede alternativer, såsom siloxaner, propylerede aromater og sulfosuccinater, anvendes til specifikke formål. De ikke-fluorerede alternativer er generelt mindre persistente og bioakkumulerende, men nogle af dem er mere giftige.

Der er i almindelighed mangel på offentliggjorte data om alternativernes egenskaber, dels fordi data som oftest er beskyttet af forretningshemmeligheder, og dels fordi det meste af den videnskabelige forskning har fokuseret på de polyfluorerede stoffer.

1. Introduction to the substance group

The Danish EPA's list of undesirable substances includes PFOA and PFOS and their derivatives, but the scope of the present report has been extended to cover more perfluorinated and polyfluorinated chemicals.

Perfluoroalkyl substances, polyfluoroalkyl substances and some types of fluorinated polymers are often collectively designated PFCs, e.g. by the OECD and other international organisations (e.g. in the context of SAICM and ICCM). Unfortunately the same acronym is used for the perfluorocarbon gases in Danish and EU regulatory contexts (e.g. in Commission Regulation (EC) No 1493/2007); consequently, some confusion may occur in using this acronym. In the absence of other acronyms covering all the relevant substances, however, PFCs will be used here in accordance with the use by OECD (2006). The group covers the following substances:

- Perfluoroalkyl and polyfluoroalkyl substances (PFASs) as defined below, and
- Chemicals (including polymers) which contain a perfluoroalkyl moiety attached to other atoms that may not be perfluorinated, and which have potential to transform to produce PFASs.

This survey does not include the following perfluorinated and polyfluorinated substances:

- Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs – another use of the acronym), hydrofluoroethers (HFEs) and other similar substances;
- Other polyfluorinated organic substances without at least two fully fluorinated carbons:
- Inorganic fluorine compounds.

1.1 Perfluoroalkyl and polyfluoroalkyl substances

The perfluoroalkyl and polyfluoroalkyl substances have recently been reviewed by Buck *et al. (*2011) who suggest a common terminology, classification and acronyms for the substances and substance groups. The suggested classification and terminology for these substances will be used, and extended as necessary, in this survey.

The entire group of perfluoroalkyl and polyfluoroalkyl substances will collectively be designated PFASs; some authorities and authors of scientific papers use this acronym only for some subgroups e.g. for the perfluoroalkyl substances or for the perfluoroalkyl sulfonates.

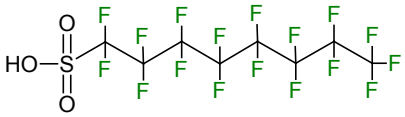
A systematic overview of manufactured perfluoroalkyl and polyfluoroalkyl substances is provided in Table 1. The table originates in a systematic overview provided in Buck *et al. (*2011). The table does not include substances which are indicated by Buck *et al. (*2011) as environmental transformation products only. Annex 1 includes a reference list of specific substance abbreviations used in this report with an indication of the chemical name, CAS No, chain length, substance group name and group abbreviation.

Perfluoroalkylated substances

The perfluoroalkylated substances consist of a large group of compounds consisting of a hydrophobic alkyl chain of varying length (typically 4 to 16 carbon atoms) and a fully fluorinated hydrophilic end group, $F(CF_2)_{n\text{-}R}$. [4]

Within the group of perfluoroalkylated substances, the perfluoroalkyl acids (PFAAs) and their salts have been the main focal point for regulatory actions until now. The main subgroups are the perfluoroalkane sulfonic acids (PFSAs) and their salts and the perfluoroalkyl carboxylic acids and their salts (PFCAs).

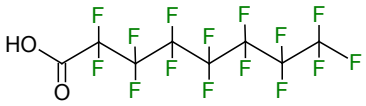
Perfluorooctane sulfonic acid (PFOS) is the most prominent of the perfluoroalkane sulfonic acids (PFSAs). PFOS has a linear perfluoroalkyl carbon chain of 8 atoms and a sulfonic acid functional group.



Perfluorooctane sulfonic acid (PFOS)

PFSAs with shorter chain lengths discussed in this report are perfluorohexane sulfonic acids (PFHxS with a 6-carbon chain) and perfluorobutane sulfonic acid (PFBS with a 4-carbon chain).

Among the perfluoroalkyl carboxylic acids (PFCAs), the most prominent member is perfluorooctanoic acid (PFOA) with an 8-carbon chain. Note that the substance has 7 perfluorinated carbon atoms only. Annex 1 list a number of PFCAs which are named according to the number of carbon atoms in the perfluorinated carbon chain. Some of the substances are commercial products, but many may be transformation products wich can be found e.g. in environmental samples or food.



Perfluorooctanoic acid (PFOA)

A distinction is made between long-chain perfluorinated compounds and short-chain perfluorinated compounds, based on the toxicity and bioaccumulation differences between the two groups (further described in Chapters 0 and 0). According to the OECD (2012), "Long-chain perfluorinated compounds" refer to:

- Perfluorocarboxylic acids with carbon chain lengths of C8 and higher, including perfluorooctanoic acid (PFOA);
- Perfluoroalkyl sulfonates with carbon chain lengths of C6 and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS), and
- Precursors of these substances that may be produced or present in products.

The designation C8, C6, etc. will be used to designate the length of the carbon chain of the perfluoalkyl moiety (part of the molecule) of the substances and not the total number of carbon atoms of the substance in this context. For the perfluorcarboxylic acids (PFCAs) and their salts, however, by tradition the C number has indicated the number of the carbon chain with the perfluorinated moiety although one of the carbon atoms in fact is not perfluorinated. PFOA, usually desribed as a C8 PFCA, consequently only includes 7 perflourinated carbons, as shown in the chemical formula above.

[4] Hydrophilic = attracted to and dissolved in water, oil repelling; Hydrophobic = water repelling, prefer non-polar solvents.

TABLE 1
OVERVIEW OF THE MAIN GROUPS OF NONPOLYMER PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (MAINLY BASED ON BUCK *ET AL.*, 2011)

Group	Subgroup	Abbreviation	Functional group $C_nF_{2n+1}R$, where R =	Examples
Perfluoroalkyl acids (PFAAs)	Perfluoroalkyl carboxylic acids	PFCAs	-COOH	Perfluorooctanoic acid (PFOA) Perfluorononanoic acid (PFNA) Perfluorohexanoic acid (PHHxA)
	Perfluoroalkyl carboxylates	PFCAs	$-COO^-$	Sodium perfluorooctanoate (Na-PFOA) Ammonium perfluorooctanoate (APFO) Ammonium perfluorononanoate (APFN)
	Perfluoroalkane sulfonic acids	PFSAs	$-SO_3H$	Perfluorooctane sulfonic acid (PFOS) Perfluorohexane sulfonic acid (PFHxS) Perfluorobutane sulfonic acid (PFBS)
	Perfluoroalkane sulfonates	PFSAs	$-SO_3^-$	Tetraethylammonium perfluorooctane sulfonate (NEt4-PFOS)
	Perfluoroalkyl phosphonic acids	PFPAs	-P(=O)(OH)2	Perfluorooctyl phosphonic acid (C8-PFPA)
	Perfluoroalkyl phosphinic acids	PFPIAs	$P(=O)(OH)(C_mF2_m+1)$	Bis(perfluorohexyl) phosphinic acid (C6/C6-PFPIA)
Perfluoroalkane sulfonyl fluorides		PASFs	$-SO_2F$	Perfluorooctane sulfonyl fluoride (POSF)
Perfluoroalkane sulfonamides		FASAs	$-SO_2NH_2$	Perfluorooctane sulfonamide (FOSA)
Perfluoroalkanoyl fluorides		PAFs	-COF	Perfluorooctanoyl fluoride (POF)
Perfluoroalkyl iodides (Telomer A)		PFAIs	-I	Perfluorohexyl iodide (PFHxI)
Perfluoroalkane sulfonamido substances	N-Alkyl perfluoroalkane sulfonamides	MeFASA, EtFASAs BuFASAs	$-SO_2NH(R')$ where $R' = C_mH_{2m+1}$ (m = 1,2,4)	N-Methyl perfluorooctane sulfonamidoethanol (MeFOSE) N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE)
	Perfluoroalkane sulfonamidoethanols and	FASEs MeASEs,	$-SO_2N(R')CH_2CH_2OH$ where $R' = C_mH_{2m+1}$ (m = 1,2,4)	N-Ethyl perfluorobutane sulfonamidoethanol (EtFBSE) Perfluorooctane sulfonamidoethanol (FOSE)

Group	Subgroup	Abbreviation	Functional group $C_nF_{2n+1}R$, where R =	Examples
	N-alkylperfluoroalkane sulfon-amidoethanols	EtFASEs BuFASEs		
	N-Alkyl perfluoroalkane sulfonamidoethyl acrylates and methacrylates	MeFAS(M)ACs EtFAS(M)ACs, BuFAS(M)ACs	$-SO_2N(R')CH_2CH_2OC-(O)CH=CH_2$ and $SO_2N(R')CH_2CH_2OC-(O)C(CH_3)=CH_2$ where$R' = C_mH_{2m+1}$ (m = 1,2,4)	N-Ethyl perfluorooctane sulfonamidoethyl acrylate (EtFOSAC)
Fluorotelomer substances	Semifluorinated n-alkanes and alkenes	SFAs SFAenes	$-(CH_2)_mH$ and $-CH=CH(CH_2)m_{-2H}$, with m = 2–16 and n = 6–16	(Perfluorooctyl)ethane (F_8H_2)
	n:2 Fluorotelomer iodides	n:2 FTIs	$-CH_2CH_2I$	8:2 Fluorotelomer iodide (8:2 FTI)
	n:2 Fluorotelomer olefins	n:2 FTOs	$-CH=CH_2$	6:2 Fluorotelomer olefin (6:2FTO)
	n:2 Fluorotelomer alcohols	n:2 FTOHs	$-CH_2CH_2OH$	4:2 Fluorotelomer alcohol (4:2 FTOH)
	n:2 Fluorotelomer acrylates and methacrylates	n:2 FTACs n:2 FTMACs	$- H_2CH_2OC(O)CH=CH_2$ and $-CH_2CH_2OC(O)C(CH_3)=CH_2$	6:2 Fluorotelomer acrylate (6:2 FTAC) 6:2 Fluorotelomer methacrylate (6:2 FTMAC)
	n:2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates	PAPs	$(-CH_2CH_2O)_xP(=O)(OH)_{3-x}$ where x = 1 or 2	10:2 Fluorotelomer phosphate monoester (10:2 monoPAP)
	n:2 Fluorotelomer sulfonic acids	n:2 FTSAs	$-CH_2CH_2SO_3H$	6:2 Fluorotelomer sulfonic acid (6:2 FTSA)
	n:2 Fluorotelomer sulfonic salts	n:2 FTSAs		6:2 Fluorotelomer sulfonyl chloride
Miscellaneous	Polyfluoroalkyl ether carboxylic acids and others		For example: $-O(C_mF_{2m})OCHF(C_pF_{2p})$ COOH	4,8-Dioxa-3H-perfluoro-nonanoate

"Precursor" is defined by OECD as a substance that has been recognized as having the potential to degrade to perfluorocarboxylic acids with carbon chain lengths of C8 and higher (including PFOA) or perfluoroalkyl sulfonates with a carbon chain length of C6 of higher. Please note the difference in chain length between the long-chain perfluorocarboxylic acids and the long-chain perfluoroalkyl sulfonates.

The fact that e.g. PFOS and PFOA can be formed by degradation/transformation of other PFASs with similar perfluorinated chain lengths influences the way the substances are currently restricted. The restriction consequently may go across the different substance groups, but specifically address substances with a similar chain length.

As an example PFOS and related substances have been restricted in the EU since 2006 and the substances have recently been included in the list of restricted substances under the Stockholm Convention as further described in the next chapter. The restriction in the EU is currently covered by the POPs Regulation, but until 2011 was included as entry 53 of Annex XVII to the REACH Regulation with a similar definition of covered substances. The substance group is defined as all substances with the chemical formula $C_8F_{17}SO_2X$ where X = OH (PFOS itself), metal salt (O-M^+), halide, amide, and other derivatives including polymers. These substances are C8 substances within the following substance groups: perfluoroalkane sulfonic acids, perfluoroalkane sulfonates, perfluoroalkane sulfonyl halides, perfluoroalkane sulfonamides and perfluoroalkane sulfonamido substances, as shown in Table 1. Furthermore, the group includes side-chain-fluorinated polymers with $C_8F_{17}SO_2$- groups attached to the carbon backbone (further discussed in section 1.2).

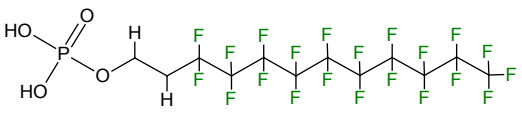
Other perfluoroalkyl and polyfluoroalkyl substances

Table 1 includes a number of other groups of perfluoroalkyl substances which are mainly used as raw materials for surfactant and surface protection products: perfluoroalkane sulfonyl fluorides, perfluoroalkane sulfonamides, perfluoroalkanoyl fluorides, perfluoro alkyl iodides and perfluoroalkane sulfonamido substances (PFAAs).

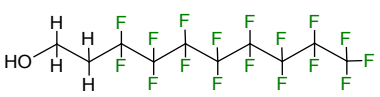
The PFAAs can be degraded to perfluoralkyl sulfonates. Most attention has been given to the aerobic biotransformation of the perfluoroalkane sulfonamido derivatives having 8 perfluorinated carbon atoms, in particular N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) and n-methyl perfluorooctane sulfonamidoethanol (MeFOSE), which are ultimately degraded to PFOS.

The main product group of polyfluoroalkyl substances are the fluorotelomers. Fluoretelomers have non-fluorine substituted hydrogen atoms (a CH_2-CH_2 group) in between the perfluorinated carbon chain and the functional group. Fluorotelomers are produced with a variety of functional groups including alcohols, sulfonamides, sulfonamidoethyl acrylates and methacrylates, and sulfonamido acetic acids.

For the naming of the fluorotelomers, a notation is used indicating the length of the perfluorinated carbon chain and the length of the chain with non-substituted hydrogen atoms. Below is a 10:2 fluorotelomer phosphate monoester (10:2 monoPAP) with 10 fully fluorinated carbon atoms and 2 non-fluorine substituted atoms and an 8:2 fluortelomer alcohol (8:2 FTOH).



10:2 monoPAP



8:2 FTOH

Fluorotelomers may be precursors of perfluoroalkyl carboxylates by degradation. The 10:2 fluorotelomer phosphate monoester shown above may thus be degraded to C10 or shorter perfluoroalkyl carboxylates.

As fluorotelomers are not degraded to perfluoroalkyl sulfonates, long-chain fluorotelomers are those with fully fluorinated carbon chains of eight or more C atoms (e.g. 8:2 fluorotelomer alcohol, 8:2 FTOH), whereas the short-chain fluorotelomers are those with less than 8 C atoms.

The majority of the fluorotelomers are used for manufacturing various fluorotelomer-based products including raw material building blocks, surfactant and side-chain-fluorinated polymers that all originate from the starting raw material, perfluoroalkyl iodide, PFAIs (Buck *et al.*, 2011). The synthesis pathway is shown in Figure 1. The final products may to some extent contain the intermediates as impurities, i.e. the side-chain-fluorinated polymers may contain FTOH as an impurity.

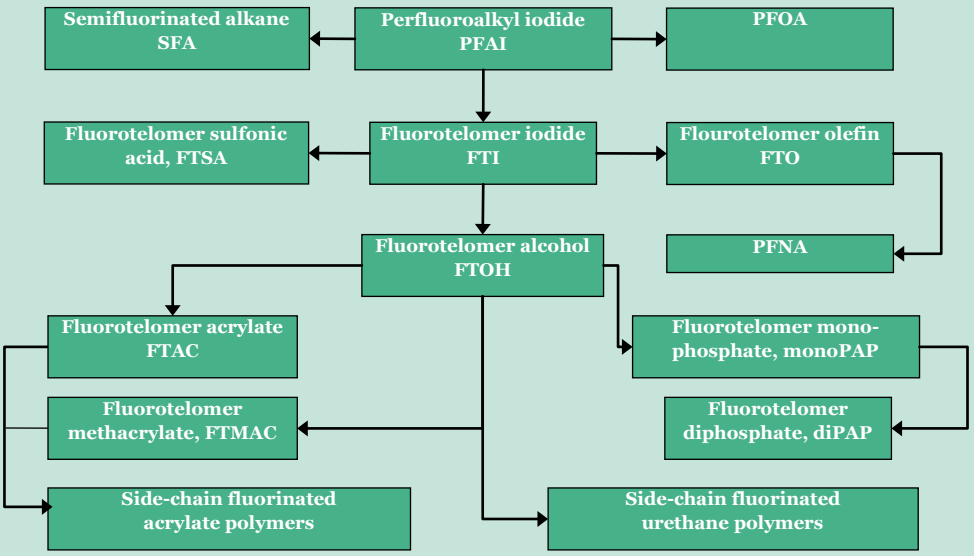


FIGURE 1
PERFLUOROALKYL CARBOXYLIC ACIS, FLUOROTELOMERS AND SIDE-CHAIN-FLUORINATED POLYMERS SYNTEHSIZED FROM PERFLUOROALKYL IODIDE (PFAI) (BASED ON BUCK *ET AL.*, 2011)

1.2 Fluorinated polymers

Many of the polyfluorinated substances on the OECD list are polymers and not covered by the definition of PFASs as used above. According to the OECD, the majority of PFOS-related chemicals are e.g. high molecular weight polymers, in which the PFOS moiety represents a fraction of the total molecular weight (OECD, 2002). The same is true for other PFASs, where the PFAS moiety also represents a fraction of the total molecular weight.

Buck *et al.* (2011) organises the fluorinated polymers into three groups as shown in Table 2.

TABLE 2
OVERVIEW OF FLUOROPOLYMERS, PERFLUOROPOLYETHERS, AND SIDE-CHAIN–FLUORINATED POLYMERS (BASED ON BUCK *ET AL.*, 2011)

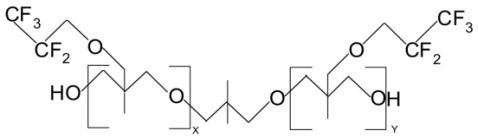
Main group	Examples	Uses
Fluoropolymers: Carbon-only polymer backbone with F directly attached to backbone C atoms	Polytetrafluoroethylene (PTFE) Polyvinylidene fluoride (PVDF) Polyvinyl fluoride (PVF) Fluorinated ethylene propylene (FEP)	Plastics for a variety of uses The presence of the fluorine atoms provides the plastics with a high thermal and chemical resistance among other properties. The issues with these polymers are the possible emissions of PFASs and other substances during the production of the polymers and possible impurities in the final material originating from non-reacted raw materials and residues of PFOA and other PFASs used as processing aids (further described in section 3.2.6).
Perfluoropolyethers (PFPEs): Ether polymer backbone with F atoms directly attached to backbone C atoms	Polymers, in whose backbone $-CF_2-$, $-CF_2CF_2-$, and possibly $-CF(CF_3)CF_2$ units are separated by O atoms	Functional fluids, surfactants, and surface protection products
Side-chain–fluorinated polymers: Nonfluorinated polymer backbone with fluorinated side chains, ending in $-C_nF_{2n+1}$	Fluorinated acrylate and methacrylate polymers	Surfactants and surface protection products e.g. water proofing, stain proofing and grease proofing finishes for textile, leather, an paper surfaces
	Fluorinated oxetane polymers	Surfactants and surface protection, mainly for textile products
	Fluorinated urethane polymers	Offered in many forms and functionalities primarily as fluorosurfactants and coatings additives

The degradation of the fluoropolymers and perfluoropolyethers cannot lead to the formation of long-chain PFCAs; these polymers are not included in the OECD list of possible precursers and are not a subject of the present survey.

In contrast to the two types of polymers described above, side-chain-fluorinated polymers are composed of variable composition backbones with polyfluoroalkyl (and possibly perfluoroalkyl) side chains. Through degradation of these polymers, the side chains may be released from the polymer chain to become PFASs. The PFASs formed will depend on the type and length of the side chains. The mechanism is further described in chapter 0. Side-chain-fluorinated polymers with side chains that may be precursors of PFOS, PFOA and other PFASs are included in the OECD surveys.

Side-chain-fluorinated polymers are mainly produced from fluorotelomers as illustrated in Figure 2. These polymers are often referred to as fluorotelomer-based polymers.

An example of polymers of this type is PolyFox™ (OMNOVA Solutions Inc.): fluorochemicals of short-chain fluorosurfactants based on fluorinated polyethers with a molecular weight greater than 1,000 and with C_2F_5 or CF_3 perfluoroalkyl side chain structures (Poulsen *et al.*, 2005). The product line includes anionic and non-ionic surfactants, UV-radiation curable acrylic monomer derivatives and polyols. The basic structure of one of the products, PolyFox™ 656 polymer with C_2F_5 side chains, is illustrated in the following figure (x + y equals about 6):



PolyFox™ 656 (UNEP, 2010)

The actual polymers produced are often complex structures with different side chains in order to obtain the desired properties. The polymer shown in the figure below have a fluorotelomer-derived perfluoroalkyl acrylate side chain to obtain water and oil repellancy and soil release, and a non-fluorinated alkyl acrylate to obtain film forming softness. Furthermore, the polymer has crosslinking monomers to provide durability.

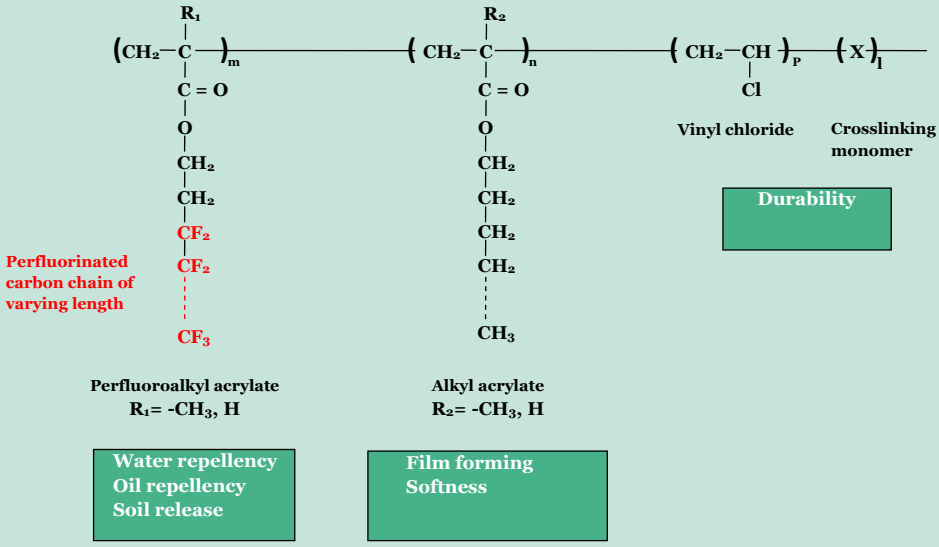


FIGURE 2
POLYMER STRUCTURE OF OIL AND WATER REPELLANTS FOR TEXTILES (BASED ON DAIKIN, 2009)

1.2.1 Polymers and REACH

Polymers may be subject to authorisation and restriction under REACH, but polymers are exempt from registration and evaluation. Nonetheless, manufacturers and importers of polymers may still be required to register the monomers or other substances used as building blocks of the polymer, as these molecules are generally recognised as of higher concern than the polymer molecule itself (ECHA, 2012c).

Of the 623 substances on the 2007 OECD list which have been pre-registered under REACH, only two include “polymer” in the chemical name used for the pre-registering. Among the five substances registered in the Danish Product Register with the highest consumption in Denmark, two are polymers which are not included in the list of pre-registered substances (further discussed in section 3.3).

In the REACH terminology the fluorinated side chains may be considered "Other reactant", which refers to a molecule that can be linked to one or more sequences of monomer units but which cannot be regarded as a monomer under the relevant reaction conditions used for the polymer formation process. Monomers and any other substances ending up chemically bound to the polymer and for which the corresponding tonnage as reagents makes up 1 tonne or more per year are to be considered for registration (ECHA, 2012).

Whereas fluorotelomers used for production of fluorotelomer-based polymers in the EU will be registered with this specific use, it is not clear how the side-chains of imported polymers are dealt with.

One of the substances with the indication of the 2013 registration intention is indicated as a "reaction mass" (generic name for multiconstituent substances) of telomers: heptadecafluorodecyl acrylate, henicosafluorododecyl acrylate and pentacosafluorotetrade. The final substance is likely a telomer-based polymer and the notation is an example of a transparent registration of these polymers.

Another issue is to what extent the PFASs in themselves may be considered polymers. Buck *et al.* (2011) briefly mention that some substances, based on certain members of a family of compounds which may potentially be alternatives to PFOS, have a sufficient number of repeating units (together with other characteristics) to enable them to be considered polymers under REACH.

FluoroCouncil has been contacted in order to clarify how the industry considers the status of the side-chain fluorinated substances under REACH, but has not answered.

The EU restriction of PFOS and related substances includes polymers with $C_8F_{17}SO_{2-}$ side chains. The restriction is currently covered by the POPs regulation, but was included as entry 53 of Annex XVII to the REACH Regulation with a similar definition of covered substances until 2011.

1.3 OECD surveys

The OECD has conducted three surveys on production and releases of PFASs and has published several lists of PFASs, the most recent full list dating back to 2007. The surveys have been used as gross lists for the previous Danish surveys of PFOS, PFOA and related compounds (Havelund, 2001, 2002; Jensen *et al.,* 2008) and are generally used as reference lists for surveys in other countries.

The 2007 list (update of the 2006 survey list) includes about 960 substances divided into four main groups:

1. PFOS and related compounds;
2. Perfluoroalkyl sulfonate and related compounds (apart from those included in the previous group);
3. PFOA and related compounds, and
4. Other PFCAs "fluorinated chemicals that potentially degrade to PFCA" (polyfluorinated carboxylic acids).

The grouping of substances is indicated in Annex 2.

The three first groups in the lists are mainly based on the chain length of the substances and include substances from different chemical groups. PFOS-related chemicals include e.g. salts of PFOS or chemicals that can degrade to PFOS.

The list of PFOS and related compounds include:

- Fully fluorinated (eight-carbon chain length) organic compounds. Both fluorinated linear and isooctane sulfonate compounds;
- PFOS-related/PFOS based substances, which may be salts of PFOS, e.g. potassium, lithium, ammonium, diethanolamine, and potassium. The related chemicals include, but are not limited to: carboxylates, amines, ethers, iodides, phosphonic/phosphinic compounds, alcohols, esters, phosphates, sulfonates, siloxanes, thioethers, urethanes, and acrylates, or polymers that contain PFOS as only a portion of the entire polymer, and
- Substances containing a mixture of C4-8 fluorinated carbon chains.

The most recent 2009 survey (OECD, 2011) has focused on collection of data on specific PFASs with chain lengths of C6 and higher (including PFOS), PFCAs with chain lengths of C8 and higher (including PFOA) and potential precursors of carboxylic acids in fluorotelomer based products. The survey results indicated that a total of 42 of the 73 perfluorinated chemicals surveyed were manufactured and/or formulated into products in 2008. The survey included requests to companies in non-OECD countries; however, no responses were received from companies in these countries.

Of the 960 substances on the 2007 OECD list, 623 substances are included in the list of pre-registered substances under REACH (ECHA, 2012b); these may potentially be relevant in an EU context. Besides these substances the list, which contains more than 100,000 pre-registered substances, may include PFASs which are not included in the 2007 OECD list. As previously mentioned, many side-chain-fluorinated polymers on the OECD list are not pre-registered.

1.4 Function of the substances for main application areas

The main functions of the substances are described in the assessments of alternatives to the substances (e.g. UNEP, 2010; UNEP, 2012; Poulsen *et al.,* 2005).

The main application area of the PFASs and the side-chain fluorinated polymers is as surfactants and surface protection agents.

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or the tension between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

Applications of perfluoroalkyl compounds have made use of their unique surfactant properties. The alkyl tails of perfluoroalkyls make these substances both hydrophobic (water-repelling) and oleophobic (oil-repelling). Thus they repel water, oil and dirt and insulate electricity.

The hydrophilic end group of the substances can be neutral (e.g., -OH and $-SO_3NH_2$), or negatively charged (carboxylates (COO^-), sulfonates ($-SO_{3-}$) and phosphonates ($-PO_{3-}$)) or positively charged (e.g., quaternary ammonium group). Thus, the resulting compounds are non-ionic, anionic or cationic surface active agents due to their amphiphilic character (EFSA, 2012).

Besides the surfactanct properties, the substances are characterised by high thermal and chemical stability. The strong carbon-fluorine bond makes the perfluoroalkyl chain present in the PFASs extremely stable and nonreactive. PFASs resist even strong acids and high temperatures.

2. Regulatory framework

This chapter gives an overview of key legislation covering fluorinated substances within the scope of this report and summarises how specific substances are addressed in existing and upcoming EU and Danish legislation, international agreements, and in eco-label criteria, as well as a number of activities in non-EU countries and organisations. The overview reflects the findings from the data search.

For readers not used to dealing with legislative issues, Annex 4 gives a brief overview of the legal instruments used in the EU and DK and how they are related. The appendix also gives a brief introduction to the chemicals legislation, explains the lists referred to in section 2.1.2, and provides a brief introduction to international agreements and selected eco-label schemes.

2.1 EU and Danish legislation

This section will first list existing legislation and then give an overview of on-going activities, focusing on which substances are in the pipeline in relation to various REACH provisions.

2.1.1 Existing legislation

Table 3 gives an overview of existing legislation addressing fluorinated substances within the scope of this report. For each area of legislation, the table will first list the EU legislation (if applicable) and then possible transposition of this into Danish law and/or other national rules. The latter will only be elaborated in case of Danish rules differing from EU rules.

The table illustrates that current EU legislation mainly focuses on PFOS and derivatives including strict restrictions on the use of such substances (see next paragraph), a requirement for export notification procedure and potential listing as a possible priority substance in the Water Framework Directive. In contrast, EU legislation relating to food contamination and monitoring focuses broadly on perfluoroalkylated substances. Four fluorinated substances are on the positive list in relation to production and polymerisation of plastic food contact materials: the ammonium salt of PFOA (high temperature sintering and polymerisation) and three substances to be used for high temperature polymerisation of fluoropolymers, including a substance indicated to be a 'mixture of telomers' and a C6-perfluorinated ether. Finally, the import/export legislation stipulateses that perfluorooctane sulfonatesqualify for PIC notification.

Perfluorooctane sulfonic acid (PFOS) and its derivatives are strictly restricted by the POPs regulation (Regulation (EC) No 850/2004) which is the main implementing instrument of the Stockholm Convention in the EU. The Regulation includes a few exemptions which are more or less identical to the “acceptable purposes” listed in Annex B to the Stockholm Convention. The exemptions generally allow very low concentration in substances, preparations and the addressed articles. The applications listed under “specific exemptions” in Annex B to the Convention are not exempt in the POPs Regulation. PFOS and its derivatives are included in the list of substances subject to waste management provisions, but without specific concentration limits. The European Commission is currently working on setting specific concentration limits for the PFOS and other new substances under the Stockholm Convention.

The European Commission has prepared a proposal in 2011 (COM(2011) 876 final) for adding PFOS and its derivatives to the list of priority substances in the field of water policy (amending the Water Framework Directive 2000/60/EC) and suggesting environmental quality standards for PFOS (amending Directive 2008/105/EC).

TABLE 3
DANISH AND EU LEGISLATION ADDRESSING PFASs

Legal instrument	Substances	Requirements
Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes I and III (POPs Regulation) **PFOS added by Commission regulation No 757/2010 of 24 August 2010 amending Regulation (EC) No 850/2004 as regards Annexes I and III**	Perfluorooctane sulfonic acid and its derivatives (PFOS) $C_8F_{17}SO_2X$ (X = OH, Metal salt (O-M +), halide, amide, and other derivatives including polymers)	The production, placing on the market and use of PFOS, whether on their own, in preparations or as constituents of articles, shall be prohibited. 1. Exemptions from control measures (Article 4(1)(b) of the regulation) shall apply to concentrations of PFOS equal to or below 10 mg/kg (0,001 % by weight) when it occurs in substances or in preparations. 2. Exemptions from control measures (Article 4(1) (b)) shall apply to concentrations of PFOS in semi-finished products or articles, or parts thereof, if the concentration of PFOS is lower than 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/m² of the coated material. 3. Use of articles already in use in the Union before 25 August 2010 containing PFOS as a constituent of such articles shall be allowed. Article 4(2), third and fourth subparagraphs shall apply in relation to such articles. 4. Fire-fighting foams that were placed on the market before 27 December 2006 may be used until 27 June 2011. 5. If the quantity released into the environment is minimised, production and placing on the market is allowed for the following specific uses provided that Member States report to the Commission every four years on progress made to eliminate PFOS: (a) until 26 August 2015, wetting agents for use in controlled electroplating systems; (b) photoresists or anti reflective coatings for photolithography processes; (c) photographic coatings applied to films, papers, or printing plates; (d) mist suppressants for non-decorative hard chromium (VI) plating in closed loop systems; (e) hydraulic fluids for aviation. 6. Once standards are adopted by the European Committee for Standardisation (CEN) they shall be used as the analytical test methods for demonstrating the conformity of substances, preparations and articles to paragraphs 1 and 2. Any other analytical method for which the user can prove equivalent performance could be used as an alternative to the CEN standards.

Legal instrument	Substances	Requirements
Limit values for POPs in waste set by Commission regulation (EU) No 756/2010 amending Regulation (EC) No 850/2004 of 24 August 2010 as regards Annexes IV and V		The substances are included in the list of substances subject to waste management provisions without specific concentration limits (jf. Commission regulation (EU) No 756/2010 of 24 August 2010)
Regulation 649/2012 concerning the export and import of hazardous chemicals	(PFOS), $C_8F_{17}SO_2X$ (X = OH, Metal salt (O-M+), halide, amide, and other derivatives including polymers) Perfluorooctane sulfonates (1763-23-1)	Subject to export notification procedure Included in list of chemicals qualifying for PIC notification
Commission Regulation (EU) No 420/2011 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs	Perfluoroalkylated substances	Member States should report to EFSA findings on perfluoroalkylated substances in food obtained in accordance with Commission Recommendation of 17 March 2010 on the monitoring of perfluoroalkylated substances in food (2010/161/EU)
Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food	Perfluorooctanoic acid, ammonium salt (CAS No 3825-26-1) Perfluoro acetic acid, α-substituted with the copolymer of perfluoro-1,2-propylene glycol and perfluoro-1,1-ethylene glycol, terminated with chlorohexafluoropropyloxy groups (CAS No 329238-24-6) Perfluoro[2-(poly(n-propoxy))propanoic acid] (CAS No 51798-33-5) perfluoro[2-(n-propoxy)propanoic acid] (CAS No 13252-13-6)	Requirements concerning the intentionally use in the manufacture of plastic layers in plastic materials and articles intended for contact with food: Only to be used in repeated use articles, sintered at high temperatures Only to be used in concentrations up to 0,5 % w/w in the polymerisation of fluoropolymers that are processed at temperatures at or above 340 °C and are intended for use in repeated use articles Only to be used in the polymerisation of fluoropolymers that are processed at temperatures at or above 265 °C and are intended for use in repeated use articles

Legal instrument	Substances	Requirements
Directive 2008/105/EC on environmental quality standards in the field of water policy,	PFOS (CAS No 1763-23-1)	Included in Annex IIII listing substances subject to review for possible identification as priority substance or priority hazardous substances
Commission Recommendation of 17 March 2010 on the monitoring of perfluoroalkylated substances in food (not a legally binding instrument)	PFOS and PFOA and, if possible, their precursors such as perfluorooctane sulfonamide (PFOSA), N-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE) and 8:2 fluorotelomer alcohol. The Member States should, if possible, include compounds similar to PFOS and PFOA but with different chain length (C4 – C15) and polyfluoroalkyl phosphate surfactants (PAPS) such as 8:2 diPAPS and 8:2 monoPAPS in order to estimate the relevance of their presence in food.	Recommend Member States to monitor the presence of perfluoroalkylated substances in food during 2010 and 2011. The monitoring should include a wide variety of foodstuffs reflecting consumption habits including food of animal origin such as fish, meat, eggs, milk and derived products and food of plant origin in order to enable an accurate estimation of exposure.
***Bekendtgørelse om kvalitetskrav til miljømålinger* [Statutory Order on quality requirement to enviromental analyses] BEK no 900 of 17/08/2011**	Perfluorooctane sulfonate (PFOS) Perfluoroctane sulfonamide (PFOSA) Perfluorohexane sulfonate (PFHxS) Perfluorodecane acid (PFDA) Perfluorononane acid (PFNA) Perfluorooctane acid (PFOA) Perfluoroundecane acid (PFUnA) Other perfluorinated substances	Sets requirements concerning quality control of chemical analyses of environmental and product samples and requirements concerning standard deviation on the measurements. Concerns analyses prepared as part of the authorities' enforcement of the Danish Environmental Protection Act, the Chemical Substances and Products Act and other legal instruments in the field of the environment and analysis prepared as part of environmental monitoring programmes.

Classification and labelling

Table 4 shows that PFOS and a number of its derivatives are subject to CLP harmonised classification and labelling, most notably for carcinogenicity, reproductive toxicity, and chronic aquatic toxicity. No other fluorinated compounds within the scope of this report are subject to harmonised classification.

Self-classifications for substances without a harmonised classification and labelling are summarised in section 2.2.

TABLE 4
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification *1	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
607-624-00-8	perfluorooctane sulfonic acid (PFOS) [1]; potassium perfluorooctane sulfonate (K-PFOS) [2]; diethanolamine perfluorooctane sulfonate [3]; ammonium perfluorooctane sulfonate (NH4-PFOS) [4]; lithium perfluo-rooctane sulfonate (Li-PFOS) [5]	1763-23-1 [1] 2795-39-3 [2] 70225-14-8 [3] 29081-56-9 [4] 29457-72-5 [5]	Carc. 2 Repr. 1B STOT RE 1 Acute Tox. 4 * Acute Tox. 4 * Lact. Aquatic Chronic 2	H351 H360D*** H372** H332 H302 H362 H411

*1 The abbreviations are added here for clarification. All substances are C8 PFSAs.
Consult Regulation (EC) No 1272/2008 for the explanation of *,** and *** which concerns the translation from Directive 67/548/EEC to the CLP Regulation for the hazard classes indicated.

Authorisation List/ REACH Annex XIV
None of the perfluorinated and polyfluorinated substances within the scope of this report are included in the Authorisation List as of August 2012.

2.1.2 Ongoing activities - pipeline

Community Rolling Action Plan (CoRAP)
Table 5 shows that REACH substance evaluations that may lead to restrictions are planned for two broadly defined fluorinated 'substances' suspected to possess PBT/vPvB properties probably due to the potential release of PFASs.

TABLE 5
SUBSTANCES IN THE COMMUNITY ROLLING ACTION PLAN (ECHA, 2012a)

CAS No	EC No	Substance Name	Substance group, number of perfluori-nated atoms	Year	Member State	Initial grounds for concern
-	700-161-3 *1	reaction mass of mixed (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)l) phosphates, ammonium salts	Mixed C6, fluoroalkyl phosphates	2013	the Netherlands	Environment/ Suspected PBT/vPvB
-	700-403-8 *1	ammonium salts of mono- and bis[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl and/or poly (substitut-ed alkene)] phosphate	fluoroalkyl phosphates, C6	2013	Belgium	Environment/ Suspected PBT/vPvB

*1 The EC Number is not available. Therefore, the number assigned to substances by the ECHA after inquiries is used.

Registry of intentions

Table 6 shows Registry of Intentions for restriction proposals, proposals for harmonised classifications and labelling and proposals for identifying fluorinated substances as Substances of Very High Concern (SVHC).

It shows that there are currently no intentions for initiation of further restriction procedures for substances within the scope of the current report, whereas SVHC intentions have been submitted for six PFCAs substances (C8 to C14, including PFOA) indicated to be CMRs or PBTs. A number of harmonised classification and labelling proposals are intended or have been submitted for four PFCAs (C8-C10, including PFOA) substances, as well as for an 8:2 fluorotelomer. All substances are suggested to be classified as reproductive toxicants, whereas for PFOA and APFO (a C8 PFCA) classification for carcinogenicity, target organ toxicity, acute toxicity and eye irritation have also been suggested. Classification for toxicity to the environment has not been suggested.

All substances are included in the OECD list of polyfluorinated substances (OECD, 2007).

TABLE 6
PFOS AND OTHER POLYFLUORINATED SUBSTANCES ON THE CANDIDATE LIST, IN REGISTRY OF INTENTIONS AND IN ANNEX XV DOSSIERS SUBMITTED

Registry	CAS No	Substances	Substance group, perfluorinated C-chain length	Scope (as indicated in the registry)	Dossier intended by	Expected data of submission
Registry of current SVHC intentions	335-67-1	Perfluorooctanoic acid (PFOA)	PFCAs, C8	CMR	Germany	28/01/2013
	3825-26-1	Ammoniumpentadecafluorootanoate (APFO)	PFCAs, C8	CMR	Germany	Submitted 03/04/2012
Registry of submitted SVHC intentions	2058-94-8	Henicosafluoroundecanoic acid	PFCAs, C11	PBT	Germany	Submitted 06/08/2012
	307-55-1	Tricosafluorododecanoic acid	PFCAs, C12	PBT	Germany	Submitted 03/04/2012
	72629-94-8	Pentacosafluorotridecanoic acid	PFCAs, C13	PBT	Germany	Submitted 03/04/2012
	376-06-7	Heptacosafluorotetradecanoic acid	PFCAs, C14	PBT	Germany	Submitted 03/04/2012
Registry of current Harmonised Classification and Labelling intentions	335-76-2	Nonadecafluorodecanoic acid	PFCAs,C10	Proposed classification according to CLP: Reproductive toxicity	Sweden	01/09/2012
	375-95-1	Heptadecafluorononanoic acid	PFCAs, C9	Proposed classification according to CLP: Reproductive toxicity	Sweden	01/09/2012
Registry of submitted Harmonised Classification	678-39-7	8:2 Fluorotelomer alcohol (8:2 FTOH)	n:2 Fluorotelomer alcohols, C8	Proposed classification according CLP: Repr. 1B, H360 D	Norway	Submitted: 20/03/2012

Registry	CAS No	Substances	Substance group, perfluorinated C-chain length	Scope (as indicated in the registry)	Dossier intended by	Expected data of submission
and Labelling intentions				[most recent version]		
	3825-26-1	Ammoniumpentadecafluorootanoate (APFO)	PFCAs, C8	Carc. 2, H351 Repr. 1B, H360D STOT RE 1, H372 STOT RE 2, H373 Acute Tox. 3, H331 Acute Tox. 3, H301 Eye Irrit. 2, H319	Norway	Submitted: 09/04/2010
	335-67-1	Perfluorooctanic acid (PFOA)	PFCAs, C8	Proposed classification according CLP: Carc. 2, H351 Repr. 1B, H360D STOT RE 1, H372 STOT RE 2, H373 Acute Tox. 3, H331 Acute Tox. 3, H301 Eye Irrit. 2, H319	Norway	Submitted: 21/02/2011

Candidate list
The Candidate list (2 August 2012) does not include any fluorinated substances within the scope of this report. ECHA launched a public consultation on 54 potential SVHC 3 September 2012; among these the four substances listed in Table 6 under Registry of submitted SVHC intentions.

Annex XIV recommendations
The lists of Annex XIV recommendations (2 August 2012) do not include any fluorinated substances within the scope of this report.

2.2 Self-classification

The Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA) contains classification and labelling information on notified and registered substances received from manufacturers and importers. The database includes the harmonised classification as well. Companies have provided this information in their C&L notifications or registration dossiers. ECHA maintains the Inventory, but does not verify the accuracy of the information (ECHA, 2012a).

Classification of PFOS and other polyfluorinated substances listed in the database is shown in Table 7.

TABLE 7
CLASSIFICATION INFORMATION FROM MANUFACTURERS AND IMPORTERS (C&L LIST) ON REGISTERED SUBSTANCES AND SUBSTANCES WITH 2013 INTENTIONS

CAS No	Substance name	Substance group, perfluorinated C-chain lenght	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
56773-42-3	Tetraethylammonium heptadecafluorooctanesulfonate	PFSAs, C8	**Total**		**75**
			Acute Tox. 3	H301	52
			Acute Tox. 4	H332	29
			Carc. 2	H351	29
			Repr. 1B	H360	29
			Lact.	H362	29
			STOT RE 1	H372	29
			Aquatic Chronic 3	H412	52
			Acute Tox. 4	H302	23
307-35-7	Heptadecafluorooctanesulfonyl fluoride	PASFs, C8	**Total**		**53**
			Acute Tox. 3	H301	28
			Eye Dam. 1	H318	51
			Acute Tox. 3	H331	28
			Repr. 1B	H360	29
			STOT RE 1	H372	29
			Aquatic Chronic 2	H411	29
			Skin Corr. 1B	H314	24
85995-91-1	Alkyl iodides, C8-14, γ-ω-perfluoro	PFAIs, C8-14	**Total**		**27**
			No classification		
90622-71-2	Alkyl iodides, C6-18, perfluoro	PFAIs, C6-18	**Total**		**28**
			No classification		
52299-25-9	Bis(nonafluorobutyl)phosphinic acid	Other, 2*C4	**Total**		**1**
			Acute Tox. 3	H301	1
			Eye Dam. 1	H318	1
62037-80-3	Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate	Other, C4	**Total**		**45**
			Acute Tox. 4	H302	45
			Eye Dam. 1	H318	45
			STOT RE 2	H373	1
17527-29-6	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl acrylate	(6:2) Fluorotelomer acrylates, C6	**Total**		**134**
			Skin Irrit. 2	H315	24
			Eye Irrit. 2	H319	24
			STOT SE 3	H335	68
2043-57-4	1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodooctane	(n:2) Fluorotelomer iodides, C6	**Total**		**99**
			Skin Irrit. 2	H315	26
			Eye Irrit. 2	H319	26
			STOT SE 3	H335	26
2144-53-8	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate	(n:2) Fluorotelomer methacrylates, C6	**Total**		**99**
			Skin Irrit. 2	H315	27
			Eye Irrit. 2	H319	27
			STOT SE 3	H335	27

CAS No	Substance name	Substance group, per-fluorinated C-chain lenght	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
27619-89-2	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctanesulfonyl chloride	6:2 Fluorotelomer sulfonyl chloride, C6	**Total** Skin Sens. 1 Resp. Sens. 1	 H317 H334	**45** 45 1
375-72-4	1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonyl fluoride	PASFs, C4	**Total** Met. Corr. 1 Acute Tox. 4 Acute Tox. 3 Skin Corr. 1B Eye Dam. 1 STOT SE 3 STOT SE 1 Aquatic Chronic 4	 H290 H302 H311 H314 H318 H335 H370 H413	**58** 1 1 1 27 1 1 2 29
647-42-7	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctan-1-ol	(n:2) Fluorotelomer alcohols, C6	**Total** Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 STOT SE 3 STOT RE 1 Aquatic Chronic 2	 H302 H315 H319 H332 H335 H372 H411	**120** 63 29 29 11 29 1 18
67584-55-8	2-[Methyl[(nonafluorobutyl) sulfonyl]amino]ethyl acrylate	*N*-Methyl perfluoroalkane sulfonamidoethyl acrylates, C4	**Total** Skin Sens. 1	 H317	**208** 119
68391-08-2	Alcohols, C8-14, γ-ω-perfluoro	Perfluoroalkyl alcohols/ketones, C8-14	**Total** Flam. Liq. 3 Acute Tox. 4 Skin Irrit. 2 Acute Tox. 4	 H226 H312 H315 H332	**113** 86 86 86 86
85631-54-5	2-Propenoic acid, γ-ω-perfluoro-C8-14-alkyl esters	Mixture of perfluoralkyl esters, C8-14	**Total**		**26**

Source : Classification and Labelling Inventory at: http://echa.europa.eu/web/guest/information-on- chemicals/cl-inventory-database

2.3 Eco-labels

Table 8 shows that PFOS and to some extent PFOA, other PFAS, PFCA and related compounds are subject to Nordic Swan and/or the EU flower ecolabelling criteria for printing chemicals paint/varnishes, footwear, playground equipment, as well as furniture and fitments. The chemicals must not be intentionally added or present in the addressed products.

TABLE 8
ECO-LABELS TARGETING PFOS AND OTHER POLYFLUORINATED SUBSTANCES

Eco-label	Substances *1	Mixtures, articles, processes	Document title
Nordic Swan	PFOS-related substances	Printing companies: must not be added to chemicals	Nordic Ecolabelling of Printing companies
	PFOA PFOS	Furniture and fitments: must not be present in/added to the chemical product or material	Nordic Eco-labelling of Furniture and fitments
	PFOA PFOS	Playground equipment: must not be present in/added to the chemical product or material	Nordic Ecolabelling of Outdoor furniture and play-ground equipment
	PFAS, PFOA, PFOS, PFCA, Related com-pounds which may degrade to PFCA	Indoor paint and varnishes: are not permitted in the product.	Nordic Ecolabelling of Indoor paints and varnishes
EU Flower	PFAS, PFOA, PFOS, PFCA, Related com-pounds which may degrade to PFCA	Indoor paints and varnishes: are not permitted in the product	Commission Decision Of 13 August 2008 establishing ecological crite-ria for the award of the Community eco-label to indoor paints and varnishes
	PFAS, PFOA, PFOS PFCA. Related com-pounds which may degrade to PFCA	Outdoor paints and varnishes: are not permitted in the product	Commission Decision Of 13 August 2008 establishing ecological criteria for the award of the Community eco-label to outdoor paints and varnish-es
	PFOS	Footwear production: shall not be used/added up until purchase.	Commission Decision of 9 July 2009 on establishing the ecologi-cal criteria for the award of the Community eco-label for footwear
German Blue Angel	No specific require-ments have been identi-fied		

*1 In this context PFAS refers to perfluorinated alkylated substances only.

2.4 International agreements

Table 9 gives an overview of how fluorinated compounds within the scope of this report are addressed by various international agreements. It shows that PFOS is addressed by the OSPAR (priority substance), Helsinki (strict restriction on use) and the Stockholm convention (also addressing PFOS related compounds). As noted earlier and shown in Table 3, the latter is transposed into the EU POPs regulation. Further, PFOA is on the Helsinki convention radar screen for action.

A guidance on the best available techniques (BAT) and best environmental practices (BEP) for the production and use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention has been developed to assist Parties in developing strategies for applying those techniques and practices and for implementing the recommendations of the Conference of the Parties (COP) on risk reduction for PFOS.

TABLE 9
INTERNATIONAL AGREEMENTS ADDRESSING PFOS AND OTHER POLYFLUORINATED SUBSTANCES

Agreement	Substances	Scope
OSPAR Convention	Perfluorooctanyl sulfonic acid and its salts (PFOS)	OSPAR list of priority substances, Part A substances
Helsinki Convention (HELCOM)	Perfluorooctane sulfonate PFOS) Perfluorooctanoic acid (PFOA)	HELCOM Baltic Sea Action Plan adopted on 15 November 2007 by the HELCOM Extraordinary Ministerial Meeting: By 2008 to work for strict restrictions on the use in the whole Baltic Sea catchment area of the Contracting States By 2009, if relevant assessments show the need, to initiate adequate measures such as the introduction of use restrictions and substitutions in the most important sectors identified by the Contracting Parties
Stockholm Convention	Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	The requirements are transposed in the EU POPs REGULATION (Regulation (EC) No 850/2004) and reference is made to Table 3
Rotterdam Convention (PIC Convention)		None of the substances within the scope of this report are included in Annex III of the Convention and subject to the PIC procedure
Basel Convention		Waste of polyfluorinated substances may be part of different hazardous waste types in Annex VIII, but are not specifically mentioned in the description of the wastes.

2.4.1 Action plan for reduction of PFOS in Denmark

As part of the updated Danish national implementation plan for Stockholm Convention submitted to the secretariat for the Convention in August 2012, an action plan for the reduction of PFOS in Denmark was developed.

The following table indicates the new initiatives that will be taken in relation to the release of PFOS throughout the substances' life cycle.

TABLE10
ACTION PLAN FOR REDUCTION OF PFOS IN DENMARK

No.	Initiative	Description	Responsible institution	Time frame
1	Report on use of PFOS in Denmark	PFOS is included in the Danish EPA list of undesirable substances (LOUS). In the period 2012-2015 all substances in LOUS will be surveyed with a view to assessing the possible need for further regulation, labelling, information or phasing-out. In step with these endeavours, a detailed investigation will be carried out of the different uses of PFOS and other per- and polyfluorinated substances in Denmark, as well as their possible substitutes.	Danish EPA	2012
2	Notification of allowed uses	Notify the uses that are being allowed and report to the Secretariat of the Stockholm Convention on the development of work to phase out PFOS.	Danish EPA	2012/ 2016
3	Information to users of PFOS on acceptable uses in Denmark	Inform users of PFOS for hard chromium plating about the provisions of the POP Regulation. Inform other possible users of PFOS via sector organisations. Prepare a register of users of PFOS.	Danish EPA	2012-2013
4	Study of PFOS/PFOA as soil and groundwater contamination	PFOS/PFOA has been used in fire extinguishing foam, and cases have been observed in both Denmark and abroad of soil and groundwater having been contaminated with PFOS at fire drill sites due to the repeated use of fire extinguishing foam. An investigation will be launched under the technology programme for soil and groundwater contamination. The project is to investigate e.g. whether there are other sources of contamination of soil and groundwater with PFOA/PFOS, and to clarify whether PFOS/PFOA contamination of soil and groundwater in connection with fire drill sites is a generally occurring phenomenon.	Danish EPA	2012-2014
5	Assessment of the presence of PFOS in household waste	On the basis of a survey under Initiative 1, an assessment will be carried out of the presence of PFOS in waste from households.	Danish EPA	2012-2013
6	Validation of destruction of PFOS	Encourage the European Commission to carry out a survey to validate whether PFOS can be adequately destroyed in ordinary waste incineration processes. The results will form the basis for assessing to what extent a change in current treatment methods for waste containing PFOS in Denmark is required.	Danish EPA	Not set
7	Possible separation of household waste containing PFOS	Depending on the results of Initiative 6, requirements will possibly be prepared for separation of certain significant fractions of household waste containing PFOS.	Danish EPA	Not set
8	Guidelines concerning articles which must not be reused and recycled	Prepare guidelines concerning articles which must not be reused or recycled because they contain PFOS in concentrations that exceed the set limit values.	Danish EPA	Not set

2.5 Activities by other non-EU organisations

The PFASs are addressed by national authorities and international organisations all over the world. The following briefly describes some of the activities of highest relevance for the current survey.

2.5.1 OECD

The OECD Web Portal on perfluorinated chemicals (abbreviated PFCs) is designed to facilitate information exchange on perfluorinated chemicals (http://www.oecd.org/ehs/pfc/). Stakeholders can share information on government activities related to their regulatory and stewardship efforts, updates on scientific developments, new technologies, available alternatives, and events related to perfluorinated chemicals.

The OECD activities related to perfluorinated chemicals include efforts to collect more reliable data of the production and use of perfluorinated chemicals, including information from producers on environmental releases of targeted substances from manufacturing and the content of targeted substances in products. The OECD has conducted three surveys on production and releases of the substances. The most recent survey is from 2009 (OECD, 2011).

The 2006 OECD workshop on PFCAs and precursors concluded with a series of recommendations, including an information clearing house, areas where governments and industry could work towards risk reduction programmes, sharing information on effective technologies to reduce environmental releases and providing information on the chemical content of articles, among others.

2.5.2 ICCM and SAICM

In May 2009, the International Conference on Chemicals Management (ICCM) adopted Resolution II/5 for the management of polyfluorinated substances (abbreviated PFCs) and transition to safer alternatives. The resolution invites governments, international organisations and other stakeholders to consider the development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals of concern in products and to work toward global elimination, where appropriate and technically feasible.

Progress of the work was summarised for the 4th ICCM meeting in September 2012 (SAICM, 2012). The conference also proposed the Terms of Reference for a global PFC group. The group's objective is to facilitate information exchange and information gathering on PFOS and PFOA, their related substances and products and mixtures containing these subtances (collectively designated as PFCs).

2.5.3 USA

In January 2006 the US EPA initiated the PFOA Stewardship Program, in which the eight major companies in the industry committed voluntarily to reduce facility emissions and product content of PFOA, precursor chemicals and higher homologue chemicals on a global basis by 95 percent no later than 2010, and to work toward eliminating emissions and product content of these chemicals by 2015.

The progress of the program can be followed at US EPA's website for perfluoroalkyl acid (PFOA) and fluorinated telomers at http://www.epa.gov/oppt/pfoa/index.html, which includes a description of the activities undertaken by the agency.

US EPA is reviewing substitutes for PFOA, PFOS, and other long-chain perfluorinated substances as part of its review process for new chemicals under the Toxic Substances Control Act (TSCA) New Chemicals Program (NCP). Through the end of 2008, over 150 alternatives of various types have been received and reviewed by EPA. US EPA reviews the new substances against the range of toxicity, fate and bioaccumulation issues that have caused past concerns with perfluorinated substances, as well as any issues that may be raised by new chemicals.

2.5.4 Canada

By an amendment to the Prohibition of Certain Toxic Substances Regulations of 30 Sep. 2010 (SOR/2010-211 September 30, 2010) Canada has prohibited four fluorotelomers, with an exemption for their presence in articles (Environment Canada, 2010). The four substances are (CAS No from UNEP, 2011 and Environment Canada, 2012b):

- Hexane, 1,6-diisocyanato-, homopolymer, reaction products with alpha-fluoro-omega-2-hydroxyethyl-poly(difluoromethylene), C16-20-branched alcohols and 1-octadecanol (CAS No. 126927-97-7);
- 2-propenoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, gamma-omega-perfluoro-C10-16-alkyl acrylate and stearyl methacrylate (CAS No 203743-03-7);
- 2-propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with butyl 2-propenoate and 2,5 furandione, gamma-omega-perfluoro-C8-14-alkyl esters, tert-Bu benzenecarboperoxoate-initiated (CAS No 459415-06-6), and
- 2-propen-1-ol, reaction products with pentafluoroiodoethane tetrafluoroethylene telomer, dehydroiodinated, reaction products with epichlorohydrin and triethylenetetramine (CAS No 464178-90-3).

The four fluorotelomer-based substances are primarily used in applications involving water-, oil-, soil- and grease-repellents for paper, fabric, leather, packaging, rugs and carpets, as well as tiles and grouts. They are also used as a levelling agent in coatings. The restriction is based on an assessments indicating that the four fluorotelomer-based substances are ultimately sources of long chain perfluorinated carboxylic acids (PFCAs) through the release of precursors (Environment Canada, 2010).

None of the four substances are included in the list of substances pre-registered under REACH. Cas No 203743-03-7 was identified as constituent of a textile impregnation spray for car interiors in a Danish survey from 2008, while CAS No 203743-03-7 was a constituent of SONAX textile impregnation (Jensen *et al.,* 2008). CAS No 203743-03-7 is registered in the Danish Product Register (quantity and application confidential).

2.6 Summary on regulatory framework

PFOS and similar substances/derivatives

This chapter shows that the main legal focus so far has been on PFOS and its derivatives (sometimes including polymers with the potential to release PFOS). This includes harmonised EU classification and labelling, strict restrictions on use (following the Stockholm Convention), requirements for export notifications and via the Water Framework Directive. PFOS is also addressed in all ecolabelling criteria (EU flower and Nordic Swan) and in all international agreements (OSPAR, Helsinki and Stockholm Conventions) identified in this survey. Denmark has a specific focus on PFOS and has prepared an action plan for reduction of PFOS in Denmark. PFOS and derivatives have also high priority in non-EU countries and organisations.

PFCAs, including PFOA

PFOA and other PFCAs are currently less regulated than PFOS, but a range of these substances are in the pipeline with intentions for identifying six substances as Substances of Very High Concern (SVHC) due to CMR or PBT properties (possibly leading to Authorisation or Restriction requirements) and five with submitted or intended harmonised classification and labelling proposals indicating similar human health problems as with PFOS and similar substances. PFOA is also on the

Helsinki convention radar screen for possible action and addressed in ecolabelling criteria for several product groups.

PFSAs
Perfluorooctane sulfonates are subject to PIC notification under the import/export legislation.

Perfluoroalkylated substances in general
This broad group of substances is addressed in EU legislation related to content and monitoring in foodstuffs, as well as in a number of ecolabelling criteria.

Fluorinated polymers
As set out in Chapter 1 of this report, release of PFOS, PFOA and similar substances during production and use of fluorinated polymers may be an issue of concern. The only regulation of the polymers is the restriction on polymers with side chains with a similar structure as PFOS under the POP Regulation. Otherwise this substance group is not specifically addressed.

Perfluoroalkyl and polyfluoroalkyl substances in general
Activities in various international fora, including OECD, ICCM/SAICM, USA and Canada point to an increased focus on substances within the scope of this report, with Canada addressing e.g. specifically a number of fluorotelomers.

3. Manufacture and uses

3.1 Data available on global and EU manufacture of PFCs

This section provides an overview of the data available on the manufacture of PFCs world-wide across the different substance groups followed by a description of manufacture and use by each of the main groups.

3.1.1 Global manufacture of PFCs

The majority of the global production of PFASs and fluoropolymers are produced by eight major companies who all participate in the US EPA 2010/2015 PFOA Stewardship Program. These major manufacturers represent more than 90% of the global annual production of perfluorinated chemicals and fluoropolymers (Posner *et al.,* 2009).

Six of these companies, Arkema France, Asahi Glass Co. Ltd., Clariant International Ltd., Daikin Industries Ltd., DuPont Company and Solvay Specialty Polymers are organised in the Global Industry Council for Fluoro Technology, FluoroCouncil (FluoroCouncil, 2012). Two of the companies participating in the stewardship program, 3M/Dyneon and BASF Corporation, are not members of the FluoroCouncil.

The FluoroCouncil has been contacted in order to obtain updated information on the overall global production and consumption of PFASs and fluorotelomer-based polymers by substances groups and application areas. The council has not been able to provide detailed information on production volumes and uses of the chemicals.

The OECD has prepared surveys of the production of PFCs in its member countries in 2004, 2006 and 2009. The most recent, the 2009 survey, focuses on the long-chain PFCs and their precursors and the emissions from the production (OECD, 2011). Of the 73 substances surveyed, 42 were manufactured and/or formulated into products in 2009. The reponse rate of the 27 companies surveyed was 33% and no responses were obtained from non-OECD countries. The survey thus gives a quite incomplete picture of the world-wide situation and, due to the low response rate, it has been difficent to demonstrate a trend in production. The main results of the surveys are indicated for each substance group below.

3.1.2 Registration of manufacture and import under REACH

Among the major manufacturers of fluorinated chemicals, three companies, Arkema (France), Clariant International Ltd. (Switzerland) and BASF Corporation (Germany), have headquarters in the EU27+2 (EU+ Norway and Switzerland), but other companies may have production sites with PFASs or side-chain-fluorinated polymers within the EU.

An overview of the production of PFCs in the EU does not exist; it has been beyond the limits of the current survey to obtain detailed information on manufactured volume directly from the individual manufacturers.

Some information on the use of PFOS and PFOA and related substances exist; this is described in the following sections, but quantitative information on the volumes of production, use and release of PFASs and the side-chain-fluorinated polymers is limited.

All manufacturers and importers of chemical substances > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). The 1st of December 2008 was the deadline for pre-registration of substances that will be produced or imported in volumes of more than 1 tonne per year and company in the EU. Pre-registered chemicals benefit from tonnage and property dependent staggered deadlines:

- 30 November 2010: Registration of substances
- manufactured or imported at 1000 tonnes or more per year,
- carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and
- substances dangerous to aquatic organisms or the environment above 100 tonnes per year;
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year, and
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

PFOS and related substances are classified carcinogenic and toxic to reproduction and should consequently be registered according to the REACH Regulation by November 2010 if manufactured or imported in quantities above one tonne. For the remaining PFASs, only substances manufactured or imported at 1000 tonnes or more per year had to be registered before 30 November 2010 while the substances manufactured or imported at 100 - 1000 tonnes per year have to be registered by 31 May 2013.

ECHA has prepared a list of substances for which companies have expressed their intentions for registration of the substances by 31 May 2013. The expression of interest could indicate that the substances are manufactured or imported in the 100-1000 tonnes range, but the tonnage may actually be lower, as is the situation for many of the substances currently registered.

Polymers are exempt from registration. This means that the majority of the relevant fluorinated substances would not be registered. However, monomers and any other substance(s) ending up chemically bound to the polymer, and for which the corresponding tonnage is above the tonnage limits, are to be considered for registration (ECHA, 2012).

Of the 960 substances on the 2007 OECD list of PFOS, PFAS, PFOA, PFCA and related compounds and chemicals that may degrade to PFCA, 623 substances are included in the list of pre-registered substances under REACH (ECHA, 2012b) and may potentially be relevant in an EU context.

Of these substances, only 2 include the text string “polymer” in the substance name.

Registered substances and substances intended to be registered by 2013 are shown in Table 11. The total tonnage of manufacture and import of the registrants is indicated in ECHA’s registration database with tonnage bands (ECHA, 2012h). For substances used as intermediates, tonnage bands are generally not provided.

Currently 9 substances are registered; of these, four are registered as used as intermediate only without tonnage bands, and for one substance tonnage and use is confidential. Twelve substances are indicated to be registered by 2013. Of these 21 substances, 7 substances were not included in the 2007 OECD list, but have been identified from the chemical names going though the list of registered substances and the list of 2013 intentions.

The total reported tonnage of registered substances is in the range of 14-140 t/y. One substance, ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate, is in the 10-100 t/y category.

In order to obtain EU-wide information on the use of the substances an information request has been forwarded to the following European trade organisations: Euratex (apparel and textile), ECRA (carpets), CEPE (paint, printing ink and artists' colours) and FEICA (adhesives). No information

was obtained. Besides, as mentioned elsewhere, the international FluoroCouncil has been contacted, but no data have been obtained.

Substances registered in ECHA's REACH registration database

The table overleaf shows substances included in ECHA's database on registered substances and substances for which industry has indicated the intention to register the substances by 2013.

3.1.3 Statistics on EU production and import/export

Production of PFASs is not covered by any specific activity code of the EU production statistics (Prodcom). PFASs are not covered by any specific commodity codes (CN8 code) of the EU external trade statistics (Comext).

TABLE 11
PFASs REGISTERED IN ECHA'S REACH REGISTRATION DATABASE OR FOR WHICH INDUSTRY HAS INDICATED ITS INTENTION OF REGISTRATION BY 2013

CAS No	EC No	Substance name *1	Abbrevi-ation	Substance group, perfluorinated chain length *2	OECD 2007 group	Registered, tonnage band , t/y *3	Inten-tion 2013 *4	Registered end uses
56773-42-3	260-375-3	Tetraethylammonium heptadecafluorooc-tanesulfonate		PFSAs, C8	PFOS	1-10		Industrial use for metal (chromium) plating
307-35-7	206-200-6	Heptadecafluorooctanesulfonyl fluoride		PASFs, C8	PFOS	Intermediate Use Only		
85995-91-1	289-100-5	Alkyl iodides, C8-14, γ-ω-perfluoro		PFAIs, C8-14	Perfluoroalkyl iodide com-pounds	Intermediate Use Only		
90622-71-2	292-474-2	Alkyl iodides, C6-18, perfluoro		PFAIs, C6-18	Perfluoroalkyl iodide com-pounds	Intermediate Use Only		
-	700-161-3	Reaction mass of mixed (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphates, ammonium salts		Undefined mixture, C6	Not included	Tonnage Data Confidential		Not indicated
52299-25-9 *5	700-183-3	Bis(nonafluorobutyl)phosphinic acid		Other, C4	Not included	1 - 10		Industrial use of reactive processing aids ; Use as labor-atory reagent
62037-80-3 *5	700-242-3	Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate		Other, C4	Not included	10 - 100		
-	700-403-8	Ammonium salts of mono- and bis[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl and/or poly (substituted alkene)] phosphate		one or two C6	Not included	1 - 10		Use as a surface active agent, industrial and professional settings, by consumers

CAS No	EC No	Substance name *1	Abbrevi-ation	Substance group, perfluorinated chain length *2	OECD 2007 group	Registered, tonnage band , t/y *3	Inten-tion 2013 *4	Registered end uses
-	700-536-1	N,N,N,-triethylethanaminium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate		PFSAs (C4)	Not included	1 - 10		Manufacture of tetrae-thylammonium perfluorobu-tanesulfonate Industrial use of tetrae-thylammonium perfluorooc-tanesulfonate for metal (chromium) plating
17527-29-6	241-527-8	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl acrylate	6:2 FTAC	(6:2) Fluorotelomer acrylates, C6	Fluoro ester compounds (F5)	Not registered	x	
2043-57-4	218-056-1	1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodooctane	6:2 FTI	(n:2) Fluorotelomer iodides, C6	Fluoro iodide compounds (F7)	Not registered	x	
2144-53-8	218-407-9	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate	6:2 FTMAC	(n:2) Fluorotelomer methacrylates, C6	Fluoro ester compounds (F5)	Not registered	x	
26650-09-9	607-977-8	Thiocyanic acid, 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl ester		Fluorotelomer halogenides, C6	Partial fluoro & miscellane-ous fluoro compounds (F17)	Not registered	x	
27619-89-2	248-576-4	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctanesulfonyl chloride		6:2 Fluorotelomer sulfonyl chloride, C6	Fluoro sul-fonate/sulfona mide/sulfonyl compounds (F11)	Not registered	x	
375-72-4	206-792-6	1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonyl fluoride	PBSF	PASFs, C4	PFAS	Not registered	x	

CAS No	EC No	Substance name *1	Abbrevi-ation	Substance group, perfluorinated chain length *2	OECD 2007 group	Registered, tonnage band , t/y *3	Inten-tion 2013 *4	Registered end uses
647-42-7	211-477-1	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctan-1-ol	6:2 FTOH	(n:2) Fluorotelomer alcohols, C6	Fluoro alcohol compounds (F1)	Not registered	x	
67584-55-8	266-733-5	2-[Methyl[(nonafluorobutyl) sulfonyl]amino]ethyl acrylate	MeFBSAC	*N*-Methyl perfluoroalkane sulfonamidoethyl acrylates, C4	PFAS	Not registered	x	
68391-08-2	269-927-8	Alcohols, C8-14, γ-ω-perfluoro		Perfluoroalkyl alcohols/ketones, C8-14	Fluoro alcohol compounds (F1)	Not registered	x	
85631-54-5	288-003-5	2-Propenoic acid, γ-ω-perfluoro-C8-14-alkyl esters		Mixture of perfluoralkyl esters, C8-14	Fluoro ester compounds (F5)	Not registered	x	
34455-22-6	608-993-8	1-Octanesulfonamide, N-[3-(dimethylamino)propyl]-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-		C6 telomer	Not included	Not registered	x	
-	915-328-8	Reaction mass of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl acrylate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafluorotetrade		Undefined mixture of C8, C10, C12 telomers.	Not included	Not registered	x	

*1 For registered substances the registered name is indicated; for other substances included in the ESIS databes (with EC number), the substance name in ESIS is indicated (http://esis.jrc.ec.europa.eu/)

*2 Describes the number of perfluorinated atoms in one chain.

*3 As indicated in the lists of registered substances at ECHA's website (ECHA, 2012h). For each separate registration (which may cover more than one manufacturer) the registered tonnage is indicated. For substances indicated as "Intermediate use only" no tonnage band is reported.

*4 Included in the list of substances that companies have told ECHA they intend to register by the 2013 REACH registration deadline. It is based on responses to a survey ECHA conducted. 31 May 2013 is the deadline for industry to register all phase-in substances manufactured or imported in the EU at or above 100 tonnes a year.

*5 CAS No not indicated in registration, but added here.

3.2 Global and EU manufacture and use of PFCs

3.2.1 PFOS and other polyfluoroalkyl sulfonates and derivatives

Global manufacture and consumption

3M was, prior to the phase-out announced in 2000, the major global producer of perfluorooctanesulfonyl fluoride (POSF) although smaller producers existed in Europe and Asia. POSF is used as an intermediate in the production of PFOS and PFOS derivatives, and the production of POSF can be used as an indicator of the total production of PFOS-related substances.

The total historical worldwide production of POSF between 1970 and 2002 was estimated by Paul *et al. (*2009) to be 96,000 tonnes (or 122,500 tonnes, including unusable wastes). The majority of this was produced by 3M. The company manufactured approximately 3,665 t/y POSF, or 78% of the estimated global POSF production of 4,650 t/y, when the production peaked in 2000.

The major uses for the POSF-derived substances were in providing grease, oil and water resistance to materials such as textiles, carpets, paper and coatings in general.

From 1970 to 2002, the main end uses of the POSF-derived substances were carpets (48,000 tonnes for the entire period), paper and packaging (24,000 tonnes), apparel (12,500 tonnes), performance chemicals (6,000 tonnes), and aqueous fire fighting foams (10,000 tonnes) (Paul *et al.,* 2009).

Between 2000 and 2003 the global production dropped sharply as a consequence of 3M's phase out of the chemical's production. However, production of POSF-derived chemicals is still ongoing in other countries, although at a much smaller scale than before 2003.

The global production and consumption of PFOS and related substances in recent years have been reviewed in a study undertaken for UNIDO in 2009 (Carloni, 2009). According to this study, China started larger-scale production of PFOS in 2003 (Carloni, 2009). Since 2005 China's annual output has grown rapidly due to the increase of the applications of PFOS in the country and overseas demand. The cumulative PFOS production for the period 2003-2008 is estimated at 250 tonnes; of this, 200 tonnes was used in China. In 2006, POSF was produced by 15 Chinese enterprises. The accumulated global production of PFOS and related compounds for the period 2003-2008 was 410 tonnes. China accounted for more than half of this. Japan and Germany ranked second and third with cumulative productions of 100 and 25 tonnes, respectively.

The 2009 OECD survey reported on production of 2.5 t/y of PFOS and related substances. The results showed that products containing PFOS are used mainly in the photolithography process as antireflective coatings, as intermediates in industrial applications (e.g. as raw material of photoacid generators,) and as precursors for ammonium PFOS production. The potassium salt of PFOS (CAS No 2795-39-3) had a variety of uses including those as a mist suppressant for chromium (VI) plating, a processing aid in the manufacture of fluoropolymers and in medical devices.

An important difference between developing countries and developed countries seems to be in the number of sectors in which PFOS is currently used. China, for example, used PFOS in a large range of applications in 2008: textiles, fire fighting foams, pesticides, metal plating, semiconductors and cleaning products. For 2008 it is reported that 100 tonnes PFOS were used for textile treatment in China (Lim *et al.,* 2011). As China is party to the Stockholm Convention, it must be expected that many of these uses will cease (or have ceased) as China implements its obligations under the Convention.

In the developed world, small volumes are still used for applications exempt under the Stockholm Convention: mainly chromium plating, photolithography, photography and in hydraulic fluids for aviation.

Consumption in the EU

The use of PFOS and its derivatives has been restricted in the EU since 2006. The substances are listed in Annex 1 (banned substances) to the POPs regulation with an exemption for five application areas.

The total consumption for these areas was estimated at about 8 t/y in 2010 (Table 12) in a study for the European Commission (ESWI, 2011). For some of the application areas, the estimate is based on data from a UK report from 2004 (RPA, 2004), which are considered the best estimate, but may not be up-to-date.

The major application area was the metal plating industry. PFOS lowers the surface tension of the chromium bath and therefore reduces the size of bubbles in the bath. The surface of the bath is therefore calmer and emissions to air are reduced. Most of the industries have switched to alternatives when it became evident that PFOS was problematic; however, in some branches a shift to other chemicals has been difficult. Today only the use in nondecorative hard chromium (VI) plating in closed loop systems is allowed. In hard chromium (VI) plating, the industry continues to use PFOS to limit chromium (VI) emissions to air from the chromium bath.

The most common PFOS-related surfactant used in the chromium plating industry in Denmark today is tetraethylammonium perfluorooctane sulfonate (CAS no. 56773-42-3) (Poulsen *et al.,* 2011).

The substance is registered for use in chromium plating with a tonnage of 1-10 t/y (Table 11).

PFOS derivatives are used in the photographic industry as ingredients in photographic material (film, paper, plate). The concentration of PFOS in films is indicated at 0.1- 0.8 µg/cm².

TABLE 12
BEST ESTIMATE OF PFOS USED BY INDUSTRY SECTOR IN THE EU 2010 (ESWI, 2012)

Industry	PFOS consumption, kg/y
Metal plating industry	6,500
Photographic industry	562
Semiconductor industry	9.3
Hydraulic fluids in aviation industry	730

Detailed flow charts showing the flow of PFOS to the different waste streams and to the environment for each application area is provided in the report from ESWI (2011) and discussed in section 4.1.1.

Perfluorooctanesulfonyl (heptadecafluorooctanesulfonyl) fluoride (POSF) which is used as an intermediate in the production of PFOS and its derivatives is registered for intermediate use only under REACH, without any tonnage band.

3.2.2 PFOA, longer chained PFCAs and related substances

Global production and consumption

Historically, commercial polyfluorinated carboxylic acids (PFCA) products were mixtures containing linear C8 or C9 PFCAs as their major component (Prevedouros *et al.,* 2006).

The estimated global production of perfluorooctanoate (PFOA) and ammonium perfluorooctanoate (APFO) from 1951-2004 is 3,600-5,700 tonnes, while the manufacturing of perfluorononanoate (PFNA) and ammonium perfluorononanoate (APFN) during the same period is estimated at 800-2,300 tonnes (Prevedouros *et al.,* 2006). In 1999, global annual APFO production was approximately 260 tonnes.

PFOA and PFNA have mainly been used as polymerisation aids in the manufacture of fluoropolymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) (Prevedouros *et al.,* 2006). Furthermore, PFOA was used as a component in aqueous fire-fighting foam from approximately 1965 to 1975. Historically the PFCAs and derivatives also had widespread use as additives in various industrial and consumer products. Manufacture of fluoropolymer was the single largest direct use of the ammonium salts APFO and APFN. They act among other to solubilise fluoromonomers to facilitate their aqueous polymerization.

As a result of the US EPA Stewardship Program (see section 2.5.3) and further activities to substitute the PFOA, precursor chemicals and higher homologue chemicals in many uses, the production of PFOA and other C8-fluorochemicals have decreased significantly at least in Europe and North America.

For the most recent OECD survey, the seven companies that reponded to the survey reported the manufacture of a total of <5.5 tonnes PFOA and related compounds (OECD, 2011). Furthermore, the mass of five different 8:2 fluorotelomers which potentially may degrade to PFOA and PFNA was reported. These substances were present as residuals or impurity of products at a total of <20 tonnes.

No data have been identified on the global production and use of PFCAs of chain lengths longer than C9. Four recently published Annex XV dossiers for C11-14 PFCAs (ECHA 2012e, f, g, h) and an ecological screening assessment for C9-C20 PFCAs (Environment Canada, 2012a) do not indicate any current uses of the substances.

Consumption in the EU

The following section is largely extracted from a report prepared for the European Commission on the risks arising from the industrial use of PFOA and APFO (RPS Advies, 2010). According to the report, the market volume of production and import of PFOA and APFO showed a decreasing trend from 2002 onwards in the EU-27 Member States. For the period 2004-2008 the average market volume is estimated to be a maximum of 100 t/y. The trend in the use of PFOA and related compounds shows a further decrease, and the report estimated that the market for 2010 would likely be less than 50 t/y.

According to the information available to RPS Advies (2010), only one manufacturer of APFO was active in the EU in 2009 and this company planned to cease production as per April 2010. The annual average sales volume of APFO of the company during the years 2004-2008 was reported to be about 40 t/y of which 10 tonnes was exported or storaged. The import of the substances into the EU was estimated at 20-25 t/year.

Three applications of PFOA /APFO were identified: fluoropolymer production, and use as surfactants in the semiconductor industry and photographic industry.

The fluoropolymer production was the major direct user of PFOA as a processing aid. PFOA may be present at residual levels in the fluoropolymer products that are placed on the market as resins or as dispersions. The study does not provide specific data on the quantities of PFOA ending up in the polymers.

APFO was used in the photographic industry in a total average annual volume of 2.6 t/. In the photographic industry PFOA and PFOA-derivatives play an essential role in manufacturing and performance of certain imaging products because these chemicals provide critical antistatic, surfactant, friction control, and dirt repellent properties. The substances also provided important safety features by controlling the build-up and discharge of static electricity and preventing employee injury, operating equipment and product damage, and fire and explosion hazards.

According to the study, the semiconductor industry had a minor usage of PFOA and related substances, and the total consumption for the entire EU semiconductor industry was estimated at less than 50 kg/year.

The total tonnage of imports of PFOA and APFO as residuals in mixtures and articles imported from countries outside the EU was estimated with high uncertainty at <5 t/y.

No data are available on the use of other long-chained PFCAs and related substances in the EU.

3.2.3 Short-chain PFCAs

Global manufacture and consumption

Limited information has been identified regarding the current production and consumption of short-chain polyfluorinated carboxylates and sulfonates and their derivatives. Information on these substances is not included in the 2009 OECD survey.

Information from industry (FluoroCouncil, 2012) indicates a general transition trend in the use of PFCAs and PFSAs:

- Surfactants:
  - Moving from ≥6 carbon to 4-carbon-based fluoroalkane sulfonate chemicals
  - Moving from 8 and 9 carbon perfluoro carboxylate polymerization aids (PFOA/PFNA) to certain mono- or poly-fluoroether carboxylates or other shorter-chain fluorinated substances;
- Surface modification polymers:
  - Moving from ≥6-carbon to 4-carbon-based fluoroalkane sulfonate chemicals
  - Moving from ≥8-carbon to 6-carbon fluorotelomer chemicals.

The 4-carbon-based sulfonate chemistry is based on perfluorobutane sulfonate (PFBS) and derivatives e.g. perfluorobutane sulfonamido-based fluorosurfactants. PFBS-based chemistry was introduced by 3M as replacement for the PFOS-based chemistry and PFBS-based substances are today used mainly for protective treatments (e.g. of textiles) and surfactants.

Information from Australia Department of Health and Ageing (NICHAS, 2005) indicates that potassium perfluorobutane sulfonate based chemicals have main applications in industrial and consumer carpet protection treatments, industrially applied corrosion resistant paints and coatings, and high performance industrial chemical applications in the metal processing industry. Further applications include electronic grade fluorochemical surfactants in etch solutions, photoresists (light-sensitive material used in several industrial processes, such as photolithography and photoengraving), photoresist strippers and edge bead removers, anti-reflective coatings, spin-on glass films and as flame retardant additives.

Consumption in the EU
Limited information is available on the use of short-chain PFSAs in the EU.

One short-chain PFSA is included in the list of registered substances: N,N,N,-triethylethanaminium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (EC Number 700-536-1; no CAS No indicated = triethylethanaminium perfluorobutanesulfonate). The registered quantity of this C4 perfluorosulfonate salt is 1-10 t/y. The use indicated in the registration dossier is manufacture of tetraethylammonium perfluorobutanesulfonate, which is used for metal (chromium) plating (ECHA, 2012h). This substance is the C4 analogue to the C8 tetraethylammonium perfluorooctane sulfonate used for metal chromium plating and mentioned in the section above. It is not clear why it is the intermediate and not the final substance which is registered.

Three other short-chain PFASs, not included in the OECD list, were registered with a total tonnage of 12-120 t/y. For two of the substances (each with 1-10 t/y) the uses were indicated as reactive processing aids, laboratory reagents and surface active agents.

3.2.4 Fluorotelomers and fluorotelomer-based polymers

Glabal manufacture and use
Fluorotelomer-based products have been manufactured since the early 1970s and used in many of the same industrial and consumer product applications as POSF-derived products (Prevedouros *et al.,* 2006). From 1985 to 2000, the global production of fluorotelomers increased from 2,000 to 11,000 t/y (Korzeniowsky, 2008).

According to US EPA (2009), world-wide production of fluorotelomers in 2006 was estimated at about 9,000 t/y and the USA accounted for more than 50 percent of this fluorotelomer production. This estimate was low compared with another estimate made by the German Umweltbundesamt (2009) that indicates that the annual worldwide production of the basic fluorinated telomer alcohols (FTOH) was estimated at 11,000 to 14,000 tonnes.

According to US EPA (2009) most of the fluorotelomers are used to produce side-chain-fluorinated polymers as described in section 1.2. No data have been identified indicating the percentages of the total used as fluorotelomer compounds and fluorotelomer-based polymers, respectively.

US EPA (2009) reports that the final application of the world-wide production of fluorotelomers in 2006 was as follows (apparently mainly used as fluorotelomer-based polymers):

- Textiles and apparel accounted for approximately 50% of the volume;
- Carpet and carpet care products accounting for the second largest share in consumer product uses, and
- Coatings, including those for paper products, are the third largest category of consumer product uses.

Limited data are available on the manufacture of fluorotelomers and side-chain-fluorinated polymers in China, but the production volume was in 2009 apparently still relatively low. In 2009, the China Dyeing and Printing Association reported that approximately 10,200–10,600 tons of fluorinated finishing agents were used each year in China (Lim *et al.,* 2011). Of this 9,800–10,200 tons were imported and 300 tons were domestically made. According to a presentation at a UNEP workshop, the imported agents are from foreign companies, such as 3M, Dupont, Clariant, Huntsman, Daikin and Asahi (ChinaPops, 2009). The total content of fluorinated substances is not indicated.

The overall trend in global manufacturing and consumption of fluorotelomer and fluorotelomer – based polymers is a shift from ≥C8 to C6 fluorotelomer chemicals (FluoroCouncil 2012).

No data, however, have been available on the distribution between the pure telomers and PFT-based polymers based on ≥C8 and C6 fluorotelomer chemistry, respectively.

Consumption in the EU

Very limited information has been available on the production and consumption of fluorotelomers and fluorotelomer-based polymers in the EU. None of the registered substances are within the group of fluorotelomers and fluorotelomer-based polymers.

Considering a worldwide production in the range of 11,000 to 14,000 t/y (Umweltbundesamt, 2009), the consumption in the EU would likely be in the range of 3,000 – 5,000 t/y. It means that none of the substances are likely to be manufactured or imported in quantities above 1,000 t/y and consequently not registered as of today.

A number of telomers belonging to the groups: (n:2) fluorotelomer acrylates, (n:2) fluorotelomer iodides, (n:2) fluorotelomer methacrylates, fluorotelomer halogenides, (n:2) fluorotelomer sulfonic salts, and (n:2) fluorotelomer alcohols are among the substances with a 2013 registration indication are. All the substances are based on C6 chemistry which is in accordance with the current shift from C8 to C6 chemistry. However, one "reaction mass" (probably telomer-based polymer) is based on C8, C10, C12 telomers.

The available data do not indicate to what extent the side-chain-fluorinated polymers are produced in the EU or imported from countries outside the EU.

3.2.5 Emission from manufacture

PFASs have historically been manufactured using four distinct routes. Today PFASs are principally manufactured by two different processes: electrochemical fluorination (EFC) and telomerisation. The brief description below is extracted from Buck *et al. (*2011).

Electrochemical fluorination (ECF) is a technology in which an organic raw material (e.g. octane sulfonyl fluoride) undergoes electrolysis, leading to the replacement of all the H atoms by F atoms. The free-radical nature of the process leads to carbon chain rearrangement and breakage, resulting in a mixture of linear and branched perfluorinated isomers and homologues of the raw material as well as perfluorocarbons and other species. The ECF process has traditionally been used to produce PFOS (via POSF) and PFOA (via perfluorooctanoyl fluoride). Today the ECF process is, among other functions, used to produce products based on perfluorobutane.

Telomerisation is a technology in which a perfluoroalkyl iodide (PFAI) is reacted with tetrafluoroethylene (TFE), to yield a mixture of perfluoroalkyl iodides with longer perfluorinated chains. The starting iodide is referred to as the "telogen" and the TFE as the "taxogen." The product perfluoroalkyl iodide mixture is often then reacted further, in a second process step, where ethylene is inserted. The perfluoroalkyl commonly known as Telomer A, resulting from telomerisation, the 1st step, and the "fluorotelomer iodides", commonly known as Telomer B, formed in the 2nd step, are raw material intermediates used to produce additional building blocks that are further reacted to create a family of "fluorotelomer-based" surfactant and polymer products. When a linear telogen and taxogen are employed in the telomerisation process, the resulting perfluoroalkyl iodides have exclusively linear perfluoroalkyl chains. Mainly linear substances are produced by the process, but branched substances may be formed if a branched telogen is employed and reacted with the TFE.

The total emission of POSF from the manufacture of 122,500 tonnes POSF (including waste) from 1970 to 2002 is estimated at 650-2,600 tonnes, while the emission of PFOS is estimated at 6.5-130 tonnes.

According to the most recent OECD survey, total releases of PFOS (and related substances) to the environment (incl. off-site landfill, underground injection and water treatment) from the manufacture by seven companies in five countries replying to the survey was <1.5 t/y in 2009. The release to the environment of other PFCs was <5.5 t/y of PFOA, <6.0 t/y of PFOA ammonium salt and perfluorooctyl iodide (in total) while the releases of C8:2 telomers were confidential.

Under the US EPA Stewardship Program, eight major companies operating in the USA have committed to reduce global facility emissions and product content of PFOA, precursor chemicals and higher homologue chemicals by 95% by 2010. The kg PFOA released per kg produced was in the 0.001-0.1 kg/kg range and the total releases in 2009 were reported to be 2-20 tonnes (US EPA, 2011).

Fluorotelomer alcohols (FTOHs) are used as intermediates in the production of other fluorotelomers and side-chain-fluorinated polymers. Fluorotelomer alcohols are volatile and the main sources are the manufacture and use of fluorotelomer-based products. No specific data on emissions of FTOHs from manufacturing processes have been identified.

3.2.6 Impurities in products

PFOA and other PFASs may be present as impurities in a variety of products. The focus has so far mainly been on PFOA and FTOHs.

PFOA in fluorotelomers

PFOA and other PFCAs may be found at very low trace levels in some fluorotelomer products as a by-product of their synthesis and as a result of residuals/precursors breaking down to PFCAs.

The total amount of PFOA as impurity in fluorotelomer products from non-US based production locations was reported to the US EPA PFOA Stewardship Programme at <50 kg/y while the total content of PFOA, PFOA precursors and higher homologues was 1 t/y (US EPA, 2011).

Residual PFOA and related substances in fluoropolymer resin products range between 0-150 mg/kg and 5-3000 mg/kg in the fluoropolymer dispersion products of the non-US based production locations. Reductions of PFOA, PFOA salts and higher homologues and precursors of PFOA in fluoropolymer dispersion products are reported as between 54% and 100% in the EPA's 2009 summary tables (US EPA, 2011).

Dupont reports that it has been possible to reduce the PFOA content in aqueous-based dispersions from 1,000-5,000 ppm to a level below 50 ppm (Shelton, 2009).

Environment Canada has made an agreement with the fluorinated products industry (some of the same companies participating in the US EPA Stewardship Program) to work towards the elimination of residual perfluorooctanoic acid (PFOA), residual long chain PFCAs and residual precursors in their fluorochemical products sold in Canada. Compared to a 2004 baseline, the reduction in 2009 was in the range of 23.6 to 99.9% depending on the company (Environment Canada, 2012c).

PFOA in PFTE and other fluoroplastics

PFOA has traditionally been used as a processing aid (surfactant) in the production of certain fluoropolymers and other grades of fluoropolymers and fluoroelastomers. The surfactant is removed when the fluoropolymer aqueous emulsion is dried. Residual surfactant may remain in the polymer and PFOA has been demonstrated to be present in articles with fluoropolymers, such as coated non-stick kitchen ware (Washburn *et al.,* 2005). As part of the US EPA Stewardship Program (see section 2.5.3), the PFOA content of fluoropolymers has been reduced significantly in recent years. Guo *et al. (*2009) found the PFOA concentration of PFTE cookware in the USA in at a level of <1.5 to 4.4 ng/g which is lower than the 4-75 ng/g previously reported by Begley *et al. (*2005).

FTOHs and FTOs in fluorotelomers and fluorotelomer-based polymers
FTOHs or fluorotelomer iodide is used to make acrylate monomer, a fundamental building block for the polymeric products representing >80% of the fluorotelomer-based products manufactured and used worldwide (Prevedouros *et al.,* 2006). The reaction of fluorotelomer alcohol to make fluorotelomer acrylate or methacrylate esters leaves 0.1-0.5 wt % unreacted residual FTOHs. Alternatively, reaction of fluorotelomer iodide with acrylic acid salt to form acrylate monomer results in 3-8 wt% FTOs (fluorotelomer) byproduct. The FTOHs and FTOs are present in the resulting sales products unless removed. Prevedouros *et al. (*2006) estimated that approximately 100 t each of FTOHs and FTOs were present annually in fluorotelomer-based products (Prevedouros *et al.,* 2006). These substances may be released from the products and can be found in the indoor environment and in the atmosphere as described elsewhere in this report.

3.3 Manufacture and use of PFCs in Denmark

PFCs are not manufactured in Denmark.

The use of PFCs in Denmark has previously been surveyed in 2001 (Havelund, 2001), 2002 (Havelund, 2002) and 2008 (Jensen *et al.,* 2008).

The 2008 survey was based on data from the Danish Product Register (retreived in 2007) on the import, production and export of preparations used for professional applications combined with estimates on the use of substances not included in the register, and import of the substances with articles. As part of the survey an extensive consultation among trade organisations, manufacturers of the substances and downstream users within the main application areas was undertaken. However, hardly any quantitative information on the use of the substances for the different application areas was obtained from the market actors. Therefore the authors had to estimate the total content of marketed articles on the basis of knowledge of the quantities of traded articles and some assumptions on the PFASs content of the articles, based on information from the literature and specifications of PFASs containing agents from major manufacturers of these agents.

It has been beyond the scope of the current survey to prepare a full update of the 2008 survey; the focus is rather to discuss new findings that may influence the total picture regarding use of the substances in Denmark.

Trade organisations covering the main application areas and a few key market actors have been contacted as part of the survey as described for each application area in the following.

3.3.1 Manufacture, import and export of PFASs and side-chain-fluorinated polymers on their own and in mixtures

The combined nomenclature (CN) used for the import/export statistics in Denmark and the EU does not have any specific commodity codes (CN8 codes) for PFASs or mixtures containing PFASs. The substances and mixtures are included in more aggregated commodity groups.

Data was retrieved from the Danish Product Register in July 2012 in order to obtain an overview of current uses of the PFASs and side-chain-fluorinated polymers in mixtures and assess any trend in their use as compared with the 2008 survey. The data represents mainly 2011 figures.

The Product Register includes substances and mixtures used occupationally and containing substances classified as hazardous in a concentration of at least 0.1% or 1% (depending on the classification of the substance). Only PFOS and derivatives have a harmonised classification (see section 2.1.1), and for the other non-classified substances the registration will only occur, if they are con-

stituents of products, which are classified and labelled as hazardous due to the presence of other constituents. The data consequently do not provide a complete picture of the presence of the substances in mixtures placed on the Danish market. Furthermore, for substances included in mixtures used for production of mixtures in Denmark (e.g. included in raw materials used for production of paint) the quantities may be doublly-accounted for as both the raw material and the final mixture are registered. The amounts registered are for occupational use only, but for substances used for the manufacture of mixtures in Denmark the data would still indicate the quantities of the substances in the final mixtures placed on the market both for professional and consumer applications.

The results of the data retrieval by substance are shown in Annex 3 together with the data from the 2008 survey. The annex also briefly describes how the list of substances was generated.

The data can further be summarised as follows:

- In total 54 PFCs were registered in the Product Register in 2012 against 92 substances in the 2008 survey.
- The total registered quantity was 3.3 tonnes, 13.2 tonnes less than the 16.5 tonnes registered in the 2008 survey.
- 48 of the substances registered in 2007 were not registered in 2012;
- 11 of the substances registered in 2012 were not registered in the 2007 survey, partly because they were not included in the 2006 OECD list used for this survey. The total import + production of these 11 substances was 0.2 tonnes while 0.0 tonnes was exported. For all except one substance the data are confidential.
- For 21 substances in the 2012 survey, the data were confidential. The total quantity for these substances was 0.2 tonnes.
- None of the substances in the database of registered substances or the list of 2013 intentions, which are not on the OECD 2007 list, were registered in the Product Register.

Five of the seven substances with highest registered quantity, which account for 83% of the total registered consumption, are shown in Table 13. Two substances for which the quantity is confidential are not indicated.

None of the substances are registered under REACH or on the list of the 2013 intentions. Three of the substances are not pre-registered, probably because they are polymers and not subject to registration under REACH. Four of the substances are side-chain-fluorinated polymers.

Besides these side-chain-fluorinated polymers, the mixtures in the Product Register may also contain fluoropolymers, which are beyond the scope of the OECD surveys and this study, because they are not considered precursors of PFASs. Three substances identified in the Jensen *et al. (*2008) (but not included in the data retrieval in the Product Register in the study) were included in the data retrieval for this study, but the data are not included in the list of substances in Annex 3. Tetrafluoroethylene polymer (CAS No 9002-84-0) in PFTE polymer-based waxes was registered in 168 products used for various applications with a total of 12 tonnes. Most likely more mixtures with fluorinated polymers are used, and the total quantity may be significantly higher than the quantities of the side-chain-fluorinated polymers. This situation illustrates the necessity to clearly distinguish between the different types of polymers.

TABLE 13
FIVE OF TOP SEVEN SUBSTANCES REPRESENTING 88 % OF THE TOTAL TONNAGE REGISTERED IN THE PRODUCT REGISTER IN 2012

CAS No	Chemical name (as indicated in OECD, 2007)	OECD class	Number of products	Production and import, t/y	Export, t/y	Application areas *1	REACH
143372-54-7	Siloxanes and silicones, (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10- heptadecafluorodecyl)oxy Me, hydroxy Me, Me, octyl, ethers with polyethylene glycol mono-Me ether	Fluorosiloxane/silicone /silanes (F12), C8	84	1.9	1.3	Paint, lacquer and varnishes	Not pre-registered
65545-80-4	Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, ether with α-fluoro-ω-(2-hydroxyethyl) poly(difluoromethylene) (1:1)	Fluoro ether (F6), n *1	10	0.9	0.0	Paint, lacquer and varnishes	Pre-registered
24448-09-7	1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-N-methyl- (MeFOSE)	PFOS, C8	21	0.5	0.08	Paint, lacquer and varnishes	Pre-registered
65530-70-3	Poly(difluoromethylene), α, α'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[ω-fluoro-, ammonium salt	Fluoro phosphate (F8), n *1	19	0.3	0.0	Paint, lacquer and varnish, polishing agents	Not pre-registered
65530-69-0	Poly(difluoromethylene), α -[2-[(2-carboxyethyl)thio]ethyl]- ω-fluoro-, lithium salt	Fluoro thioether (F14)	17	0.2	0.2	Polishing agents, cleaning/washing agents	Not pre-registered

*n Notation from the OECD list (OECD, 2007), "n"presumeably indicate a polymer of various lengths.

*1 As indicated for Denmark in the SPIN database of the Nordic Product Registers. Most of the substances are also used for confidential applications.

PFOS and related substances

Six of the registered substances are included in the OECD classes of PFOS and PFOS/PFAS. The total registered production and import was 0.52 tonnes while the registered export was 0.08 tonnes. Of this MeFOSE (CAS No. 24448-09-7) shown in the table above accounted for 85%. The substance with the CAS No 68298-62-45, with a registered consumption of 0.04 t/y in 32 mixtures, is a multiconstituent substance and included in the OECD class PFOS/PFOA. It contains $C_8F_{17}SO_2$- moieties and is consequently subject to restriction. The main registered application area is paint, varnishes and lacquers.

[5] 2-Propenoic acid, 2- [butyl [(heptadecafluorooctyl)sulfonyl]amino]ethyl ester, telomer with 2-[butyl[(pentadecafluoroheptyl) sulfonyl]amino]ethyl 2-propenoate, methyloxirane polymer with oxirane di-2-propenoate, methyloxirane polymer with oxirane mono-2-propenoate and 1-octanethiol

Tetraethylammonium perfluorooctanesulfonate (CAS no. 56773-42-3) is used for non-decorative chromium (Poulsen *et al.,* 2011), one of the exempt applications further described below, but the total quantity is confidential.

The total registered consumption of the PFOS and PFOS/PFAS substances in the 2008 survey was 2 tonnes.

As mentioned below, the total identified consumption of PFOS for exempt applications in Denmark was estimated at 0.020-0.028 t/y in 2010. The discrepancy between this amount and the 0.5 tonne registered in the Product Register may be due to inadequate update of the notifications or uses not in compliance with the POP Regulation.

PFOA and related substances
The total registered production and import of substances in the OECD class PFOA was 1 kg. The consumption of substances from this class was also insignificant in the 2008 survey.

The main issue with regard to PFOA is consequently to what extent some of the registered fluorotelomers and side-chain fluorinated substances may contain perfluorinated moieties that may be precursors for PFOA when the substances degrade.

Side-chain fluorinated polymers
Fourteen of the registered substances include "poly" in the substance name. In total these substances accounted for 77% of the total consumption. The major application areas were paint, lacquers and varnishes, polishing agents and cleaning/washing agents.

Other substances
Fluorotelomers and short-chained PFAS in total accounted for 0.2 t/y corresponding to 7% of the total. The actual substances and applications are confidential.

3.3.2 End-use of PFASs in articles and mixtures

The total registered quantities of the substances by application area are shown in Table 14. The table includes the minimum and maximum estimates of the quantity of the substances in end-products from the 2008 survey. The minimum estimate was mainly based on data from the Product Register and is thus comparable with the 2012 data shown. For paint, however, the data from the Product Register were used as the maximum estimate. The maximum estimate was based partly on the data from the Product Register, partly on expert estimates based on knowledge on tonnage of articles and mixtures and some assumptions regarding the likely content of the fluorinated substances.

The total registered quantity in 2012 is 3.2 tonnes. Two of the major registered application areas in the 2008 survey were releasing agents and glues, which accounted for more than half of the registered quantity. In 2012 the registered consumption for these application areas was close to zero.

For some of the application areas the registered consumption was higher in 2012: cleaning agents, impregnating agents and soldering agent. For some of the registered use areas in 2012, the 2008 survey did not indicate any use, such as fuel additives and process-regulating agents.

For two major application areas, carpets and impregnated clothing, the 2008 survey did not base the estimates on the Product Register data, but on general knowledge of the use of these substances for the manufacturing of such articles.

For paint and lacquers, polish and car-care products it was assumed that the substances were present in mixtures which were not notified to the Product Register because they do not contain con-

stituents classified as hazardous. For many of the use areas it was assumed that the total quantity was higher than the minimum estimate but no data were available to make any qualified estimates.

The total in 2007 was estimated at 38 tonnes. Considering that the global production of fluorotelomers and telomer-based substances is estimated at 11,000 to 14,000 t/y, and that these account for the majority of global use of the substances concerned, it can be assumed that the total consumption in Denmark with end-products would be in the range of 10 to 100 tonnes.

TABLE 14
TOTAL ESTIMATED QUANTITY OF PFCs IN END-PRODUCTS IN 2007 AND QUANTITY REGISTERED IN THE PRODUCT REGISTER IN 2012

Use area	Estimated quantity of PFCs in end-products in 2007, kg/y		Quantity registered in the Product Register in 2012 *1 kg/y
	Min. estimate	Max. estimate	
Releasing agents	7,200	>7,200	7
Paint, lacquers and varnishes	100	3,500	544
Printing inks	15	>15	0
Adhesives	2,500	>2,500	1.2
Surface active agents	1,100	>1,100	614
Cleaning agents	100	>100	208
Polish and care products	170	590	7
Auto polish and wax	*0.08*	*358*	
Floor polish	*0.24*	*60*	
Carpets	745	18,000	*2
Sunshades/awnings, tents, umbrellas, parasols etc.	not estimated	not estimated	*2
Impregnated clothing	400	3,500	*2
Footwear	not estimated	not estimated	*2
Impregnating agents	170	340	309
Impregnation agents for footwear only	*12*	*24*	
Impregnation agents for car textiles only	*1.8*	*1.8*	
Galvano-technical products	760	>760	0 *3
Fire inhibitors	400	>400	confidential
Pesticides	180	>180	0
Soldering agents	280	>280	441
Other surface treatment agents for metal	not indicated	not indicated	6
Fuel additives	not indicated	not indicated	151
Process-regulating agents	not indicated	not indicated	767
Application not indicated and other	not indicated	not indicated	225
Total	14,120	> 38,465	3,258

*1 Registered consumption with the mixtures placed on the market in Denmark = production + import – export

*2 Agents used for manufacturing of these articles may be included in the group “impregnating agents”.

*3 It is known that PFCs are used in galvano-technical products, but they are not indicated as such in the Product Register. May be included in the product group “process-regulating agents”.

As mentioned it has been beyond the scope of this study to prepare a full update of the survey, but readily available newer information is briefly discussed in the following.

Hard chromium plating
PFOS is used in non-decorative hard chromium plating in Denmark which is one of the exempt applications of PFOS. Around the year 2010, 10-28 kg of PFOS was used annually in hard chromium plating in Denmark (Poulsen *et al.,* 2011). In hard chromium plating, a thin layer of chromium is applied electrochemically to the surface of metals. The PFOS substances were used to limit the formation of Cr (VI) aerosols, which are considered of concern in terms of both occupational health and safety and the environment. The most commonly used PFOS substance for this purpose was tetraethylammonium perfluorooctanesulfonate (CAS no. 56773-42-3). This chemical substance is typically found in preparations with a concentration of 5-10%; e.g. Fumetrol® 140. Some users were contacted in May 2012 as part of the preparation of the updated national implementation plan for the Stockholm Convention. PFOS is still being used for this purpose by about 5 companies in Denmark, and there are currently no plans to phase out PFOS. PFOS is used in recirculating systems without wastewater drainage outlet. The substances are decomposed gradually in the baths, which are subsequently disposed of to the hazardous waste treatment plant, Kommunekemi.

In a project under the programme *"Miljøeffektiv Teknologi – Substitution af problematiske kemikalie*r" (Environmentally efficient technology - substitution of chemicals of concern) (Poulsen *et al.* 2011), feasible chemical and physical alternatives to PFOS were developed with support from the Danish EPA in 2009-2011. Several chemical and physical alternatives were evaluated. The results showed that a 6:2 fluorotelomer substance 1H,1H,2H,2H perfluorooctane sulfonic acid (Fumetrol® 21, CAS No. 27619-97-2) in a large scale test:

- works as effective as PFOS as mist suppressing agent,
- seems to have the same durability as PFOS as mist suppressing agent,
- has the same price level as PFOS as mist suppressing agent,
- can be substituted right away, when PFOS is burnt out in the chrome bath, without the need of changing the entire chrome bath chemicals, and
- is an environmental improvement as it is less persistent, less bioaccumulative, and less toxic than PFOS (Poulsen *et al.,* 2011).

Paint and lacquers
The data from the Product Register demonstrates that the fluorinated substances are widely used as surfactants in paint.

The trade organisation Danmarks Farve- og Limindustri (DFL, Danish Paint and Adhesives Industry) was contacted. An enquiry to the members revealed that the fluorinated substances were not used as substances on their own in the industry, but are likely to be present in some of the imported raw materials. The 2008 survey describes the discrepancy between the registered quantities in the Product Register (3.5 tonnes) and answers from the industry which did not recognise the fluorinated substances registered in the Product Register. For this reason the total quantity in paints was estimated at 100 kg, aminimum estimate.

A likely explanation is that the fluorinated substances are included in raw materials, but not specified in safety data sheets as the substances are used in concentrations below 0.005%. The registered quantities have remained at a level of several tonnes, making it likely that it reflects actual use in Denmark.

Impregnated clothing
As mentioned in section 3.2.4, the production of apparel is estimated to consume around 50% of the global production of fluorotelomer-based substances. It is further indicated that in 2009 approxi-

mately 10,000 tons of fluorinated finishing agent (the quantity in terms of fluorinated substances is not indicated) were imported to China for the production of apparel and other textile products.

The fluorinated agents are typically used for clothing for outdoor uses to make the clothing water and soil repellent. It was reported that about 400 kg fluorinated substances being used for impregnation of textiles in Denmark (excluding carpets) in the 2008 survey. The average content of fluorinated substances in the agents was about 17%. However, the majority of the impregnated textiles is imported and in 2007, the production was 15-20% of the imported amounts.

The main issue is to what extent PFASs are present in trace concentrations in the textiles or formed from side chains released from the fluorinated polymers. The 2008 survey (Jensen *et al.,* 2008) quoted Norwegian and Swedish investigations of PFASs in all-weather jackets showing an unbound content of fluorotelomer alcohols (FTOH) of 25 to 1000 µg/m² of textile, an unbound content of PFCA between <5 and 400 µg/m² of textile and an unbound content of PFOS-related compounds between <5 and 100 µg/m² of textile (Schulze and Norin, 2006; Berger and Herzke, 2006 as cited by Jensen *et al.,* 2008).

A study of PFASs in 11 textiles (mainly all-weather apparel) marketed in Norway by the Norwegian Pollution Control Authority (SFT, 2006) found the following levels of unbound PFASs in the textiles (number of samples with detectable content of the substances indicated in bracket): FTOH: 0-10,683 µg/m²(10), FTS/-FTCA: 0-6 µg/m²(7), PFSAs :0-31 µg/m²(9), PFCAs :3-170µg/m²(11), FASA/-FASE:0-23µg/m²(8), PFOS: <0.02-30 µg/m²(9), PFOA: 0.4-34 µg/m²(11).

A recent report by Greenpeace (2012) has found similar levels in 13 items of outdoor clothing from major brands purchased in Germany, Austria and Switzerland. The highest concentration of PFOA was 5 µg/m² while the total sum of the analysed PFCAs reached 11 µg/m². The highest concentrations for the FTOHs were 352 µg/m² 6:2 FTOH and 240 µg/m² 8:2 FTOH. PFOS was not detected in any of the samples.

Similar levels as cited above can be expected to be found in outdoor clothing marketed in Denmark by major brands.

Carpets

Carpets have historically been the major application area for PFOS in the EU. The 2008 survey estimated that carpets may likely be the major application area of the fluorinated substances in Denmark. It was confirmed by manufacturers of carpets that fluorinated agents were used for the carpets, and it was assumed that between 56 and 90% of the carpets in Denmark were impregnated with fluorinated substances, but information on which specific substances were used was not obtained.

A major supplier of fluorinated substances for carpets has been contacted but no specific information has been obtained.

Packaging

The 2008 survey did not specifically estimate the total use of the substances for packaging which was not within the scope of the survey. The use for packaging may have been included in the aggregated group “surface active substances”. On a global scale, coatings, including those for paper products, are the third largest category of consumer product uses of fluorotelomer-based substances. In particular the use of the substances for food contact materials, and the possible consumer exposure to the substances in the packaging, has been intensively studied in recent years.

A recent Danish study explored the identity of a range of polyfluorinated surfactants used for food contact materials, primarily to impart oil and water repellancy to paper and board. More than 115 molecular structures were found in industrial blends from the EU, USA and China, belonging to the groups of polyfluoroalkyl-mono and diester phosphates (monoPAPS, diPAPS and S-diPAPS),-ethoxylates, -acrylates, -amino acids, -sulfonamide phosphates and -thio acids, together with residuals and synthesis byproducts. In addition, a number of starting materials such as perfluorooctane

sulfonamide N-alkyl esters were analysed. Dialkylated and trialkylated PAPS and S-diPAPS were found in migrates from European food contact materials (Trier *et al.,* 2011).

In fourteen screened food-contact materials collected in Denmark, both diPAPS and S-diPAPS were identified above the detection level in four of the materials while one of the materials contained diPAPS only (concentrations not indicated). In popcorn migrates, diPAPS and S-diPAPS was detected semi-quantitatively at 0.2–0.7 mg/kg food which correlate well with levels found in studies from the USA (Trier *et al.,* 2011).

In 2012, the Danish Veterinary and Food Administration screened 84 food-contact materials for the presence of PFASs (DVFA, 2012c). In 41 of the materials, the screening indicated that the substances were not present. The remaining 43 materials were subsequently analysed for 36 PFASs.

The substances were divided into two groups of substances: those which can be degraded to PFOA and PFCA, and those which can be degraded to PFOS and PFSA. None of the materials contained substances that can be degraded to PFOS and PFSA. Most of the 43 materials contained PFOA/PFCA precursors in the µg/kg range while three materials contained more than 1 mg/kg of the substances, calculated as total PFOA equivalent to 1.5 mg/kg, 2.2 mg/kg and 10.2 mg/kg respectively. In these materials the main PFASs were 6:2/8:2 DiPAPs, 8:2 FTOH and 10:2 FTOH.

In a study of migration of PFASs from food contact materials, the Danish Veterinary and Food Administration analysed the content of PFCAs, PFSAs, PFSAAs, FTOHs, monoPAPs, diPAPs and S-diPAPs in 66 samples of paper and cardboard (DVDA, 2012d). In 10 of the samples, the concentration of one or more PFASs was above the detection limit. For these 10 samples, migration to the food and to a food simulator of 50% ethanol was measured. The migration of the substances to the simulator was generally higher than the migration to the food items. The highest migration was found originating from packaging and parchment paper to cakes. Migration of PFASs from the packaging or parchment paper to the cakes was detected for all five cake samples. In one of the samples, migration of six different PFAS was found. In popcorn popped in packaging with a content of PFHxA and PFBA, the latter substance was found in a concentration of 24 µg/kg popcorn. In another popcorn sample, the packaging contained FTOH and other FPASs, but these substances could not be detected in the popcorn after it was popped. No migration from the packaging to coffee and flour could be detected.

In response to the results demonstrating the presence of a wide range of PFASs in packaging, the Danish trade organisation for the packaging industry "Emballageindustrien" (Emballageindustrien, 2012) undertook a survey of PFASs used in food-contact packaging materials in late 2011. The survey covered 85% of the members of the trade organisation which produce food-contact packaging. The survey included paper, cardboard and printing inks used for manufacture. According to the survey, the food-contact packaging produced in Denmark does not contain PFAS. However, it is indicated that some of the suppliers of cardboard use PFASs of the type that are recommended by the German Federal Institute for Risk Assessment (BfR) on paper and board for food contact (BfR, 2012). The recommendation lists 14 fluorinated substances with a maximum content in the range of 0.4-1.2% based on dry fibres weight, depending on the actual substance. The substances are mainly polymers and co-polymers based on short-chain fluorochemicals.

The trade organisation has been contacted as part of the present survey in order to obtain more information on the actual substances and quantities used, but specific data have not been obtained.

Cleaning products

A survey of the chemical substances in cleaning products for ovens, cookers and ceramic hobs from 2010 did not find PFOS the four mixtures analysed for the content of PFOS (Andersen *et al.,* 2010).

Fire extinguishers

PFOS-related substances have traditionally been used in fire fighting foams in Denmark as well as other countries (Havelund, 2002). The remaining PFOS-containing foams were allowed to be used until June 2011. Investigation of sites contaminated by the former use of fire extinguishers is addressed by the Danish action plan for PFOS (section 2.4.1).

In the 2008 survey, 400 kg/y of PFCs were registered for use in fire-fighting foams. In 2012 three different PFCs were registered as used for this application area in the Product Register, but names of the substances and the registered quantities are confidential. According to a study of alternatives to FPOS and PFOA from 2005, both PFC-based fire-fighting foams and fluorine-free foams were used in Denmark at that time (Poulsen *et al.,* 2005). It was indicated that a significant amount of the foams came from the company Solberg Scandinavia which still market fire-fighting foams with PFCs and fluorine-free foams. The foams were based on C6 fluorinated compounds (e.g. dodecafluoro-2-methylpentan-3-one, a mixture of different C6 fluorinated telomers possibly containing some C8 fluorinated compounds as well) and protein-based foams or synthetic detergent foams (Poulsen *et al.,* 2005). It has not been attempted to make an updated survey of the use of PFCs in fire-fighting foams.

Trace content of PFOS in products

A Norwegian study analysed PFOS and other PFAS in 30 consumer products in 2009 (Herzke, 2012). Notably, PFOS, which has been strictly regulated in Norway since 2007 and is regulated in the EU, was found in amounts close to or exceeding the EU regulatory level in 4 of the 30 analyzed products, all within the leather or carpet product groups. Two pooled (n=8) leather samples (38 and 21.2 μg/m²) exceeded the EU regulatory level of 1 μg/m², whereas two pooled (n=4) carpet samples (0.7 and 1.04 μg/m²) were close to the regulatory limit. One of the carpets was labelled as Teflon®, which is a PTFE fluoropolymer, but it apparently contained PFOA 6:2 FTS, PFHxS, PFHxA, PFHpA and PFOA at trace levels.

A recent report by Greenpeace (2012) did not fnd PFOS-related substances in any of the samples of outdoor garments.

The Norwegian results indicate that many textiles or other coated materials which are coated with a fluoropolymer or other fluorinated agents may contain PFOS above the limit value of 1 μg/m².

3.4 Summary on the use of PFCs in the EU and Denmark

Table 15 summarises information on the use of PFCs at EU level and consumption of the substances registered in the Danish Product Register in 2012.

The consumption of PFOS, PFOA and APFO at EU level has recently been surveyed in studies for the European Commission. Limited information is available at EU level on the use of PFCs other than PFOS and PFOA by application area. The registrations under REACH provide limited information on the current use of the substances in the EU. Apart from PFOS and some derivatives, the substances do not have a harmonised classification and all substances are apparently imported or produced in tonnages below 1,000 t. After 2013 more information will be available, as companies have notified of their intentions for registration of 12 substances more. It is, however, unclear how fluorinated side chains of imported side-chain-fluorinated polymers, which are not subject of registration, arepre-registered.

The total registered tonnage is in the range of 15-150 t/y, but the total consumption of PFCs with end-uses, considering global production, is likely in the 2,000-4,000 t/y range (excl. of fluorotelomers used as intermediate in the production of fluortelomer-based polymers in order to prevent double counting).

The international industry organisation FluoroCouncil are not able to provide aggregated data on consumption by substance group at EU level. More information would be needed to assess the use of the substances at EU level and monitor any changes from long-chain fluorochemistry to short-chain (e.g. ECHA, 2012g).

In Denmark, the total consumption with mixtures registered in the Product Register has decreased from 16.5 tonnes in 2007 to 3.2 tonnes in 2012. A significant part of the decrease was due to a decrease in the use of “releasing agents” from 7.2 t/y to nearly zero. Of the 3.4 tonnes in 2012, side-chain-fluorinated polymers accounted for 77% of the total. Of the 92 substances registered in 2007, 48 substances were not registered in 2012, while 11 new substances where registered in 2012. Notably 0.5 tonnes of PFOS-related substances were registered for uses not in compliance with the restrictions of the POP Regulation.

The actual consumption in Denmark in mixtures is probably significantly higher than the quantity registered in the Product Register, as notification of the register is only required for mixtures defined as hazardous. Areas with a significant consumption not registered could be agents for treatment of carpets and textiles, water-based paints and adhesives, and fire-fighting foams.

The total quantity of PFC in end-products in Denmark has not been updated, but it is expected that the total quantity for the main application areas may be at the same level as in 2007. The total in 2007 was estimated to be in the range of 14 to in excess of 34 t/y (no upper limit indicated). The major application areas were estimated to be releasing agents (probably used in the plastics industry), surface active agents (probably used for production of articles), paint, lacquers and varnishes, adhesives, carpets, impregnated clothing, and galvano-technical products (probaby surfactants used in the industry). A significant part of this total may be imported in clothing (taking up 50% of global consumption), carpets, packaging and other articles treated with PFCs.

TABLE 15
CONSUMPTION OF THE PFCs IN THE EU AND DENMARK

Substance group	EU		Denmark	
	Estimated consumption in 2011, t/y	Use areas, remark	Consumption registered in the Product Register in 2012, t/y	Use areas, remark
PFOS and related substances	8 Registrations : 1-10	Metal plating industry (81%) Photographic industry Semiconductor industry Hydraulic fluids in aviation industry	0.5 0.02 *1	Registered uses in non-compliance: Paint, laquers and varnishes Metal plating industry
PFOA and APFO	25-50	Fluoropolymer production (majority) Photographic industry Semiconductor industry	0.001	PFOA may be present at low levels as contaminant of fluoropolymers
Longer chained PFCAs and related substances	no data no registrations	no data		
Short-chain PFASs	Registrations : 30-130 Probably significantly higher	Limited data: Surfactants, reactive processing aids	0.4	For the main part uses are confidential
Fluorotelomers	No registrations	Probably same as world market: Textiles and apparel (50%) Carpet and carpet care products Coatings, including those for paper products		
Side-chain-fluorinated polymers	Probably some 2,000-4,000 based on world-wide consumption		2.3	Paint, lacquers and varnishes, polishing agents, cleaning agents (+ non confidential uses)

*1 Not registed in the Product Register. Data from Poulsen *et al.*, 2011.

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4. Waste management

4.1 EU

Detailed information is available on PFOS in waste at EU level, whereas limited information has been identified on other PFASs in the waste streams at EU level.

4.1.1 PFOS in waste

This section is mainly based on selected information contained in the report prepared by the ESWI consortium on behalf of the European Commission, DG Environment, "Study on waste related issues of newly listed POPs and candidate POPs" (ESWI, 2011).

In the past, perfluorooctane sulfonic acid and its derivatives have been used for a wide range of products and processes. Among these uses are pesticides, plumbing fluxing agent, medical applications and devices, flame retardants, coatings and coating additives, adhesives as well as uses in rubber and plastics, upholstery, and the leather and carpet industries.

At present, PFOS is used in the metal plating industry, as content in hydraulic fluids in the aviation industry, in the photographic industry and the semiconductor industry as described in section 3.2.

Current PFOS uses in metal plating and photographic industries, as well as use in hydraulic fluids in the aviation industry, are considered relevant sources of PFOS to waste. In case of the photographic industry there has been a continuous reduction of the use of PFOS, but due to the existing storages of pictures in households or x-rays in hospitals, this application area generates a relevant PFOS-containing historical waste stream. The current use of PFOS in the semiconductor industry is not considered relevant for waste.

With respect to past uses, upholstery and carpets are considered relevant due to their long lifetime regarding PFOS entering the waste stream.

Industries with products having a shorter lifetime, such as textiles, paper and cardboards, do not significantly influence the current waste stream anymore, even if they still contribute to current and future PFOS emissions, in particular as releases from waste disposal or contaminated sites. Industries which used PFOS during their production processes with end-products not containing PFOS, such as the mining industry, do not pose a current input of PFOS to waste streams.

The results of ESWI (2011) are summarised in Table 10. According to the study, generally there was a considerable drop in the use of PFOS in the EU in the period from 2000 to 2004, where many uses of PFOS ceased before the use PFOS for the applications was restricted at EU level. Articles in use in society will therefore primarily be articles with relatively long lifetimes, such as leather furniture and carpets made of synthetic fibres. The EU study calculates specific amounts in the waste stream from leather furniture and carpets. The study indicates that use of PFOS for the two product groups ceased in 2002.

In the years up to 2002, an estimated 146 tonnes of PFOS per year were used for production of carpets in the EU27, and the average concentration of PFOS in PFOS-impregnated carpets was 88 mg/kg. It is also estimated that about 146 tonnes per year of PFOS will be disposed of in the period

from 2012 to 2016 in a waste volume of 1.9 million carpets (both with and without PFOS) with an average content of 75 mg/kg.

In the years up to 2002, about 6 t/y of PFOS were used in the EU27 for leather furniture, and in 2010 a corresponding amount was disposed of with this furniture in a total waste volume of about 71,000 tonnes of upholstered furniture (both with and without PFOS) with an average content of PFOS of 2.4 mg/kg. Calculations in the study assume PFOS concentrations in leather furniture of typically around 80 mg/kg (in the furniture where PFOS was used in production). Calculations in the study also assume an average lifetime of 10 years for the articles and that everything will have been disposed of by 2012. Considering the uncertainty of the lifetime estimates and the fact that the leather articles are generally expensive, there may still be amounts to be disposed of in 2012 and the following years.

Certain types of fire-extinguishing foam produced before 2002 may contain PFOS. Based on information on the operational lifetime of fire extinguishing foam, the EU study estimates that the amounts of PFOS in fire extinguishing foam stored in the EU fell from 122 tonnes in 2004 to about 84 tonnes in 2011, and that at the cut-off date on 27 June 2011, between 54 and 87 tonnes of PFOS in fire extinguishing foam were still being stored. After this date the fire extinguishing foam containing PFOS was to be destroyed. However, some stocks of PFOS containing fire fighting foams remain in the EU, but are in the process of disposal (EC, 2012).

TABLE 1
PFOS IN ARTICLES IN USE AND IN WASTE IN THE EU (ESWI, 2011 AS SUMMARISED BY DANISH EPA, 2012)

Articles	Amounts used in the EU	Lifetime	Amounts in articles in use in the EU in 2012	PFOS concentration in waste	PFOS amounts in waste in the EU in 2012
Carpets	Before 2002, 146 tonnes of PFOS were used annually in 1.7 million tonnes of carpets, i.e. the average content of PFOS in these carpets was 88 ppm.	14 years	About 584 tonnes of PFOS in 2012, corresponding to 4 years consumption in the period up to 2002.	It is assumed that the concentration of PFOS in the total amount of carpets disposed of is 75 ppm as not all carpets contain PFOS	About 146 tonnes of PFOS in a total waste fraction of 1.9 million tonnes of carpets (will continue at this level until 2016).
Leather upholstery in furniture and car interiors	Until 2002, about 5.7 tonnes of PFOS in 71,342 tonnes of leather upholstery were used annually (3% of the market for leather upholstery). Leather furniture is assumed to represent 50% whereas vehicles make up the remaining 50%.	10 years	0 tonnes (assuming that everything is disposed of by 2012).	PFOS represents about 0.04% of the used leather, and leather represents 20% of upholstery, i.e. PFOS represents 80 ppm in leather upholstered articles treated with PFOS	0 tonnes (assuming that everything is disposed of by 2012).

Articles	Amounts used in the EU	Lifetime	Amounts in articles in use in the EU in 2012	PFOS concentration in waste	PFOS amounts in waste in the EU in 2012
Other textiles, cardboard and paper	It is assumed that PFOS has been used for these but the volumes are not indicated.	Paper: 1 year Textile: 4 years	0 tonnes (assuming that everything is disposed of in 2012).	Not stated.	0 tonnes (assuming that everything is disposed of in 2012).
Fire extinguishing foam	About 18 tonnes/year until 2006. About 144 tonnes were accumulated in the EU in 2006.	15 years	0 tonnes (requirement that all stocks be destroyed as at 27 June 2011).	Typically 0.5-1.5% in the foam but there are also examples of concentrations up to 10%.	0 tonnes (requirement that all stocks be destroyed as at 27 June 2011).

Overall substance flow

The management of the relevant waste streams related to PFOS' specific occurrence is described in detail in the ESWI study (2011). The following figure shows the overall results of the PFOS mass flow analysis showing the situation in 2010.

"In Product" represents the existing stock of the substance in product in use. Due to limited data for a number of sectors and countries, the mass flow is partly based on assumptions and extrapolation. However, the mass flow provides an impression of the dynamics of the PFOS flow to the environment and to waste and on the relative contribution of major relevant sectors related to PFOS.

It is important to consider that fire fighting foams had to be destroyed by 27 June 2011 and do not currently significantly contribute to the PFOS substance flow.

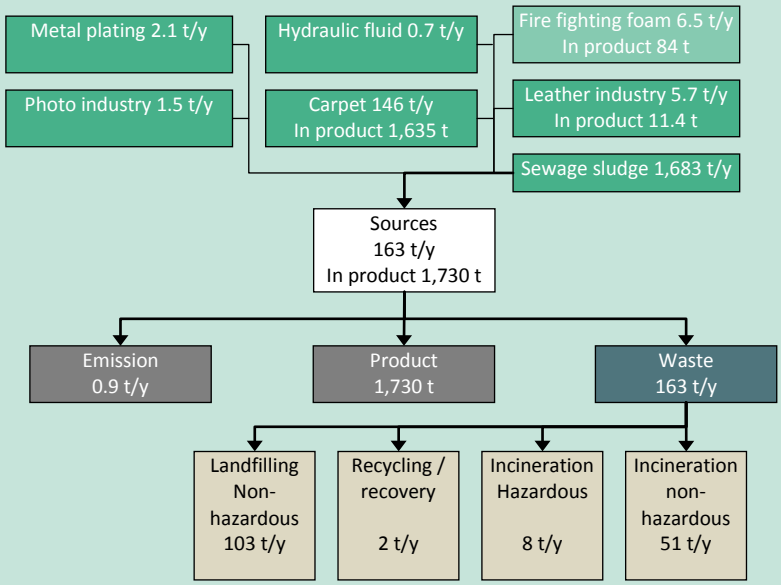


FIGURE 3
OVERALL MASS FLOW FROM PFOS FROM SOURCES TO CURRENT DISPOSAL/RECOVERY OPERATIONS IN THE EU (NOTE: THE FIGURE ILLUSTRATES THE SITUATION IN 2010. CURRENTLY (2012) FIRE FIGHTING FOAMS ARE NOT ANY MORE RELEVANT. IN ORDER TO GIVE AN ESTIMATE ON THE CURRENT SITUATION, THE FIGURES IN THE ILLUSTRATION CAN BE ADJUSTED AS FOLLOWS: FIRE FIGHTING FOAM = NOT RELEVANT, SOURCES = 157 T/Y, EMISSION = 0.42 T/Y, PRODUCT = 1646, WASTE = 157 T/Y, INCINERATION HAZARDOUS = 44,55 T/Y)

Contribution of the relevant sectors

Table 16 shows the contribution of the different sectors to the European PFOS flow to emissions, products and waste.

Considering the current situation (i.e. without fire fighting foams), the table shows that the overall discharge of PFOS from the investigated sources in Europe to the environment and to waste accounts for about 158 t/y. Almost all of the PFOS is discharged to waste (157 t/y), whereas only a small fraction (0.41 t/y) reaches the environment.

Emission to the environment from current processes (0.4 t/y) is dominated by metal plating (90%). Other relevant source sectors are the photo industry (7 %) and hydraulic fluids from aviation (4%). The leather and carpet sector do not contribute to PFOS emissions to the environment. Losses during their lifetime have not been considered due to the lack of data.

PFOS discharge to waste is dominated by waste resulting from the carpet industry (93 %), followed by the leather industry (4%), metal plating (1%), sewage sludge (1%), photo industry (1%) and hydraulic fluids for aviation (0.5%).

TABLE 16
CONTRIBUTION OF THE RELEVANT SECTORS IN THE EU 27 TO PFOS IN EMISSIONS, PRODUCTS AND WASTE (BASED ON ESWI, 2011)

Sector/Activity	Emission t/y	Product t/y	Waste t/y	Total t/y
Metal plating	0.37	0	2	2
Photo industry	0.03	0	1	1
Hydraulic fluid	0.02	0	1	2
Fire fighting foams (FFF) *1	0.45	84	6	91
Leather industry	0	11	5	17
Carpet industry	0	1,635	146	1,781
Sewage sludge	0	0	2	2
Total (including FFF) *1	0.87	1,730	163	1,895
Total (excluding FFF)	0.41	1,646	157	1,804

*1 The fire fighting foams should be disposed of by June 2011.

Sewage sludge

PFOS is concentrated in sewage sludge from waste water treatment. Emissions to the environment occur to water (PFOS which is not concentrated in sewage sludge) and to soil when the sewage sludge is used for agricultural purposes. About 5.3 million tonnes of sewage sludge with a content of approximately 770 kg of PFOS result in additional possible emissions to the environment. The substance flow of PFOS in sewage sludge at EU level is shown in the figure below.

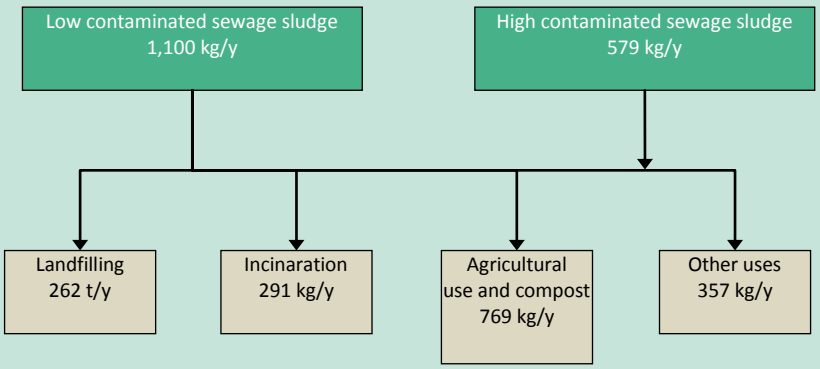


FIGURE 4
SUBSTANCE FLOW OF PFOS IN SEWAGE SLUDGE IN THE EU LEVEL (BASED ON ESWI,2011)

Waste incineration
As shown above, the majority of the PFOS-containing waste in the EU is disposed of to municipal waste incineration or landfilling. In Denmark, the majority is disposed of using incineration, as described in the following. Destruction of the PFOS by incineration is a key issue in relation to the disposal of PFOS-containing waste and is discussed separately in section 4.3.

4.1.2 Other PFCs in solid waste

Assessments of other PFCs in solid waste at EU level have not been identified.
The analysis of the risks arising from the industrial use of PFOA and APFO and from their use in consumer articles (RPS Advies, 2010) contains hardly any information on PFOA in waste and waste water. It is noted that the release from the use of PFOA in the semiconductor industry may give rise to 4 kg/y in emissions though waste water.

4.1.3 PFCs in waste water and sewage sludge

As part of the EU project "Perfluorinated organic compounds in the European environment" (PERFORCE), the presence of perfluorinated substances in influent, effluent and sewage sludge in six MWWTP in four EU Member States were analysed (de Voogt *et al.,* 2006). The report does not provide mean and median values for the results. The highest concentration in the dissolved phase of the influent was found for PFOS (10-200 ng/L), PFOA (20-65 ng/L), PFNA (8-45 ng/L) and FTS (15-300 ng/L). The particular phase of the influent contributed significantly to the overall concentration in the case of the carboxylic acids (53-95% of the total) but less for the sulfonates (15-48%) and for PFOSA (55%). The concentrations in the effluents were: PFOS (15-200 ng/L), C4-PFSAs (2-50 ng/L), C6-PFSAs (2-59 ng/L), PFHpA (4-18 ng/L), PFOA (20-111 ng/L), and PFNA (2-19 ng/L). The removal efficiencies in the MWWTPs for the PFSAs were found to be in the range of 0-47%, while for the PFCAs the efficiencies were higher, in the range of 20-80%. The PFCAs showed the following order (from higher to lower efficiency): C12>C9=C7>C8>C11>C10. For PFOSA, large differences between plants were observed with a mean value of 28% (de Voogt *et al.,* 2006).

In the sewage sludge PFOS and 6:2 FTS were the most abundant of the analysed PFASs, ranging from <d.l. to 110 µg/kg for PFOS and <d.l. to 110 µg/kg for FTS. The PFCAs concentrations were generally in the 0-25 µg/kg range with the following general order: C9>C8=C10>C11>C12>C14 (de Voogt *et al.,* 2006).

In a screening study supported by the Nordic Council of Ministers, sewage sludge samples from 15 MWWTPs in six Nordic countries were analysed for seven perfluoralkyl substances (Kallenborn *et*

al., 2004). The total of the seven substances ranged from 0.6 to 1.5 µg/kg dry weight. The predominant substances in the Danish sludge samples were PFOS, PFOA and PFNA, as shown in the map below. The map shows the median concentrations of the substances in the sludge from the six countries. As shown in the map, a high variability in sewage sludge composition was found across the various Nordic countries. PFOS and PFOA were the predominant perfluoroalkyl substances in sludge samples from all the countries apart from Finland, where PFHxA ranked second among the analysed PFAS.

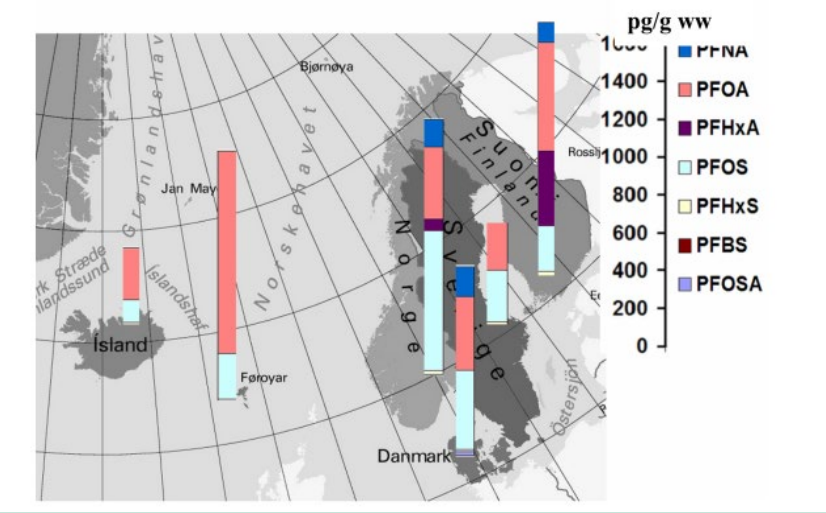


FIGURE 5
MEDIAN CONCENTRATION OF 7 PERFLUORALKYL SUBSTANCES IN SEWAGE SLUDGE FROM NORDIC COUNTRIES. (KALLENBORN *ET AL.*, 2004)

Sweden has a national monitoring programme of hazardous substances in sewage sludge which includes PFASs (Haglund and Olufson, 2010 as cited by Jensen *et al.,* 2012). In 2009, the average concentrations of PFOS and PFOA in sludge from eight different WWTP were 15.9 (1.6-37.4) and 4.9 (0.8723.9) µg/kg dry weight, respectively. Generally, the concentrations have been stable over the last five years, but with a small tendency to a decline.

Compared to the data from the Nordic countries, significantly higher concentrations of PFOS have been reported from the USA and Germany. In Germany, the mean concentration of PFOS in 61 waste water treatment plants in 2008 was reported to be 271 µg/kg (range 14 – 2,615 µg/kg) (UBW, 2009 as cited by Jensen *et al.,* 2012).

4.2 Denmark

4.2.1 PFOS and other PFASs in solid waste

If the use of PFOS in Denmark corresponds to the use in a number of EU countries up to 2016, on the order of 1-2 tonnes of PFOS will be disposed of annually in carpets, with an average concentration of around 75 mg PFOS/kg. Similarly, it is assessed that there may be smaller quantities of PFOS that will be disposed of with leather furniture, containing an average concentration of around 80 mg PFOS/kg (Danish EPA, 2012).

Considering the use of PFCs in Denmark in 2007, it must be expected that the majority of PFCs in solid waste would be in discarded carpets and impregnated clothing with a total quantity in the 10-30 t/y range; of this, the majority would be present as various side-chain fluorinated polymers.

There is no selective waste collection of articles containing PFOS or other PFCs. In Denmark today, carpets, textiles, upholstered furniture, packaging and other articles that may be surface-treated with PFOS and other PFCs, are disposed of via waste incineration with energy recovery. The main question in this respect is the fate of the incinerated substances, as discussed in section 4.3.

In a letter of 16 May 2011, the Danish EPA informed the Danish Emergency Management Agency, the safety industry and the largest dealers of fire extinguishing foam that PFOS, after 27 June 2011, must no longer be found in fire extinguishing foam. This information was to be further communicated to customers and collaboration partners alongside the requirement that the municipality must classify waste and provide instructions as to where to dispose of the waste (Danish EPA, 2012). Many users, however, disposed of the foams years ago. For example, in 2005 all fire extinguishing foam containing PFOS from DONG's offshore installations in Denmark were destroyed (Danish EPA, 2012).

In the context of the NOVANA programme, in 2004-2005 leachate from two landfills was analysed for PFOS and a number of perfluorinated substances (Strand *et al.,* 2007). PFOS was found in a concentration of 3.8 ng/L in a single sample of leachate from Stige landfill. In all other samples, the concentration of all of the substances was below the detection level of 0.2 to 2.2 ng/L, depending on the substance.

For comparison, in a German study, samples of untreated and treated leachate from 22 landfill sites in Germany were analysed for 43 PFCs (Buch *et al.,* 2010). ∑PFC concentrations ranged from 31 to 12,819 ng/L in untreated leachate and 4–8,060 ng/L in treated leachate. The dominating compounds in untreated leachate were perfluorobutanoic acid (PFBA) (mean contribution 27%) and perfluorobutane sulfonate (PFBS) (24%). The discharge of PFCs into the aqueous environment depended on the cleaning treatment systems. The mass flows of ∑PFCs into the aqueous environment from the landfills ranged between 0.08 and 956 mg/day.

4.2.2 Recycling

Recycling of waste containing PFOS is prohibited. Waste containing PFCs is generally not recycled in Denmark.

4.2.3 Waste water and sewage sludge

A study of seven PFASs in the influent, effluent and sludge from Danish waste water treatment plant was carried out as part of the NOVANA programme (Strand *et al.,* 2007). The same data are published in English by Bossi *et al. (*2008).

Measurements were carried out at nine MWWTP and in three industrial waste water treatment plants. In the influent of the MWWTPs the highest median concentrations were found for PFOA (14.7 ng/L), PFHxA (7.4 ng/L), PFOS (3.4 ng/L) and PFNA (2.5 ng/L). The highest concentrations in effluents were found for PFOA (13.4 ng/L), and PFOS (4.5 ng/L). The concentrations of PFOS and PFOA in the effluents were of approximately the same concentration in the influent.

PFOS was found in the sewage sludge from all 9 MWWTPs, in concentrations ranging from 4.8-74.1 µg/kg dry matter and with a median concentration of 8.6 µg/kg dry matter. The concentration of PFOS in the sludge was considerably higher than the concentration of other fluorinated substances. It was also about 10 times higher than the concentrations reported from the Nordic study described in section 4.1.3 (Kallenborn *et al.,* 2004).

Of the other substances, the highest concentrations were found for PFUnA (3.3 µg/kg d.m., mistakenly not indicated on the figures), PFHxS (1.8 µg/kg d.m.) and FPOA (1.0 µg/kg d.m.).

A risk evaluation of perfluorinated compounds and four other groups of persistent organic contaminants in sewage sludge has recently been published (Jensen *et al.,* 2012). For the risk evaluation Jensen *et al. (*2012) used the highest concentration of PFOS and PFOA found in sewage sludge from Danish MWWTPs. According to the study, a comparison of the lowest test concentration, where no significant effects were observed, and the predicted concentrations in soils after sewage sludge amendment, reveals a margin of safety which is on the borderline of what would be accepted according to the risk assessment procedure outlined in REACH. On this basis it is concluded that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystem and that more information on the fate and effects of PFCs is needed (Jensen *et al.,* 2012). The study notes that the restrictions in the use of PFOS in Denmark and the EU are likely to result in concentration in sewage sludge in the future.

4.3 Destruction of PFASs by waste incineration

The majority of PFOS and other PFASs used in consumer products will ultimately end up in municipal waste incinerators in Denmark. Because of the very strong C-F binding, the perfluoroalkyl chain is extremely resistant to heat and the fate of the PFOS and other PFASs by the incineration is one of the main issues concerning the management of the substances in the waste stream.

According to the Stockholm Convention on persistent organic pollutants (POPs), PFOS and other POPs should be disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of POPs, or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option (SC, 2009).

The updated draft European Community implementation plan for the Stockholm Convention (EC 2012) states that full scale tests with assessment of destruction efficiency and degradation products have not been published for municipal solid waste incinerators and sewage sludge incinerators. Comparable information from municipal waste incinerators and sewage sludge incinerators should be gathered for an assessment of the appropriateness of destroying PFOS in incinerators operating at conditions according to Directive 2000/76/EC but below 1,100°C.

The available literature about the subject is briefly reviewed below.

The 2008 survey of PFASs in Denmark (Jensen *et al.,* 2008) discuss the results of Yamada *et al. (*2005) who investigated the thermal degradation of a small polyester/cellulose fabric substrate treated with a fluorotelomer-based acrylic polymer under laboratory conditions. The conditions conservatively represented typical combustion conditions of time, temperature, and excess air level in a municipal incinerator, with an average temperature of at least 1000˚C and two second residence time. The fabric was destroyed by this treatment and no PFOA was detected, only SiF_4. Yamada *et al. (*2005) concluded that under typical municipal waste incineration conditions no significant quantity of PFOA would be formed from the incineration of a textile or paper substrate treated with a fluorotelomer based acrylic polymer, even without consideration of post-combustion pollution control equipment for acid gas scrubbing in place at municipal incinerators. This conclusion is questioned by Poulsen *et al. (*2008) who underline the fact that actual waste incineration is performed on a larger scale and is inhomogeneous and less controlled.

In a German study, the PFOS content of contaminated sludge which was incinerated in a sewage sludge incinerator at conditions in accordance with Directive 2000/76/EC was largely destroyed i.e. measured at below the detection limit of 15 ng/m³ in the exhaust air and below detection limits of all other output fractions (<10 µg/kg dry matter for solid residues and <25 ng/L for water discharges) (NRW, 2007). The incinerator was operating at a temperature up to 900°C and the following technical conditions: Above the fluidized bed, secondary air was fed to the process in order to en-

sure the burn-off of exhaust gas with an O_2 content of at least 6%. On the way to the exit of the afterburning chamber, the off-gas reaches a temperature of at least 850°C for at least 2 seconds.

A US laboratory-scale incineration study of PFOS and C8 perfluoro sulfonamides determined that a properly operating full-scale (high temperature) incineration system can adequately dispose of PFOS and C8 perfluorosulfonamides (UDRI, 2003). The study also indicated that incineration of these substances was not likely to be a significant source of PFOS into the environment. The C-S bond was completely destroyed, indicating that transformation of any combustion products to form PFOS was also highly unlikely.

A Norwegian study investigated emissions from incineration of fluoropolymers in municipal waste (Otterlei et al, 2011). The objective of the study was to investigate to what extent fluorine-containing gases, which are strong greenhouse gas contributors, may be formed and emitted from Norwegian waste incineration plants incinerating fluoropolymers. The study did not address incineration of PFCs.

A Swiss substance flow analysis for PFOS and PFOA from 2009 reviewed the existing literature with the aim of establishing the destruction efficiency of PFOS by waste incineration (Buser and Morf, 2009). Apart from the literature mentioned above, the study quotes research on the efficiency of destruction of perfluorinated substances in carpets (Lemieux *et al.,* 2007). In this study the content of perfluorinated substances in the stack from a pilot-scale rotary kiln incinerator simulator to qualitatively and, where applicable, quantitatively assess the potential for emissions of fluorinated compounds from combustion devices was measured. The concentration was below 1 µg/m^3 in the stack, and the concentrations were relatively independent of kiln feed. According to Lemieux *et al. (*2007) the results indicated that the perfluorinated substances were effectively destroyed even under mild combustion conditions and that the trace levels that were found were due either to trace contamination of the sampling duct with fluorinated compounds due to historical use of Teflon and other fluoropolymers, or sampling artefacts. The Swiss substance flow analysis concludes on the basis of the review that the available information in the literature was not sufficient for establishing a destruction efficiency coefficient.

In summary, a few studies show that PFOS is effectively destroyed at 1,100˚C (comparable to high-temperature hazardous waste incineration), and the studies available suggest that this may also be the case at a temperature of 850˚C. On the other hand, there are no studies which document clearly that destruction is complete at 850˚C.

4.4 Summary on waste management

The waste situation for PFOS is well described on both the EU-level and in Denmark. The majority of the solid waste containing PFOS and other PFCs in Denmark is disposed of to municipal solid waste incinerators, and the main issue is to what extent the substances are destroyed at the temperatures used in municipal solid waste incinerators. Limited data are available on the destruction efficiency under the actual conditions in the incinerators, and more studies are necessary to clarify whether it would be necessary to dispose of PFOS-containing waste to hazardous waste incinerators in order to comply with the requirements of the Stockholm Convention.

PFOS and PFOA are the main substances among the analysed PFCs in effluents from municipal waste water treatment plants, but PFNA, PFDA and PFHxS are found in measureable concentrations as well. The removal efficiencies in the waste water treatment plants are relatively low and, in measurements in Danish plants, the effluent concentration of PFOS and PFOA were comparable to the influent concentration. PFOS is the predominant substance in the sewage sludge. For PFOA the data are more variable. Measurements from Danish plants showed relatively low concentrations of PFOA in the sludge, but in another study with data from all Nordic countries, PFOA was the main

substance in the sludge. Both PFHxA and PFDA are present in the sludge in measureable concentrations.

Data on sources of the substances'emissions to waste water are scarce and more information on sources and levels of other PFASs than PFOA and PFOS would be of advantage.

A Danish risk evaluation of perfluorinated compounds in sewage sludge concludes that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems and that more information on the fate and effects of PFCs is needed. It should, however, be noted that the concention of PFOS may already have descreased significantly as a consequence of the current regulation and the fact that PFOS-containing articles in service are gradually being disposed of.

5. Environmental effects and fate

PFOA, PFOS and other long-chain perfluorinated chemicals are found world-wide in environmental compartments, in biota and in humans. These chemicals are all highly persistent in the environment due to the inherent high strength of the C-F covalent bond and they show bioaccumulative properties in higher animal life, including humans. Therefore, there is a growing concern that in the long term they may have significant adverse effects at population level in wildlife as well as in human populations (US EPA, 2009).

PFOS, PFOA and related substances being present globally in the environment today may originate from different sources:

- Emission from the manufacture of the substance or industrial processes where the substance is used as an intermediate, as a raw material or a process aid for the manufacturing of fluoropolymers;
- Emission from industrial processes where the substances are used for formulation of mixtures, or mixtures including the substances are used for processing articles;
- From the use and disposal mixtures and articles that intentionally include the substances;
- From use and disposal of mixtures and articles that may contain them as an impurity, and
- From the abiotic or biotic degradation of derivatives or larger functional derivatives and polymers that contain a perfluoroalkyl moiety and degrade in the environment to form the substances.

5.1.1 PFOS and other perfluoroalkyl sulfonates

Fate in the environment

Abiotic degradation

PFOS does not undergo hydrolysis; in a study conducted at 50 °C to enhance possible transformation processes, no indications of reaction were observed. The half-life of PFOS was set to be greater than 41 years (UNEP, 2006). Likewise, there was no evidence of direct or indirect photolysis in a US EPA guideline study, in which the indirect photolytic half-life in water at 25 °C was calculated to be more than 3.7 years (UNEP, 2006).

In 3M studies, the PFOS-related substances N-EtFOSE and N-MeFOSE were found to have hydrolytic half-lives of 35 and 99 days respectively at neutral pH. However, there are also reports of much longer half-lives; 6.3 years for N-MeFOSE and 7.3 years for N-EtFOSE. No photolysis occurred in the studies (Brooke *et al.,* 2004).

Regarding atmospheric degradation there are no experimental data, but the AOP program estimates a rate constant leading to an estimated half-life of 114 days, indicating that degradation in the atmosphere is not likely to be significant. The volatility of PFOS is low (Environment Agency, 2004).

The substance N-EtFOSE is calculated to be more reactive in the atmosphere with an estimated half-life of 16 hours; however, it probably only results in formation of the PFOS backbone (Brooke *et al.,* 2004).

Biodegradation
Brooke *et al. (*2004) refers to previous assessments by OECD (2002) and 3M (2003) both concluding that PFOS is not biodegradable either under aerobic or under anaerobic conditions. Only a MITI-test showed a small (3 %) removal of the parent compound, while in no other tests wasany degradation was observed. There appears to be no degradation in soil either.

N-EtFOSE and N-MeFOSE are believed to undergo primary degradation in sewage sludge, likely leading to the formation of PFOS and PFOA. The rate of biodegradation is not indicated (Brooke *et al.,* 2004).

Adsorption and distribution
According to Jensen *et al. (*2012), PFOS adsorbs to soil, sediment and sludge with distribution coefficients (K_d) ranging from 9.7 L/kg to 35 L/kg and not desorbing readily, once adsorbed to these matrices. The average K_d for three soils was 26.9 L/kg.

EUSES 2-Modeling of the environmental distribution of PFOS gave the result shown in the following table.

TABLE 17
ENVIRONMENTAL DISTRIBUTION OF PFOS BY EUSES MODELLING (BROOKE *ET AL.,* 2004)

Compartment	Release to		
	Air	Water	Agricultural soil
Freshwater	0.38%	83.18%	0.26%
Seawater	0.04%	9.06%	0.03%
Air	<0.01%	<0.01%	<0.01%
Soil (combined)	99.55%	3.42%	99.7%
Freshwater sediment	0.02%	4.20%	0.01%
Marine sediment	<0.01%	0.14%	<0.01%

Therefore, once released to the aquatic environment, PFOS will stay in the water compartment while soil is the sink for releases to air and soil.

Bioconcentration
Because PFOS is both hydrophobic and lipophobic it does not follow the typical pattern of partitioning into fatty tissues followed by accumulation, the typical pattern of many persistent organic pollutants. Instead, it binds to proteins in the plasma and, as a result, is present in highly perfused tissues such as the liver and kidneys rather than lipid tissue. Therefore, the mechanism of bioaccumulation likely differs from most other bioaccumulative chemicals (UNEP, 2006).

UNEP (2006) uses references from studies with fish BCFs in the range 2,800-3,100, i.e. below the "standard" Stockholm Convention criteria for bioaccumulation. However, monitoring data from top predators at various locations show highly elevated levels of PFOS and demonstrate the substantial bioaccumulation and biomagnification (BMF) properties of PFOS. Notable is that the PFOS concentrations in polar bears (1,700-2,000 ng/g) exceed all other individual organohalogens. A BMF >160 has been estimated based on concentrations in Arctic seals. BMFs of 10-20 relative to prey items have been calculated for the bald eagle. The levels of PFOS in biota have been shown to be increasing since the 1970s, e.g. in a retrospective Swedish study on guillemot eggs where the level was about 100 ng/g in 1975 and about 600 ng/g in 2005 (UNEP, 2006).

The bioaccumulation potential of PFOS and other PFASs in the soil environment has been shown to be significantly lower than in the marine environment. A BSAF (biota-to-soil accumulation factor) of up to 4.7 was found for earthworms (*Eisenia fetida*), while accumulation in plants was lower (Jensen *et al.,* 2012).

Environmental effects

Ecotoxicity data for PFOS are mainly found for aquatic organisms such as fish, invertebrates and algae, and for birds. The acute toxicity (LC_{50}) of PFOS to a number of freshwater and saltwater fish species were found to be in the range 4.7-133 mg/L with *Pimephales promelas* being the most sensitive species in the review by Brooke *et al. (*2004). The lowest long-term (42 days) NOEC was 0.30 mg/L, also for *P. promelas.*

According to Brooke *et al. (*2004), the acute toxicity (EC/LC_{50}) to aquatic invertebrates is in the range of 2.66-223 mg/L *(D. magna* most sensitive) and a lowest long-term (21 days) NOEC = 0.25 mg/L for the mysid shrimp *Mysidopsis bahia*.

A 10-day NOEC = 0.049 mg/L has been reported for the aquatic midge *Chironomus tentans* (UNEP, 2006). The authors consider chironomids to be 2-3 times more sensitive to PFOS than other aquatic organisms probably due to an interaction with haemoglobin, which is unique to this group of organisms. The lowest toxicity values for algae are for the green alga *P. subcapitat,* with a 96-hour IC_{50} = 48.2 mg/L and NOEC = 5.3 mg/L (UNEP, 2006).

The most sensitive endpoints for different groups of aquatic organisms are summarized in the table below. The harmonised classification is Aquatic Chronic 2 with the hazard statement H411: "Toxic to aquatic life with long lasting effects".

TABLE 18
OVERVIEW OF AQUATIC TOXICITY OF PFOS (MOST SENSITIVE ENDPOINTS) (BROOKE *ET AL.,* 2004)

Acute	Fish	Fathead minnow (Pimephales promelas) (96-h): LC_{50} = 4.7 mg/L Rainbow trout (Oncorhynchus mykiss - saltwater) (96-h): LC_{50} = 13.7 mg/L
	Invertebrates	Daphnia magna (48-h): EC_{50} = 27 mg/L Mysid shrimp (Mysidopsis bahia - saltwater) (96-h): LC_{50} = 3.6 mg/L
	Algae	Selenastrum capricornutum (96-h): EC_{50} = 126 mg/L Skeletonema costatum (saltwater) (96-h): EC_{50} > 3.2 mg/L
Long-term	Fish	Fathead minnow (Pimephales promelas) (42-day): $NOEC_{survival}$ = 0.3 mg/L
	Invertebrates	Daphnia magna (28-day): $NOEC_{reproduction}$ = 7 mg/L Mysid shrimp (Mysidopsis bahia - saltwater) (35-day): $NOEC_{reproduction}$ = 0.25 mg/L
	Algae	Selenastrum capricornutum (96-h): NOEC=44 mg/L Skeletonema costalum (saltwater) (96-h): NOEC>3.2 mg/L Duckweed (Lemna gibba) (7-day): NOEC = 15.1 mg/L

Mallard duck and bobwhite quail were exposed to PFOS in a 21 week study (UNEP, 2006). At a dose of 10 mg/kg diet PFOS, effects in male mallards included reduced testes size and decreased spermatogenesis. For quails, at the same dose level, minor effects were observed in adults including increase in liver weight and in incidence of small testes size, and a reduction in survivability in quail chicks.

Doses of 4.5 mg/kg bw/day were lethal to Rhesus monkeys over a seven week exposure period. Sub-lethal and biochemical effects observed in rats exposed to PFOS were considered to show that PFOS can affect the neuro-endocrine system in rats (UNEP, 2006; Brooke *et al.,* 2004).

A 14 -day LC_{50} = 373 mg/kg soil dw and corresponding NOEC = 77 mg/kg soil dw have been reported for earthworms (Brooke *et al.,* 2004).

The POP Review Committee under the Stockholm Convention considers PFOS to meet all the POP criteria (persistence, bioaccumulation, long-range transport potential and toxicity) (UNEP, 2006).

5.1.2 PFOA and other perfluoroalkyl carboxylic acids

Fate in the environment
The fate properties of PFOA are similar to those of PFOS. Once in the environment, PFOA is extremely persistent and not known to undergo significant further abiotic or biotic degradation under relevant environmental conditions.

PFOA is highly soluble in water (3.5 g/L) and predominantly present as an anion in solution under environmental conditions (pKa = 2.5). It has a relatively low vapour pressure (2.2 Pa), and therefore the aquatic environment is expected to be the primary sink with some additional partitioning to sediment. The presence in PFOA in the Arctic environment is most likely attributable to long range transport via ocean currents and/or of volatile precursors via the atmosphere (Environment Canada, 2012b).

There is experimental evidence indicating that PFOA is not highly bioccumulative in fish. Reported BCFs for fish species range from 3.1-27. However, fish may not be the most relevant group of organisms to consider (Vierke *et al.,* 2012) and the results cannot be extrapolated to non-aquatic species since gills provide a mode of elimination that air-breathing animals do not possess. Monitoring studies and field studies indicate that biomagnification in various terrestrial and marine mammals occur (prey: predator BMFs from 0.03 to 31 have been reported). The polar bear in particular appears to accumulate PFOA and related substances, ringed seal:polar bear BMFs of 45-125 have been reported (Environment Canada, 2012b) and PFOA concentrations in polar bear as high as 3.4 mg/g with an increasing trend from 1990 to 2006 (Vierke *et al.,* 2012).

Precursors
Exposure to PFOA can be due to releases of PFOA itself, but there also exist a considerable number of precursors which can lead to PFOA exposure in the environment. Environment Canada (2012) defines precursors as substances where the perfluorinated alkyl moiety has the formula C_nF_{2n+1} (where n=7 or 8) and is directly bonded to any chemical moiety other than a halogen atom. Potential precursors include e.g. fluorotelomer alcohols (FTOHs), fluorotelomer iodides and fluorotelomer olefins. A total of 27 PFOA precursors have been listed by Environment Canada.

The precursors listed by Environment Canada have been evaluated by Nielsen (2012), who, based on their physico-chemical properties, found that seven of the 27 precursors listed were actually not PFOA precursors, while another two could only partially be considered PFOA precursors.

Environmental effects
PFOA exhibits moderate to low toxicity in traditional acute studies with aquatic species such as fish (LC_{50} ranging from 70-2470 mg/L) and in general PFOS appears to be about 10 times more toxic to aquatic organisms than PFOA (Jensen *et al.,* 2012). The most sensitive pelagic organism reported is the freshwater green alga *Pseudokirchneriella subcapitata* for which a 96-hour NOEC = 2.0 mg/L was calculated, while for *Daphnia magna* the lowest EC_{50} reported was 34 mg/L. The 10-day NOEC to the benthic organism *Chironomus tentans* was found to be 100 mg/L (Environment Canada, 2102).

There are studies in aquatic organisms showing potential of PFOA to affect endocrine function, e.g. in rare minnows at PFOA concentrations of 3-30 mg/L, thyroid hormone biosynthesis genes were

inhibited, vitellogenin expression was induced in males, oocytes developed in the testes of male fish and caused ovary degeneration in females. Other studies show hepatotoxicity, immunotoxicity and chemosensitivity in other different organisms such as mussels, seals, dolphins, turtles and rats (Environment Canada, 2012b).

The toxicity of PFOA to reproduction of earthworms was studied and a NOEC = 80 mg/kg soil was determined. PFOA is less toxic to earthworms than PFOS (Jensen *et al.,* 2012).

One study is available where the toxicity of PFOA and its salts to avian wildlife was tested. PFOA was found not to have an effect on embryonic pipping success for white leghorn chickens at concentrations up to 10 µg/g of embryos but to bioaccumulate 2.9-4.5 times in the liver of the embryos (Environment Canada, 2012b).

Precursors
No relevant data on the ecotoxicity of the precursors of PFOA were identified.

5.1.3 Other PFASs and side-chain-fluorinated polymers

Fate in the environment
Long-chain PFCAs
Recently, Annex XV dossiers have been prepared for four long-chain perfluoroalkyl carboxylic acids; henicosafluoroundecanoic acid, tricosafluorododecanoic acid, pentacosafluorotridecanoic acid and heptacosafluorotetradecanoic acid (ECHA, 2012a, b, c, d). Only very few experimental studies on the fate of the four substances are available and the assessment therefore to a large extent builds on the read-across approach and use of data from other PFCAs such as PFOA. For all four substances it is concluded in the dossiers (ECHA 2012a, b, c, d) that they fulfil the vP as well as the vB criterion and thus are to be regarded as vPvB-substances according to Article 57 e) of REACH.

A number of C14-C15 PFCAs have been found to bioaccumulate as they are present ubiquitously in fish, invertebrates and top predators (e.g. seals and polar bears) even in Arctic regions far away from any sources (US EPA, 2009).

Short-chain PFCAs and PFSAs
Due to the increasing concern about the persistence and bioaccumulation of PFOS, PFOA and other long-chain perfluorinated alkyl carboxylic acid and alkyl sulfonic acids, a number of shorter chain alternatives, notably butane-based products (e.g. PFBS), have been introduced. These substances have been shown not to bioaccumulate due to rapid elimination in multiple organisms tested. However, as a result of this conversion, increasing levels of e.g. PFBS in surface waters have been observed (Buck *et al.,* 2011). This indicates that the alternatives are also significantly persistent in the environment.

Modelling exercises indicate that the BCFs of C4-PFSas and C4-PFCAs are about 3 orders of magnitude lower than the corresponding C8-chain compounds (PFOS and PFOA) (Rayne *et al.,* 2009).

Fluorotelomers
Buck *et al. (*2011) provides the following description of the transformation and degradation of fluorotelomer alcohols (FTOH) to e.g PFOA: "*The aerobic biodegradation and metabolic degradation pathways for fluorotelomer alcohols have been well studied. The pathways and yields of transformation products depend on the matrix in which the environmental microbial degradation or metabolism takes place and the length of the perfluoroalkyl chain in the fluorotelomer alcohol. Ultimately the fluorotelomers will be degraded to stable transformation products, including PFCAs. A n:2 fluorotelomer alcohol (n:2 FTOH) may ultimately be degraded to perfluoroalkyl acids with n or less than n atoms. As an example the 8:2 FTOH may ultimately be degraded to*

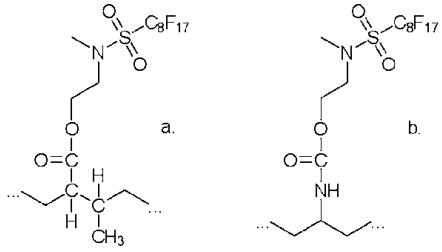
PFOA (perfluoreoctanoate), PFHxA (perfluorohexanoate) or PFhpA (perfluoroheptanoate), but also other degradation products are formed."

Parsons *et al. (*2008) refers to results of biodegradation studies conducted with 8:2 FTOH in diluted sewage sludge from a domestic WWTP and conclude that the results demonstrate that perfluorinated carbon atoms in 8:2 FTOH are indeed defluorinated and the products are degraded by microorganisms from WWTPs to form shorter chain products.

Frömel & Knepper (2010) studied the biodegradation of fluorotelomer ethoxylates (FTEO) and found that they were de-ethoxylated relatively rapidly down to seven intact ethoxy units at which level further degradation virtually ceased (no degradation observed in 48 days).

Aqueous phase photo-oxidation of $CF_3(CF_2)_6CH_2OH$ will result in the formation of PFOA. Gas phase photo-oxidation will lead to the formation of $CF_3(CF_2)_6CHO$ and subsequently in part to formation of PFOA (Wallington *et al.,* 2006 as cited by Nielsen, 2012).

(X)



Conceptual representation of example copolymers:
a. ester-linked NMeFOSE methacrylate
b. urethane-linked NMeFOSE

Most recently, Russell *et al. (*2010, as cited by Martin *et al.,* 2010) investigated degradation of a fluorotelomer urethane polymer and observed an average half life of 102 years (range 28–241 years). PreFOS based urethanes (e.g.Xb.) are also known to have been incorporated into 3M's ScotchGard line of products, and thus it is reasonable to speculate that these also may yield free PreFOS, and ultimately PFOS, via similar pathways. The important unknowns are the overall emission of such copolymers to the environment, and the rate of degradation, which needs to be assessed experimentally (Martin *et al.,* 2010).

Results from analyses of PFASs in polar bears indicate that fluorotelomers also contribute to the total bioaccumulation of per- and polyfluorinated compounds in these animals because perfluorononaic acid (PFNA) was almost only found in its linear form while both linear and branched isomers were observed for PFOA (Ellis *et al.,* 2004).

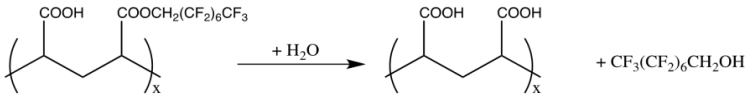
Smog chamber experiments have shown that FTOHs can degrade in the atmosphere by OH-initiated oxidation pathways, with the intermediates FTCAs and FTUCAs, to PFCAs. A half-life of approx. 20 days for the FTOHs was estimated (Ahrens, 2010).

Side-chain fluorinated polymers

By degradation of side-chain fluorinated polymers, the side chains may be released from the polymer chain to become PFASs. The PFASs formed will depend on the type and length of the side chains.

The principle is shown below, exemplified with the degradation of the side-chain-fluorinated polymer 2-propenoic acid, 2-methyl-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl ester (CAS No 53515-73-4) (Nielsen, 2012). This co-polymer contains ester side-chains $>C\text{-}C(O)OCH_2(CF_2)_6CF_3$ and may in principle undergo hydrolysis to give 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-

octanol (CAS No 307-30-2). Gas phase photo-oxidation will lead to $CF_3(CF_2)_6CHO$ and subsequently in part to PFOA.



Source: Nielsen, 2012

Environmental effects

Very little information is available about the environmental effects of PFASs other than the perfluorinated alkyl carboxylic acids and the perfluorinated alkyl sulfonic acids. Overall, these substances are not regarded to be as toxic as PFOS and PFOA.

Long-chain PFCAs

Environment Canada has made an ecological screening assessment of long-chain PFCAs, i.e. C9-C20 PFCAs, and their salts and precursors (Environment Canada, 2012b). They find that in standard toxicity studies with long-chain PFCAs, the acute toxicity of this group of substances was low to moderate with acute EC/LC_{50} values ranging from 8.8 to 285 mg/L. Two terrestrial studies on long-chain PFCAs exist: In one study with chickens, no adverse effects were observed up to 1.0 mg/kg bw dosed three times/week for three weeks with C10 PFCA. In another study with a soil-dwelling nematode, the acute LC_{50} was 306 mg/L while multi-generation effects (decreased fecundity) was observed at 0.000464 mg/L, i.e. a much lower level than the acute effect level.

Various biochemical responses to long-chain PFCAs, including vitellogenin induction, oxidative stress and chemical sensitization, have also been observed in a number of species such as marine mussels, rainbow trout and Baikal seals (Environment Canada, 2012b).

Short-chain PFCAs and PFSAs

No data on the ecotoxicity of the shorter chain fluorinated carboxylic and sulfonic acids have been identified.

5.2 Summary of environmental effects and fate

PFOS, PFOA and other long-chain perfluorinated carboxylic and sulfonic acids and their salts, and the longer chain homologues, are all extremely persistent in the environment (abiotically and biotically) and they bioaccumulate in particular in mammals and birds, despite not fulfilling the traditional bioaccumulation criteria based on bioconcentration in fish. They are not very toxic to aquatic and other organisms based on standard toxicity endpoints, but there are indications that they have certain endocrine disrupting properties. Annex XV concluded that they fulfill the vPvB cirteria.

Precursors like FTOHs may undergo some initial transformation and degradation but eventually result in formation of the corresponding carboxylic or sulfonic acid compounds.

Some shorter chain (e.g. butane-based) alternatives also appear to be persistent but not to bioaccumulate to the same extent, as they are excreted rapidly from the organisms studied.

No data on the ecotoxicity of the shorter chain fluorinated carboxylic and sulfonic acids have been identified.

6. Human health effects

There are more than 600 preregistered polyfluorinated chemicals (PFC) in REACH but most of these substances are chemical intermediates, and the general population seems only to be directly exposed to a few of them, and analytical chemistry methods only exist for the most important perfluoroalkylated substances (PFAS), such as perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) and for polyfluorinated substances, such as fluorotelomer alcohols (FTOH) and some metabolites.

Most detailed studies of toxic and adverse health effects are done for PFOS and PFOA, although more and more data for fluorotelomers and shorter chain homologues are published. For the less investigated polyfluorinated chemicals, preliminary properties may be estimated from structure and homologues.

In population studies several perfluoroalkylated acids (PFAAs) are normally measured/monitored in blood and tissues, and the sum of all or of the most abundant (PFOS and PFOA) are used for studying associations.

Although the perfluoroalkane sulfonic acids and the perfluoroalkyl carboxylic acids (PFCAs) are closely related structurally, these chemicals elicit different biological responses *in vitro* and *in vivo*. The acute lethal toxicities of PFOS and PFOA correspond to a classification as Acute tox 3 or 4. PFOS is more toxic than PFOA, and the toxicity of PFAAs increases generally with the length of the alkyl chain.

6.1 Introduction to human health effects of PFOS and other polyfluorinated substances

Uptake, distribution and elimination

It is known from animal studies that perfluoroalkylated substances (PFASs), such as PFOS and PFOA, are well absorbed orally but poorly eliminated; they are not metabolised, and undergo extensive uptake from enterohepatic circulation (Lau *et al.,* 2004; 2007). Inhaled PFOA is also easily absorbed in rodents and may also be absorbed through the skin (Hinderliter *et al.,* 2006). The oral uptake of perfluorohexanoate (PFHxA) in rats and mice was also rapid and complete (Gannon et al. 2011).

An oral dose of 8:2 FTOH was readily absorbed in rats but the skin absorption was negligible (Fasano *et al.,* 2006).

Perfluoroalkylated substances (PFASs) such as PFOS and PFOA have, contrary to most other persistent organic pollutants (POPs,) a low affinity to lipids but bind to proteins. PFASs are associated with cell membrane surfaces and accumulate in various body tissues of exposed organisms with especially high concentrations in the blood, liver, kidneys and spleen, but also in the testes and brain. The accumulation in fats and muscles is minimal.

In the blood PFASs are bound to plasma/serum proteins (Bischel *et al.,* 2010). Regarding PFOA, more than 90% is bound to serum albumin in both rodents and humans (Han *et al.,* 2003). PFOS

binds to serum albumin at a ratio of 2:1 (Luo *et al.,* 2012) and displaces hormones from sex-hormone binding and corticosteroid-binding globulins (Jones *et al.,* 2003).

Both in animals and humans these chemicals cross the placenta and are excreted in the milk. In rats, levels of PFOA in the blood of the foetus were about half of the maternal levels. The levels of PFOA in the maternal blood were about 10 times higher than in their milk, and milk levels were comparable with plasma levels in the pups (Hinderliter *et al.,* 2005).

Regarding PFCAs with fluoroalkyl chain length (C7 - C10), the longer the chain, the more of the compound was accumulated in the liver of male rats (Kudo *et al.,* 2001).

In the tissues, PFAS have affinity for binding to β-lipoproteins and the liver fatty acid-binding protein (L-FABP) which can contribute to the toxicities of these chemicals (Luebker *et al.,* 2002). The binding of PFOA to this protein has an affinity of an order of magnitude less than the natural ligand, oleic acid, and has at least 3:1 PFOA: L-FABP stoichiometry (Woodcroft at al. 2010).

The mean blood elimination half-lives for PFASs depend on the chemical and animal species and sex. The blood half-lives of PFASs:

- are longer for sulfonates than for carboxylates,
- are shorter for branched isomers,
- are often shorter in females mainly due to the difference in renal clearance (and hormones),
- increase with chain length for carboxylates,
- in rodents were hours or a few days,
- in monkeys were a little longer, and
- in humans blood half-lives were measured in years.

In retired fluorochemical workers, half-lives were 5.4 years for PFOS (av. 800 ng/mL), 8.5 years for PFHxS (perfluorohexane sulfonate) (av. 290 ng/mL), and 3.8 years for PFOA (av. 690 ng/mL) (Olsen *et al.,* 2007). Later studies have reported half-lives of about 1 month for PFBS (perfluorobutane sulfonate) and 2-4 days for PFBA (perfluorobutanoic acid) (Olsen *et al.,* 2009; 2011; Chang *et al.,* 2009).

In a study of populations in USA being exposed to PFOA via drinking water polluted by an industrial facility, serum half-lives were determined at 2.9 and 8.5 years for water districts with higher and lower exposure levels, respectively (Seals *et al.,* 2011). A highly exposed (180 ng PFOA/mL compared to an average of 4 ng/mL in USA) subset of these populations which was studied previously exhibiting a serum half-life of 2.3 years (Bartell *et al.,* 2009). These studies indicate that the half-lives are dose-dependent (Seals *et al.,* 2011).

The whole body half-life may be longer, since the elimination of these chemicals from the human body appears to be insignificant compared to the experimental animals (Harada *et al.,* 2005).

Elimination

Once absorbed in the body and distributed via the blood, PFOA is eliminated as the free carboxylic acid mainly with the urine and to a lesser extent in faeces. Therefore, renal elimination has been considered critical for detoxification (Vanden Heuvel *et al.,* 1991).

The elimination with the urine of PFAS is also greater in female rats than in males and increases with age and decreases with increasing chain length. These differences may be due to the actions of sex dependent organic anion transporters (OATs) in the kidney (Kudo *et al.,* 2002; Hinderliter *et al.,* 2006). For the shorter chain PFHxA, 100% of an oral dose in rats and mice was eliminated in the urine within 24 hrs (Gannon *et al.,* 2011).

The sex-related clearance of PFOA differs between animal species (Hundley *et al.,* 2006). In hamsters it is the opposite of what happens in rats. Male and female hamsters excreted respectively 99% and 58% of a dose in 5 days. In mice and rabbits there was no sex difference, and mice had a slower excretion rate than male rats, and rabbits hadfaster excretion rates than female rats.

The elimination half-lives in male and female Cynomolgus monkeys for PFOA were 33 days and 21 days, respectively, and the urine was the major excretion route (Butenhoff *et al.,* 2004a).

For the non-polar fluorotelomers such as 8:2 FTOH, the majority was excreted unchanged with faeces. A small part (about 1%) was excreted in the urine as the metabolite PFOA (Fasano *et al.,* 2006).

PFOS has a slower elimination rate than PFOA, and the half-life of PFOS in the female Cynomolgus monkey was about 200 days, about 40 times more than that for males (Kudo & Kawashima 2003; Seacat *et al.,* 2002; Andersen *et al.,* 2006).

Perfluorooctane sulfonamide (PFOSA) is also eliminated rapidly in rodents with a half-life of a few days. Branched isomers have a faster half-life than linear isomers (Benskin *et al.,* 2009; Ross *et al.,* 2012). The shorter-chain perfluorobutane sulfonate (PFBS) has a serum elimination half-life of about 5 hours in rats, 95 hrs in monkeys and 26 days in humans (Olsen *et al.,* 2009).

In humans there is no active excretion by the kidneys. The renal clearance in humans is almost negligible and approximately 1/5 of the clearance is based on the blood serum half-life, assuming accumulation in other body compartments. The sex differences seen in rats are not always found in humans. Although active excretion also was absent for PFOA and PFOS in monkeys their renal clearances were still 300-1000 times greater than those in humans, making extrapolations from animal data questionable (Harada *et al.,* 2005).

Biotransformation

PFOA, PFOS and other PFAAs are considered to be metabolically inert. The strong C-F bonds exclude any normal degradation pathway (Clark *et al.,* 1973). Other perfluoroalkyl acids with shorter or longer alkyl chains do have similar persistence. Any functional derivative (precursor) will ultimately be transformed to the acids.

For example, in mice and rats, the fluorotelomer alcohol 8:2 FTOH and its phosphates were transformed to PFOA, PFNA (perfluorononanoic acid) and other metabolites (Hagen *et al.,* 1981; Kudo *et al.,* 2005; Fasano *et al.,* 2006; Henderson and Smith 2007; D'Eon and Mabury 2007). The transformation in the liver is catalysed by cytochrome P_{450} (Martin *et al.,* 2005).

Perfluoroalkane sulfonamides (and *N*-substituted) are precursors of perfluoroalkane sulfonates but may sometimes also occur in environmental and human samples. That is the case for e.g. perfluorooctane sulfonamide (PFOSA).

Regarding EtFOSE (*N*-ethyl perfluorooctane sulfonamidoethanol), about 20% of an oral dose of 100 ppm is metabolised to PFOS in male rats (Thomford *et al.,* 2002). Rat liver microsomal fractions also degrade EtFOSE by de-ethylation to FOSE (perfluorooctane sulfonamidoethanol), further to PFOSA and finally to PFOS (Xu *et al.,* 2004).

Toxicology and mode of action

In general, the knowledge about the toxicology of other polyfluorinated compounds than PFOS and PFOA is rather sparse, and although the perfluoroalkane sulfonic acids and perfluoroalkyl carbox-

ylic acids are closely related structurally, these chemicals elicit different biological responses *in vitro* and *in vivo*.

The acute lethal toxicities correspond moderately to a classification as Acute tox 3 or 4. PFOS is more toxic than PFOA, and the toxicity of perfluorinated chemicals increases generally with the length of the alkyl chain. Further, PFCAs with a branched alkyl chain seem to be less toxic than linear isomers.

The liver is the primary target organ for PFOS and PFOA both in rodents and humans, and because these PFAAs are analogue ligands to natural long-chain fatty acids, they may displace them in biochemical processes (Vanden Heuvel *et al.,* 2006). This interference may contribute to the toxicity of these chemicals.

In the liver, polyfluorinated chemicals are mainly associated with either the peroxisome proliferator-activated receptor-α (PPARα) or the liver-fatty acid binding protein (L-FABP) receptor.

In an *in vitro* test of various perfluorinated chemicals PFOS had the most potent interference with L-FABP followed by EtFOSA, EtFOSE, and PFOA (Luebker *et al.,* 2002).

The binding of fluorinated chemicals to PPARα, which is one of three isoforms of PPAR encoded by separate genes and differentially expressed in various tissues found in all mammalian species examined to date, induces peroxisome proliferation, which is a well-known toxicological mechanism.

The activation of PPARα by PFOA and PFOS is more selective but less potent than the fatty acids. PFOA is more capable than PFOS in activating PPARα, and rodents are more responsive than human in test systems (Takacs and Abbott 2007).

The liver toxicity and peroxisome proliferation potency in rats depends on the carbon chain length. The doses of PFBS required for producing similar increases in the enzyme hepatic acyl CoA oxidase activity (a measure of proliferation) was about 50 times higher than those of PFOS and PFHxS (Ehresman *et al.,* 2007).

Ligands for PPARs have been widely developed for the treatment of various diseases, including dyslipidaemias and diabetes. Some hypolipidemic drugs, solvents and environmental chemicals are ligands for PPARα and can induce peroxisome proliferation; for example, clofibrate, phthalates, chloroform, perchloroethylene, trichloroethylene, HFC-123, and MTBE. Humans do not exhibit the same liver toxicities by these chemicals as found in rodent models (Peraza *et al.,* 2006).

Endocrine disruption

The peroxisome proliferation in rodents may cause lipid accumulation in the liver and uncoupling of the mitochondrial oxidative phosphorylation process, as well as induction of various enzymes involved in lipid- and steroid metabolism with the results that serum cholesterol, thyroid hormones, and testosterone are reduced but levels of estradiol are increased. Thus PFOA, PFOS and other PFAS are likely to be endocrine disruptors (Jensen and Leffers, 2008).

The competitive binding of poly- and perfluorinated compounds to the thyroid hormone transport protein transthyretin has been studied by Weiss *et al. (*2009). In Table 19 some of the data are shown:

TABLE 19
COMPETITIVE BINDING TO TRANSTHYRETIN

Compound	T4-TTR binding, %	IC_{50} nM
PFBA	106	nd
PFHxA	43	8,220
PFHpA	7	1,565
PFOA	4	949
PFNA	18	2,737
PFDcA	46	8,954
PFUnA	74	21,560
PFDoA	91	46,894
PFBS	69	19,460
PFHxS	3	717
PFOS	1	940
8:2 FTOH	117	nd
FOSA	32	6,124

T_4-TTR binding (%) =% inhibition of T4-TTR at max conc.

IC_{50} (nM) = conc. at 50% inhibition

It is clear that the binding potency decreased in the order of PFHxS>PFOS>PFOA>PFHpA>PFNA etc.

Some polyfluorinated chemicals have also estrogenic effects in cell cultures (”E-screen assay”) (Soto *et al.,* 1995). For example, the fluorotelomer alcohols 6:2 FTOH and 8:2 FTOH induce MCF-7 breast cancer cell proliferation and up-regulates the estrogenic receptor, but PFOS, PFOA and PFNA had no estrogenic effect in that test (Maras *et al.,* 2006; Vanparys *et al.,* 2006).

Immunotoxicity

The immunotoxicity potential of PFOS and PFOA have been shown and evaluated in an *in vitro* test system with cytokine release by immune cells (Corsini *et al.,* 2011). It was shown that both PFOS and PFOA suppress cytokine secretion; of these, PFOS was the most potent. It was also shown that PFOA and PFOS have different mechanisms of action.

Genotoxicity

The genotoxicological potential to generate reactive oxygen species (ROS) and to induce oxidative DNA damage in human HepG2 cells has been studied for the perfluorinated chemicals PFOA, PFOS, PFBS, PFNA and PFHxA (Eriksen *et al.,* 2010). PFOA was most active followed by PFOS and PFNA. Perfluorobutane sulfonate (PFBS) and perfluorohexanoic acid (PFHxA) did not generate ROS or DNA damage in that test.

Effects on cell membranes and intercellular communication

PFOS, PFOA and other PFAAs are substances attracted to surfaces, and PFOS and to a lesser extent PFOA can partition into model bilayers and cell membranes, where they cause changes in membrane structure, properties and function. An increased fluidity may change cell membrane surface potential and enhance calcium channels with the result of increased intracellular Ca^{2+} (Harada *et al.,* 2005; Liao *et al.,* 2008). That is the case for cultured hippocampal neurons where PFOS was most potent followed by PFTA, PFDA PFHxS and PFOA (Liao *et al.,* 2009).

PFOS, PFOSA, PFHxS and PFCAs with carbon chain lengths of 7-10 can rapidly and reversibly inhibit gap junction intercellular communication (GJIC) in a dose-dependent manner in animals, with PFDA inhibiting more than PFOA. GJIC is the major pathway of intracellular signal transduc-

tion; it is therefore important for normal cell growth and function. Defects in this communication may lead to teratogenesis, neuropathy, infertility, diabetes, autoimmune disorders, cancer, and other diseases (Upham *et al.,* 2009).

6.2 Toxicology of PFSA, including PFOS and derivatives

Acute toxicity

The acute lethal toxicity of PFOS moderately corresponds to a classification as Acute tox 4. The oral rat LD_{50} for PFOS is 250 mg/kg bw (3M 1999); therefore, PFOS is a little more toxic than PFOA. The oral LD_{50} in newborn mice was as low as 10 mg/kg bw/d (Lau *et al.,* 2004).

Short-term exposures

Toxicological studies have demonstrated that the liver is the primary target organ for PFOS, and body weight loss, increased liver weight, liver cell hypertrophy and changed lipid metabolism with reduction in serum cholesterol are early responses in experimental animals (Seacat *et al.,* 2003).

The no-observed-adverse-effect-level (NOAEL) for liver effects in male rats exposed for PFOS during 14 weeks feeding was 5 mg/kg/d (Seacat *et al.,* 2003).

Rats seem to tolerate somewhat higher liver concentrations of PFOS than monkeys, because the NOAEL for changes in thyroid hormone values (T3↓ and TSH↑) in a 6-month monkey study was 0.15 mg/kg/d (Seacat *et al.,* 2002).

The sub-chronic toxicity of potassium perfluorobutanes ulfonate (PFBS) has been studied in rats at doses of 60, 200, and 600 mg/kg-day bw for 90 days (Lieder *et al.,* 2009a). No treatment-related mortality, bodyweight, or neurological effects were noted. Red blood cell counts, haemoglobin, and haematocrit values were reduced in males receiving 200 and 600 mg/kg-day. The NOAEL for the female rat in this study was 600 mg/kg-day (highest dose of study). The NOAEL for the male rat was 60 mg/kg-day based on haematological effects.

PFOS did affect the neuroendocrine system in rats, when female rats were injected intraperitoneally with 0, 1 and 10 mg PFOS/kg bw for two weeks (Austin *et al.,* 2003). The oestrous cycle was affected, serum corticosterone level was increased, and serum leptin concentration and norepinephrine concentration in the paraventricular nucleus of the hypothalamus were decreased.

The immune system in mice seems to be highly sensitive to PFOS, and various immune parameters were affected at much lower levels than expected B-cells were identified as potential targets (Keil *et al.,* 2008; Peden-Adams *et al.,* 2008; Qazi *et al.,* 2010; Fair *et al.,* 2011). The lowest observed effect levels (LOAEL) in a 28 days' oral mouse study was 0.05 mg PFOS/kg total administered dose.

Reproductive and developmental effects

Many studies have shown that gestational exposure to PFOS may cause developmental toxicity in rats and mice, including reduction of foetal weight, cleft palate, oedema, delayed ossification of bones, and cardiac abnormalities (reviewed by Lau *et al.,* 2004 and 2007), and the developmental toxicity of PFOS is higher than that of PFOA. Structural abnormalities were only found in the highest PFOS dose groups, where significant reductions of weight gain and food consumption were also observed in the pregnant dams. Thus the relevance of these effects may be questioned.

Exposure to PFOS during pregnancy in rats (1-10 mg PFOS/kg/d from gestation day 2-21) and mice (1-20 mg PFOS/kg/d from gestation day 1-18) indicated that *in utero* exposure to PFOS severely compromised postnatal survival and caused delay in growth and development accompanied by hypothyroxinemia in the surviving pups (Lau *et al.,* 2003). In a two-generation reproduction study the NOAEL value in rats for PFOS was 0.1 mg/kg/d (Luebker *et al.,* 2005). Concurrent exposure to

PFOS and restraint stress enhance effects (Fuentes *et al.,* 2007). PFOS was associated with reduced epididymal sperm counts in mice (Wan *et al.,* 2011).

High doses of EtFOSE (*N*-ethyl-*N*-(2-hydroxyethyl)perfluorooctane sulfonamide or *N*-ethyl perfluorooctane sulfonamidoethanol) also caused reduced maternal body weight and foetal weight in rodents and had effects quite similar to its metabolite PFOS. Both PFBS and PFHxS have been assessed for developmental and reproductive effects. Maternal exposure to PFBS potassium salt did not produce any adverse effect on embryo/foetal development, and no significant alterations were noted in a two-generation study in rats at doses of up to 1 mg/kg/d (NOAEL). PFHxS was only examined in a screening system at lower doses without any effect observed (Lau *et al.,* 2003, 2004).

The potential reproductive and developmental toxicity of perfluorohexane sulfonate (PFHxS) was studied in an experiment with rats dosed by gavage at 0.3, 1, 3, and 10 mg/kg/d 14 days prior to cohabitation, during cohabitation, and until the day before sacrifice (21 days of lactation or presumed gestation day 25 (if not pregnant) for females and minimum of 42 days of treatment for males). Offspring were not dosed by gavage but were exposed by placental transfer in utero and potentially exposed via milk. At all doses reductions in serum total cholesterol and other biochemical changes in the blood but no reproductive or developmental effects were observed, and there were no treatment-related effects in dams or offspring (Butenhoff *et al.,* 2009a).

In a more recent two-generation reproduction study with the potassium salt of perfluoro butanesulfonate the parental-generation (P) rats were dosed orally by gavage with 0, 30, 100, 300 and 1000 mg PFBS/kg/day for 10 weeks prior to and through mating (males and females), as well as during gestation and lactation (females only). First generation (F1) pups were dosed similarly, beginning at weaning (Lieder *et al.*, 2009b). Second generation (F2) pups were not directly dosed but potentially exposed to PFBS through placental transfer and nursing, and the study was terminated 3 weeks after their birth. At the two high doses, increased liver weight and some effect on the kidneys were observed. NOAEL for the parental generations was 100 mg/kg bw/day.

Similar effects to what is mentioned for rodents happen in rabbits exposed to PFOS and EtFOSE during gestation. The no-observed-effect-level (NOEL) for PFOS in rabbits was 0.1 mg/kg/d (Case *et al.,* 2001).

Cancer and mutagenicity

PFOS and derivatives are not mutagenic in various test systems but may increase the genotoxicity of other chemicals. An example is that the genotoxicity of cyclophosphamide in the micronucleus assay with hamster lung V79 cells was increased manifold by simultaneous exposure to PFOS (Jernbro *et al.,* 2007).

In a two-year rat feeding study with PFOS, a modest liver tumour response (hepatocellular adenomas and one carcinoma) was observed in the high dose group of 20 ppm PFOS as potassium salt corresponding to an exposure of 1.5 mg PFOS/kg/d (Seacat *et al.,* 2003).

A dietary exposure to 100 ppm EtFOSE over a two-year period caused an increase of hepatocellular adenomas (+ one carcinoma) in female rats and hepatocellular adenomas thyroid follicular cell adenomas in males rats (Thomford *et al.,* 2002). It was estimated that 20% of an oral dose of EtFOSE was metabolised to PFOS.

6.3 Toxicology of PFCAs including PFOA and derivatives

The toxicology of PFOA has been reviewed by Kennedy *et al. (*2004), among others. The toxicological information about PFOA precursors and PFCAs with other chain lengths is sporadic.

Acute toxicity
The acute lethal toxicity of PFOA is moderate, corresponding to a classification as Acute tox 4; for instance, the oral LD_{50} is reported to be between 430 and 1800 mg/kg for adult rats of both sexes with most data in the lower end (Kennedy *et al.,* 2004). Newborns are twice as sensitive with oral LD_{50} of about 250 mg/kg (The U.K. Committee on Toxicity 2006). In mice and guinea pigs the oral LD_{50}s are 457 and around 200 mg/kg, respectively. The dermal acute toxicity is lower with skin LD_{50} of 7000 mg/kg in rats and 4300 mg/kg in rabbits probably because of limited uptake. PFOA is a mild skin- and eye irritant – maybe because of its acidity. PFOA is also moderately toxic by inhalation as dust with a $^{4h}LC_{50}$ of 0.98 mg/L.

For PFOA and PFDA (perfluorodecanoic acid) the rat intraperitoneal LD_{50}s are 189 and 41 mg/kg, respectively. Thus PFDA with a longer alkyl chain is much more acutely toxic, and it also has delayed effects (Olson and Anderson, 1983). This is in accordance with the general finding that the toxicity of perfluorinated chemicals increases with the length of the fluoroalkyl chain.

Short-term exposures/repeated-dose toxicity
The liver is the target organ, and early responses in animals are dose-related body weight reduction, liver weight increase, hepatocellular hypertrophy and changed lipid metabolism with reduction in serum cholesterol (Kennedy *et al.,* 2004).

The no-observable-adverse-effect-level (NOAEL) and lowest-observable-adverse-effect-level (LOAEL) for liver effects (weight reduction) by PFOA in male rats exposed by feeding in 13 weeks were estimated at 0.06 and 0.64 mg/kg bw/day, respectively (Perkins *et al.,* 2004). Another repeated-dose study found a similar LOAEL of 0.3-1 mg/kg bw/day for PFOA in male rats, and the branched isomers of PFOA had lower toxicity than the linear forms (Loveless *et al.,* 2006).

PFOA is less liver toxic in monkeys with a LOAEL of 3 mg/kg/d in a six month study. The only change in the monkey was liver enlargement (Butenhoff *et al.,* 2002).

PFDA having a longer chain than PFOA was more toxic in rat, hamster, mouse and guinea pig (van Rafelgheim *et al.,* 1987; Kawashima *et al.,* 1995; Ohmori *et al.,* 2003).

Sequential 28-day and 90-day oral toxicity studies were performed in male and female rats with ammonium perfluorobutyrate (PFBA) at doses up to 150 and 30 mg/kg-d, respectively, and ammonium perfluorooctanoate (PFOA) was used as a comparator at a dose of 30 mg/kg/d in the 28-days study (Butenhoff *et al.,* 2012). Female rats were unaffected by PFBA. Effects in males included: increased liver weight, slight to minimal hepatocellular hypertrophy; decreased serum total cholesterol; and reduced serum thyroxin. The no-observable-adverse-effect-levels (NOAELs) were 6 and >150 mg/kg/d for male and female rats in the 28-day study and 6 and >30 mg/kg/d in the 90-day study, respectively. Unlike with PFBA, dosing with 30 mg/kg/d PFOA resulted in increased incidence of clinical signs of toxicity (e.g. hunched posture), increased liver weight in females as well as males, and a major (75%) reduction in body weight of males. Thus, the relative response of rats to dosing with PFBA as compared to PFOA was likely the result of both the more rapid pharmacokinetic clearance and lesser pharmacodynamic potency of PFBA.

For the sodium salt of perfluorohexanoic acid (PFHxA), a NOAEL for sub-chronic toxicity in rats after 90 days gavage exposure was determined at 20 mg/kg bw/day (Loveless *et al.,* 2009). In another study based on liver effects, the NOAELs were estimated at 50 mg/kg bw/day and 200 mg/kg bw/day, respectively, for males and female rats (Chengelis *et al.,* 2009).

Perfluorobutanoic acid (PFBA) has also been tested in a 90 days gavage study with rats (Foreman *et al.,* 2009; Bjork and Wallace 2009). At the highest dose (30 mg/kg bw/day) there was an increase

in liver weight and reduced thyroid hormone in males indicating a higher toxicity than PFHxA but lower than PFOA. The toxicity was mediated by PPARα and not considered relevant for humans.

Toxicological mechanism
Polyfluorinated acids are analogue ligands to natural long-chain fatty acids and may displace them in biochemical processes and at receptors, such as PPARα and the liver-fatty acid binding protein (L-FABP).

Perfluoroalkanoates, particularly PFOA, PFNA and PFDA but not PFHxA, are highly potent peroxisome proliferators in rodent livers and affect mitochondrial, microsomal, and cytosolic enzymes and proteins involved in lipid metabolism (Ikeda *et al.,* 1985; Vanden Heuvel 1996; Upham et. al., 1998; Kudo *et al.,* 2000). PFBA has a slighter effect on indicators of peroxisome proliferation (Ikeda *et al.,* 1985).

Kudo and co-workers (2001) studied PFCAs with different chain lengths (C7 - C10) in male rodent liver. Increase in hepatic fatty acid β-oxidation activity (acyl-CoA oxidase) was used as a biochemical measure of peroxisome proliferation. The result indicated that the liver concentration and not the chain length was decisive, but the longer the chain the more of the compound was accumulated in the liver.

In vitamin A deficient mice, PFOA had a stronger effect and caused a 3-6 times increase in the β-oxidation of fatty acids (Sohlenius *et al.,* 1995).

The differences between animal species are significant for PFDA. Peroxisome proliferation was greatest in mice and almost absent in guinea pigs. However, accumulation of lipid droplets in liver cells was more pronounced in hamsters and guinea pigs than in rats and mice exposed to PFDA (van Rafelgheim *et al.,* 1987).

Immunotoxicology
The potential of PFOA to be toxic for the immune system has been discussed by deWitt *et al. (*2009). PFOA is an immunosuppressant through induction of PPARs and enhances the IgE-mediated hypersensitivity response to ovalbumin, and in this way it may provoke asthma (Fairley *et al.,* 2007). PFNA has also shown immunotoxicity (Fang *et al.,* 2008; 2010).

Reproductive and developmental effects
Many studies have shown that gestational exposure to PFOA may cause developmental toxicity especially in mice (reviewed by Lau *et al.,* 2004 and 2007).

Dose-dependent growth deficits and reduced birthweight were observed in offspring of pregnant mice which were exposed by gavage for PFOA during gestation days 1-17. At exposures ≥ 5 mg/kg/d postnatal survival was also reduced and eye-opening was delayed up to 2-3 days. The maternal LOAEL was determined at 1 mg/kg bw/day and the foetal NOAEL was maternal exposure to 3 mg/kg bw/day (Lau *et al.,* 2006; Wolf *et al.,* 2007).

A more recent mouse study observed higher body weight and increased insulin and leptin levels in post pubertal female offspring after low-dose in utero exposures to PFOA (Hines *et al.,* 2009).

The mammary gland has, specifically, proven to be a sensitive tissue with respect to various developmental endpoints, including functional lactation, milk protein gene expression, and developing neonatal and peripubertal structures. Some animal studies have shown that gestational exposure of pregnant (female) mice to doses from 3 mg PFOA/kg bw/d may result in delayed mammary gland development for offspring, which persisted into adulthood. These impacts were both a matter of

doses and of exposure timing (White *et al.,* 2009; Yang *et al.,* 2009; Tan *et al.,* 2007 and 2009; Zhao *et al.,* 2010).

PFOA exposure in offspring either during lactation or through the intra-uterine route induces delayed mammary gland development. This delay was visible as early as birth and has been found to extend into adulthood. In a multigenerational mice study P_0 dams were exposed by gavage to either up to 5 mg PFOA/kg/d on gestational days 1-17 *or* 1 mg/kg/d during gestation. The F_1 and F_2 offspring was exposed continuously to 5 ppm PFOA in their drinking water. The F_1 dams exposed to PFOA exhibited diminished lactational morphology. All exposed F_1 females and highest exposed P_0 and F_2 females had delayed mammary gland differentiation. It was concluded that gestational PFOA exposure of mice induced delay in mammary gland development and/or lactational differentiation across three generations (White *et al.,* 2011). The exposure levels were similar to concentrations occasionally found in contaminated drinking water supplies in the USA.

For the sodium salt of perfluorohexanoic acid (PFHxA), a NOAEL for developmental toxicity in rats after 90 days gavage exposure was determined at 100 mg/kg bw/day (Loveless *et al.,* 2009).

A study exposing pregnant mice to perfluorobutanoic acid (PFBA) in doses of 35, 175 and 350 mg/kg bw/day showed maternal liver effects at the two high doses but no significant effects on the offspring (Das *et al.,* 2008). Thus PFBA has lower developmental toxicity than PFOA.

Effects on fertility

The effects on hormone levels in rodents are reflected in changes in the testis, where exposure to PFOA results in Leydig cell hyperplasia and eventually development of Leydig cell adenomas (Biegel *et al.,* 1995).

A study of effects on testis in adult rats exposed to perfluorododecanoic acid (PFDoA) also showed a reduced gene expression of many genes involved in cholesterol transport and steroidogenesis and a reduced serum testosterone level (Shi *et al.,* 2007). Thus, it seems that exposure to some PFAAs can severely affect proliferation and function of Leydig cells in the adult rat. Leydig cells in the testis are the main sites for testosterone biosynthesis.

This is of considerable concern, because Leydig cell hyperplasia is common among infertile men (Holm *et al.,* 2003) who, as a group, also shows lower testosterone levels than comparable normal controls (Andersson *et al.,* 2004). Reduced testis function has been linked to the testicular dysgenesis syndrome (TDS) (Skakkebæk *et al.,* 2001). The TDS hypothesis states that in utero exposure to endocrine disruptors can damage testis development and lead to reduced testis function in the adult, with symptoms ranging from a moderately reduced semen quality to testis cancer. The best animal model for TDS consists of rats exposed to long-chain phthalates in a critical time window during development, which results in testis dysgenesis with Leydig cell hyperplasia and clustering of the Leydig cells in the centre of the testis, resulting in reduced testosterone levels and compromised fertility in the adults (Sharpe 2006; Hallmark *et al.,* 2007).

The sodium salt of perfluorohexanoic acid (PFHxA) was not a reproductive or neurobehavioural toxicant in rats after 90 days gavage exposure at 500 mg/kg bw/day (Loveless *et al.,* 2009).

Cancer and mutagenicity

PFOA was non-mutagenic in the Ames test using five strains of *Salmonella typhimurium* and in a single strain of Saccharomyces cerevisiae (Griffith and Long 1980). Several other mutagenicity studies of PFOA published by contract laboratories support the inactivity of PFOA (Kennedy *et al.,* 2004). PFDA is also negative in the Ames-Test and various other test systems. However, PFDA was active in a chromosome aberration assay in the presence of S-9 mix and in an S-phase DNA synthesis assay (Godin *et al.,* 1992). The sodium salt of perfluorohexanoic acid (PFHxA) was neither mu-

tagenic in the Ames test nor induced chromosome aberrations in human lymphocytes (Loveless *et al.,* 2009).

Long-term animal bioassays have been conducted with CD rats belonging to a strain that has a low spontaneous incidence of relevant tumours. The rats were exposed to up to 300 ppm (corresponding to about 15 mg/kg/d) PFOA in the diet for two years; hyperplasia and a dose-dependent increase in testicular Leydig cell adenomas and increase of benign hepatocellular and pancreas tumours were observed (Cook *et al.,* 1992; Biegel *et al.,* 1995; Liu *et al.,* 1996; Biegel *et al.,* 2001). These tumours could be a result of peroxisome proliferation and endocrine changes, because reduced aromatase activity and a sustained increase in serum estradiol were observed. Nevertheless, US Environmental Protection Agency has classified PFOA as an animal carcinogen (US EPA 2002).

6.4 Toxicology of other polyfluorinated substances

These substances include for example fluorotelomers of various sorts and perfluoroalkyl phosphorous compounds. The toxicological data is limited.

Polyfluoroalkyl phosphate formulations are fluorotelomer-based commercial products with a high potential for human exposure, containing a mixture of fluorinated chain lengths as well as phosphate mono-esters (monoPAPs), di-esters (diPAPs) and tri-esters (triPAPs). Animal experiments with 4:2-, 6:2-, 8:2- and 10:2 monoPAPs and diPAPS showed that the diPAPs were bioavailable, with bioavailability decreasing as the chain length increased from 4 to 10 perfluorinated carbons (D'Eon & Mabury 2011). The monoPAPs were not absorbed from the gut; however, they found evidence to suggest phosphate-ester cleavage within the gut contents. Biotransformation to the PFCAs was observed for both monoPAPs and diPAPs congeners.

The mono- and di-substituted perfluorinated phosphonic acids (mono-PFPAs and di-PFPAs) are a new class of fluorinated acids, high volume chemicals (surfactants) used. as wetting agent in waxes and coatings and as defoaming additives in pesticides, among other uses, and found occasionally in the environment and in human blood in Canada. In rats these chemicals (with C6-C12 fluoroalkyl chains) are absorbed a little slower than PFCAs and the absorption decreases with chain length and di-PFPAs less than mono-PFPAs. The blood half-lives of a few days are similar to PFOA and PFOS but the renal clearance is much slower. The faecal excretion is lower than 10%. Preliminary data indicates that these chemicals are long-lived in humans (D'Eon & Mabury 2010).

The fluorotelomer alcohols 6:2 FTOH and 8:2 FTOH induce MCF-7 breast cancer cell proliferation and up-regulates the oestrogen receptor (Maras *et al.,* 2006; Vanparys *et al.,* 2006).

Various polyfluorinated alkyl iodides have been studied for estrogenic activity in some *in vitro* test systems (Wang *et al.,* 2012). The perfluorohexyl- and perfluorooctyl iodides were the only tested substances promoting the proliferation of MCF-7 cells, induced luciferase activity in MVLN cells, and up-regulated the expression of two estrogen-responsive genes, TFF1 and EGR3. All tested substances showed estrogenic effects. The optimal chain length for estrogenic effect was C6-perfluoroalkyl iodides.

6.5 Human epidemiological studies of the effect of exposures to polyfluoroalkylated chemicals

Workplace exposures and cancer

The experience from the work environment has not indicated any important direct adverse health effects among workers exposed to either PFOS (Olsen *et al.,* 1999) or PFOA (Olsen *et al.,* 2000), besides the retrospective cohort mortality study of a cohort of 2083 workers potentially exposed to perfluorooctane sulfonyl fluoride (PFOSF) at least 1 year at the 3M Minnesota (Alexander *et al.,* 2003). PFOSF can be metabolised into PFOS. A total of 145 deaths were identified, and that was less than expected for the general population and the total cancer deaths were also less than ex-

pected (healthy worker effect). However, for the *highly exposed,* two deaths of liver cancer (SMR 3.08) and three deaths of bladder cancer (SMR 12.77) were observed. For the whole cohort there was an increased mortality of bladder cancer (SMR 4.81).

These results have been dismissed by The U.K. Committee on Toxicity (2006) because of:

- inadequacy of exposure assessment using job categories;
- potential co-exposure to carcinogenic aromatic amines, and
- lack of evaluation across PFOS manufacturing sites.

However, an exposure assessment based on job categories is normal for occupational cohort studies, and in addition the U.K. Committee on Toxicity did not mention that blood concentrations were available for the various job categories. The potential exposures to aromatic amines are likely to have been insignificant compared to the larger PFOSF exposures but an additive effect or promotion cannot be excluded. Finally, the factory studied in Minnesota was the major (only?) production facility in the World in that period.

Cancer risk in non-occupational groups

In a Danish prospective cohort of about 57 000 healthy individuals aged 50-65 selected from 1993-1997 and followed until July 2006, no significant cancer risk related to PFOS and PFOA levels was indicated (Eriksen *et al.,* 2009).

In Greenland the incidences of breast cancer have been increasing over recent years. A case-control study in Greenland compared serum levels of various environmental contaminants in breast cancer patients with levels in a control group (Bonefeld-Jørgensen *et al.,* 2011). The following PFAAs were measured: PFSA (PFOS, PFHxS, and PFOSA), PFCAs (PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA and PFTrA) with PFOS and PFOA as the dominating species. Breast cancer cases had significantly higher serum levels of PFOS (medians: 45 ng/mL – 21.9 ng/mL) and ΣPFCA (medians: 8.0 ng/mL – 5.2 ng/mL) than controls.

Population studies with effect on lipid metabolism etc.

A recent review of epidemiological evidence on the health effects of PFOA was published by Steenland *et al. (*2010a). They reported that a positive association of PFOA with cholesterol levels in blood was observed in six occupational studies, three studies of a highly exposed community and one general population study. Several studies also showed an association between PFOS and lipids of a similar magnitude.

One study of a large population in mid-Ohio Valley exposed via contaminated drinking water and with mean serum concentration of 69 ng PFOA/mL and 23 ng PFOS/mL, respectively, showed that PFOA was significantly associated with increased total cholesterol and low density lipoproteins (Frisbee *et al.,* 2010). PFOS was significantly associated with increased total cholesterol, low density lipoproteins and high density lipoproteins.

In the same population a later study showed a positive association between PFOS and PFOA serum levels and serum levels of alanine transferase (ALT) – a biomarker for liver damage (Gallo *et al.,* 2012).

The population study used data for 860 individuals from the 2003-2004 National Health and Nutrition Examination Survey (NHANES) and found a positive association between total cholesterol and serum concentrations of PFOS (mean 25 ng/mL), PFOA (mean 4.6 ng/mL) and especially PFNA (mean 1.3 ng/mL) (Nelson *et al.*, 2010a).

Three cross-sectional studies have reported positive association between PFOA and uric acid, a natural product of purine metabolism. In one study of adults with elevated community exposure to PFOA (Steenland *et al.,* 2010b), both PFOA and PFOS were significantly associated with uric acid but PFOA more, and the concentrations in the blood of PFOA were also higher than PFOS.

A study of gene expression profiles in postmenopausal woman from Norway showed significant effects of PFOA on fatty acid metabolism and increased expression of CYP_{4A22} and on insulin signalling pathways (Rylander *et al.,* 2011).

In a prospective cohort of 665 Danish pregnant women, it was found that their serum PFOA levels were positively associated with overweight/obesity at 20 years of age in their female offspring (Halldorsson *et al.*, 2012). In addition, maternal PFOA concentrations were positively associated with serum insulin and leptin levels, and inversely associated with adiponectin levels in female and male offspring. In another study of a young hypertension cohort in Taiwan, serum PFNA concentrations were associated with elevated serum adiponectin (Lin *et al.,* 2011).

Population studies of reproductive effects

In humans PFOS and PFOA are transferred from the pregnant mother to the foetus (Inoue *et al.,* 2004; Needham *et al.,* EST 2011; Beeson *et al.,* 2011; Mondal *et al.,* 2012; Gützkow *et al.,* 2012).

A study was performed in the USA of the Danish National Birth Cohort, which included data from more than 90 000 pregnant Danish women obtained from March 1997 to November 2002 (Fei *et al.*, 2007). This study found an inverse association between maternal plasma levels of PFOA - but not PFOS - and birth weight. The mean plasma concentrations were 35.3 ng PFOS/mL and 5.6 ng PFOA/mL.

An analysis of birth records linked to a survey from the PFOA drinking water contaminated mid-Ohio Valley showed some suggestion of an association with early preterm birth, and measures of growth restrictions showed weak and inconsistent association with PFOA (Savitz *et al.,* 2012ab).

A cross-sectional study, which was conducted in 2004-2005 of about 300 mothers and their newborn from Baltimore in the USA, found a negative association between concentrations of PFOS and PFOA in the mothers' serum and the birth weight and birth size of the newborn, although the serum concentrations were much lower in this study with medians of 5 ng PFOS/mL and 1.6 ng PFOA/mL (Apelberg *et al.,* 2007ab). However, in a later study from Japan, where serum levels were similar with means of 5.6 ng PFOS/mL and 1.4 ng PFOA/mL, no such correlation was found (Washino *et al.,* 2009).

A follow-up study of the Danish cohort found that maternal PFOA levels in early pregnancy were associated with smaller abdominal circumference and birth length. For each ng/mL increase of PFOA, birth length decreased by 0.069 cm an abdominal circumference decreased by 0.059 cm (Fei *et al.,* 2008).

A study of a large cohort from Avon in the UK with prenatal blood concentration (medians) of 19.2 ng/mL PFOS, 3.7 ng/mL PFOA and 1.6 ng/mL PFHxS showed that mothers from the upper tertile gave birth to girls weighing 140 gram less than for the lower tertile but at 20 months the girls with high PFOS exposure weighed 580 grams more (Maisonet *et al.,* 2012). These results should be evaluated with the paper discussed above in mind (Halldorsson *et al.,* 2012)

Another study discovered an association between PFOS and PFOA in maternal serum and decrease of duration of breast feeding in multiparous women (Fei *et al.,* 2010).

Another follow-up reported an association between reported time to pregnancy and maternal plasma levels of PFOA and PFOS in 1400 pregnant women; therefore, these chemicals may cause reduced subfecundity (Fei *et al.,* 2009). Another prospective cohort study of 222 Danish couples could not confirm that PFAAs may affect time-to pregnancy (Vestergaard *et al.,* 2012).

That may not be a problem of the mother alone, because another Danish study found that high PFAA levels (medians: 24.5 ng PFOS/mL, 4.9 ng PFOA/mL and 6.6 ng PFHxS/mL) in blood serum were associated with fewer normal sperm in studied normal young men (Joensen *et al.,* 2009).

Another more recent study of 256 American infertility patients reported no association between PFOS and PFOA levels (medians: 32.3 ng PFOS/mL and 49.2 ng PFOA/mL) and sperm quality (Raymer *et al.,* 2011).

In an European study of the sperm quality of 588 partners to pregnant women from Greenland, Poland and Ukraine, a negative association was found between PFOS serum levels and sperm morphology in the two European populations but not in the Inuits from Greenland, who had the highest serum levels with a median of 44.7 ng PFOS/mL against 18.5 ng PFOS/mL in Poland and 7.6 ng PFOS/mL in Ukraine (Toft *et al.,* 2012). It was suggested that PFOS interact with the sperm membrane function.

In a population of the contaminated area of mid-Ohio Valley, a study discovered that children showed a later age (3-6 months delay) of puberty correlated with PFOS/PFOA concentrations in the blood (Lopez-Espinosa *et al.,* 2011).

A very recent study has discovered a significant association between serum PFOA and PFNA levels and endometriosis in the operative samples (Louis *et al.,* 2012).

Kidney diseases

An association between serum PFAAs, insulin resistance and metabolic syndrome has been found indicating a possible diabetic effect and effect on the kidneys (Lin *et al.,* 2009).

Chronic kidney Disease (CKD) is a major public health problem with increased prevalence in the USA and elsewhere (Coresh *et al.,* 2011). Since, it is known that the kidneys are an important target organ for polyfluorinated chemicals a study from West Virginia of examined the relation between serum levels of PFOS and PFOA and CKD (Shankar *et al.,* 2011). The population studied was 4500 adults of both sexes from NHANES surveys 1999-2008 for which there were serum PFAA measurements. For the fourth quartile (>29.5 ng PFOS/mL and >5.9 ng PFOA/mL) they found a positive association between these fluorinated chemicals and CKD which was independent of normal confounders.

Endocrine disruption

Data from the NHANES 1999-2006 surveys including almost 4000 individuals found that higher concentrations in serum of PFOS (>36.8 ng/mL) and PFOA (>5.7 ng/mL) were associated with current thyroid disease in the US general population (Melzer *et al.,* 2010).

Effects on the immune system

An investigation of children aged 5 and 7 years from Faroe Island in the Atlantic showed that commonly prevalent exposures to PFOS, PFOA, PFHxS, PFNA and PFDA measured in blood serum were associated with lower antibody responses to childhood immunizations (vaccinations) and an increased risk of antibody concentrations below the level needed to provide long-term protection against diphtheria and tetanus (Grandjean *et al.,* 2012).

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Children's behaviour
Data from the NHANES 1999-2004 and the C8-Health Project in the USA surveys showed positive association between some serum PFAA levels and attention deficit-hyperactivity disorder (ADHD) in children (Hoffman *et al.,* 2010; Stein and Savitz, 2011). The later study found an association with ADHD and PFHxS blood levels.

Higher blood levels of PFOS, PFNA, PFDA, PFHxS and PFOSA (but not PFOA) were associated with significantly shorter "Impaired Response Inhibition" (IRT) during the "differential reinforcement of low rates of responding" (DRL) tasks measuring children's impulsivity (Gump et al. 2011).

6.6 Risk assessment

The risk characterisation for the general population exposed to PFOA shows a sufficient margin of exposure and safety for children adults and the elderly, according to Butenhoff *et al. (*2004).

The U.K. Committee on Toxicity (2006) has recommended a provisional Tolerable Daily Intake (TDI) for PFOA and PFOS of 3 μg/kg bw/d and 0.3 μg/kg bw/d, respectively, using an uncertainty factor of 100. They conclude that for some small children the TDI may already be exceeded.

In 2008 EFSA's CONTAM Panel performed a risk assessment and established a tolerable daily intake (TDI) of 150 ng/kg bw per day for PFOS and 1,500 ng/kg bw per day for PFOA (EFSA 2008). EFSA has not suggested TDIs for other PFASs.

A 2012 report concluded that dietary exposures to PFOS and PFOA are highly unlikely to exceed the TDIs (EFSA, 2012).

These assessments have all been based on results of animal experiments, which may be highly arbitrary and unreliable because the renal clearances of PFOA and PFOS are almost insignificant in humans, contrary to a significant active excretion in experimental animals. These differences in excretion of PFAAs are mentioned by EFSA but not taken into account in their assessment.

Therefore, these chemicals in humans leave the blood mainly by redistribution to internal organs and not by elimination from the body. This lack of elimination may considerably increase the inter-

nal exposure time in critical organs, and might be the explanation for the many effects found in lower exposed human populations.

6.7 Summary on human health effects

Information related to human health is available for only a few of the several hundreds of polyfluorinated chemicals (PFCs) used in industry and consumer products.

The perfluoroalkyl sulfonic acids (PFSAs) and the perfluoroalkyl carboxylic acids (PFCAs) are closely related structurally because of the perfluorinated chain. Nevertheless, these chemicals elicit different biological responses *in vitro* and *in vivo*. PFOS is more toxic than PFOA and the toxicity of perfluorinated chemicals increases generally with the length of the alkyl chain. PFCAs with a branched alkyl chain seem to be less toxic than linear isomers. Biological half-lives are much longer in humans compared to experimental animals

PFOS and four of its derivatives have a harmonised classification as carcinogenic, toxic to reproduction, acute toxic and toxic to specific target organ by repeated exposure [6]. A similar classification has been proposed for PFOA and APFO.

The precursors and functional derivatives of PFOS and PFOA will ultimately be transformed to the basic acids in the body and result in similar effects as the PFOS and PFOA. For example, the fluorotelomer alcohol 8:2 FTOH may be transformed in mice and rats to PFOA, PFNA and other metabolites. In the same way *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) is metabolised to perfluorooctane sulfonamidoethanol (PFOSE), perfluorooctane sulfonamide (PFOSA) and finally to perfluorooctane sulfonate (PFOS).

Population studies have discovered positive associations between serum levels of perfluoroalkylated acids (PFAA) and uric acid levels, thyroid disease, overweight, insulin- and leptin levels, and Chronic Kidney Disease (CKD), which is a major public health problem with increased prevalence. An investigation of children from Faroe Island in the Atlantic showed that commonly prevalent exposures to PFAAs were associated with lower antibody responses to childhood immunizations (vaccinations). The immune system seems to be highly sensitive to PFAAs, and various immune parameters were affected at levels which are found in exposed human populations.

Human population studies have found associations between maternal PFAA exposure and reported time to pregnancy, preterm birth, and lower birth weight and birth size of newborns. Some population studies also indicate that PFAAs can have an adverse effect on semen quality.

The short-chain analogues have shorter half-live times in humans. The mean half-live in human blood of is about one month for PFBS and 2-4 days for PFBA as compared to half-lifes of 5.4 years for PFOS, 8.5 years for PFHxS, and 3.8 years for PFOA.

The available information, mainly based on relatively few animal studies, indicates that the short-chain analogoues to a lesser degree have less effect than the long-chain PFAAs are linked to adverse effects such as developmental toxicity and carcinogenic potential.
In general the knowledge about the toxicology of most perfluorinated compounds is rather sparse, and it will take some years and much effort, before we will have sufficient information for evaluation of the full impact of the present levels in humans.

[6] Hazard Class and Category Code(s) according to the CLP Regulation as concern human health: Carc. 2, Repr. 1B, STOT RE 1, Acute Tox. 4; see Table 4.

7. Monitoring data and exposure

7.1 PFASs in the environment

7.1.1 Monitoring of PFOS and other PFASs in the environment and releases from point sources

The Danish national environmental monitoring and assessment programme, NOVANA, includes measurements of seven PFAS in point sources and streams and PFOS in marine animals (Table 20). Occationnally sceening surveys of a number of PFASs in more environmental compartments are undertaken

TABLE 20
PFOS AND OTHER POLYFLUORINATED SUBSTANCES INCLUDED IN THE NATIONAL MONITORING AND ASSESSMENT PROGRAMME FOR THE AQUATIC AND TERRESTRIAL ENVIRONMENT, NOVANA 2011-2015

Substance	Acronym	Point sources	Marine animals
Perfluorooctane sulfonic acid	PFOS	x (small and large sewage treatment plants)	x
Perfluorooctane sulfonamide	PFOSA	x	
Perfluorohexane sulfonic acid	PFHxS	x	
Perfluorooctanoic acid	PFOA	x	
Perfluorononanoic acid	PFNA	x	
Perfluorodecanoic acid	PFDA	x	
Perfluoroundecanoic acid	PFUnA	x	

7.1.2 Results from the Danish NOVANA monitoring programme

A number of studies exist of the presence of PFOS and other perfluorinated substances in the environment in Denmark.

A NOVANA screening survey from 2007 of PFOS and other PFASs in the environment, as well as discharges from point sources, has identified the presence of a number of different PFAS compounds near point sources, and in freshwater and marine environments in Denmark (Strand J. *et al.,* 2007). The survey included the following PFASs: PFOS, PFOSA, PFHxS, PFOA, PFNA, PFDA and PFUnA. PFOS and PFOA were generally the predominant components of the measured PFASs in both the point sources and in the aquatic environment as shown in Figure 6.

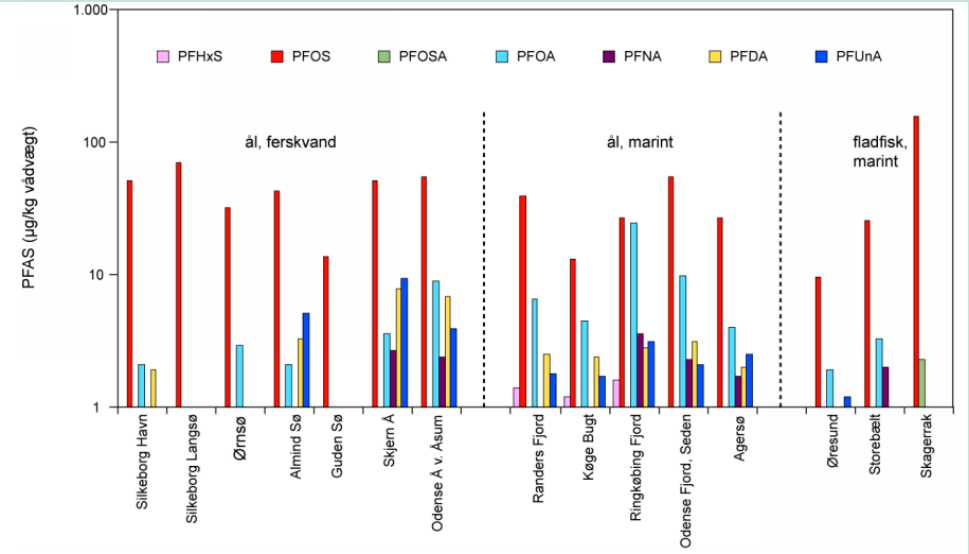


FIGURE 6
MEDIAN CONCENTRATIONS OF PFOS OG OTHER PERFLUORATED COMPOUNDS IN LIVER OF FISH FROM MARINE AND FRESHWATER RECIPIENTS (STRAND *ET AL.*, 2007). [ENHED OG NAVNE PÅ FISK OVERSÆTTES, MEN STEDNAVNE BEVARES PÅ DANSK]

Increased concentrations of PFOS locally in eel, e.g. from the Silkeborg Lakes and Odense Fjord, indicated that local sources can impact the environment. PFASs were only detected in fish, not in sediments and mussels from freshwater and marine environments.

The survey assessed the level of PFOS to represent an environmental risk especially to fish-eating birds and mammals at the highest trophic levels of the food chain, as most of the fish samples exceed the PNEC value of 17 µg/kg (predicted no-effect concentration) for PFOS in animal food. It should, however, be noted that only the liver and not the entire fish was analysed in the survey (Strand *et al.,* 2007). No conclusion was drawn for the other analysed FPASs.

The most recent data from the NOVANA programme is shown in the table below.

TABLE 21
MOST RECENT MONITORING DATA FOR PFOS AND OTHER POLYFLUORINATED SUBSTANCES IN THE ENVIRONMENT FROM THE NATIONAL NOVANA PROGRAMME

Substance	Point source	Number of samples *1	Median (maximum) concentration, mg/kg dw	Year	Source of information
PFOS	Lake sediment	18 (18)	<0.010 (<0.010)	2009	Bjerring et al. 2010
	Fish liver	15 (15)	44.4 (156.0)	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<1.0	2006	Strand J. *et al.*, 2007
	Marine sediment	0 (8)	<1.0	2006	Strand J. *et al.*, 2007
PFOSA	Lake sediment	18 (18)	<0.010 (<0.010)	2009	Bjerring et al. 2010
	Fish liver	1 (15)	2.3 (2.3)	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.9	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.9	2006	Strand J. *et al.*, 2007
PFHxS	Lake sediment	18 (18)	<0.010 (<0.010)	2009	Bjerring et al. 2010
	Fish liver	3 (15)	1.4 (1.6)	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.7	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.7	2006	Strand J. *et al.*, 2007
PFOA	Lake sediment	18 (18)	<0.010 (<0.010)	2009	Bjerring et al. 2010
	Fish liver	12 (15)	6.18 (24.5)	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.4	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.4	2006	Strand J. *et al.*, 2007
PFNA	Lake sediment	18 (18)	<0.010 (<0.010)	2009	Bjerring et al. 2010
	Fish liver	6 (15)	2.45 (3.6)	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.7	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<0.7	2006	Strand J. *et al.*, 2007
PFDA	Lake sediment	18 (18)	<0.010 (<0.010)	2009	Bjerring et al. 2010
	Fish liver	9 (15)	3.64 (7.9)	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<1.0	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<1.0	2006	Strand J. *et al.*, 2007
PFUnA	Lake sediment	18 (18)	<0.010 (<0.010)	2009	Bjerring et al. 2010
	Fish liver	9 (15)	3.42 (9.4)	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<1.7	2006	Strand J. *et al.*, 2007
	Fresh water sediment	0 (8)	<1.7	2006	Strand J. *et al.*, 2007

*1 Number of positive samples in bracket

7.1.3 The Baltic Sea and North Sea environments

HELCOM concluded in a 2010 assessment report that the PFOS levels in many fish species and sub-regions of the Baltic Sea are higher than the estimated PNEC (predicted no effect concentration) level for the protection of predators, such as mammals and predatory birds, via secondary poisoning (HELCOM, 2009). The risks and threats of PFOA on the Baltic marine environment are currently difficult to estimate due to the lack of ecotoxicological information (i.e. PNEC value has not been comprehensively assessed) according to the study.

The results demonstrate relatively high concentrations of PFOS in the Kattegat and inner Danish waters, compared with levels found in the Baltic Sea (HELCOM, 2009). The concentrations of PFOS in the liver of seals from Danish waters were in the range of 565 to 977 µg/kg while the range for PFOA was 0.3-1.3 µg/kg. For herring and other fish, levels were more uniform across the region. In the Danish waters the concentration of PFOS ranged from 10 to 60 µg/kg ww, while for PFOA it ranged from 1 to 10 µg/kg ww.

The assessment did not include data for other PFASs.

In a screening of perfluorinated substances in the Nordic environment (Kallenborn, 2004) found that lake water, seawater and rainwater (precipitation) samples were contaminated at relatively low levels. However, measurable amounts of PFAS were found in all samples. The Nordic biota samples showed signals of species-dependent distribution and levels. The highest PFAS levels were found in the top predator, the Danish harbour seal (*Phoca vitulina*) samples with PFOS as the predominant PFAS contaminant.

A study of the distribution of PFASs in sediments from the North Sea and the Baltic Sea analysed the spatial and temporal variation the concentrations of PFBS, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFNA, PFDA, and PFOSA (Theobald *et al.,* 2011). PFASs could be detected in sediments from all 15 stations which had been sampled. In most samples from the German Bight and western Baltic Sea, PFOS had the highest concentrations (0.02 to 2.4 ìg/kg dry weight), followed by PFOA at 0.06 to 1.6 ìg/kg dry weight. Levels of the other PFASs were five to ten times lower. In order to assess the potential of sediments for the investigation of PFAS time trends, a segmented core from an accumulating area in the Skagerrak (northern North Sea) was analysed. PFOS and PFOA concentrations clearly increase from the lowest layers to the surface layer, indicating a steady increase in PFAS concentrations over the last years. The PFOS and PFOA curves show a nearly parallel temporal development. Similar trends were observed for the other PFCAs (PFHxA, PFHpA, PFNA, PFDA), though at lower concentration levels. The time trends of the PFASs differ fundamentally from those of the “classical” pollutants like PCBs, DDT and HCB, for which used ceased earlier. The data demonstrates that the increase in PFOS concentrations started in the mid-1980s and accelerated for both PFOA and PFOS since approximately 1995.

Ahrens *et al. (*2010) examined the spatial distribution of 15 PFCs in surface water in the North Sea, Baltic Sea and Norwegian Sea. In the North Sea, the highest concentration was found near the coast, whereas the PFC concentration decreased rapidly from 18.4 to 0.07 ng/L towards the open North Sea. The river Elbe could be identified as a local input source for PFCs into the North Sea, whereas perfluorobutanoicacid (PFBA) was transported into the sampling area with the easterly current. In contrast to the North Sea, the distribution of PFCs in the Baltic Sea was relatively homogenous, where diffuse sources dominated. In general, the composition profile was influenced from local sources caused by human activities, whereas atmospheric deposition of PFCs were negligible, but according to the authors, the deposition could possibly have an influence on lesser-contaminated sites like the open North Sea or Norwegian Sea.

7.1.4 PFASs in the Arctic environment

PFASs have been detected in air, water, sediment, wildlife and human beings all around the world. Atmospheric transport and global ocean currents have been suggested as the pathways of the PFASs’ global transport.

Volatile precursors, such as FTOHs, can undergo long-range atmospheric transport and can be degraded via abiotic and biotic mechanisms. The detection of FTOHs in the Arctic and Antarctic air agreed with the model prediction and conclusion, and supported the hypothesis of atmospheric transport toward remote regions. Dreyer *et al. (*2009) found that total gas-phase concentrations of ship-based samples ranged from 4.5 pg/m^3 in the Southern Ocean to 335 pg/m^3 in European source regions. Concentrations of 8:2 FTOH, the analyte that was usually observed in highest concentrations, were between 1.8 and 130 pg/m^3. PFC concentrations decreased from continental regions toward marine regions and from Central Europe toward the Arctic and Antarctica. According to the authors, the study gives further evidence that volatile PFCs undergo long-range atmospheric transport to remote regions and may contribute to their contamination with persistent PFCAs and PFSAs.

The significance of precursors to the levels of PFASs found in the Arctic is not well understood for all substances.

Most modelling results address transport of PFOA; these conclude that the degradation of FTOHs is likely toy be a minor source of PFSAs in the Arctic.

Ionic PFCAs and perfluoroalkyl sulfonates (PFSAs), which have higher water solubility, are mainly distributed in surface waters. Global transport by marine ocean currents was indicated as the major pathway of PFASs' delivery to non-emission regions by both monitoring and modelling results (Zhao *et al.,* 2012).

Stemmler and Lammel (2010) used a global multicompartment model, including fully coupled three-dimensional ocean and atmospheric general circulation models, to approximate the transport of PFOA to the Arctic. In addition to primary emissions, the formation of PFOA in the atmosphere from degradation of 8:2 FTOH was included as a PFOA source. According to the model Oceanic Transport, 8–23 t/y was delivered to the Arctic; this pathway constituted the dominant source of PFOA to the Arctic. Formation of PFOA in the atmosphere led to episodic transport events (timescale of days) into the Arctic The total atmospheric deposition of PFOA in the Arctic in the 1990s was estimated at about 1 t/y and was dominated by primary emissions of PFOA rather than secondary formation from FTOH.

In accordance with this work, Prevedouros *et al. (*2006) calculated the amount of perfluorooctanoic acid (PFOA) transported to the Arctic Ocean by water as 2-12 t/y.

Zhao *et al. (*2012) detected elevated levels of ∑PFASs in the North Atlantic Ocean with the concentrations ranging from 130 to 650 pg/L. In the Greenland Sea, the ∑PFAS concentrations ranged from 45 to 280 pg/L, and the five most frequently detected compounds were perfluorooctanoic acid (PFOA), perfluorohexanesulfonate (PFHxS), perfluorohexanoic acid (PFHxA), perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS).

The presence of PFASs in the Arctic environment has been extensively studied, among others as part of the Arctic Monitoring and Assessment Programme (AMAP). The available data have been reviewed by Butt *et al. (*2010) as part of the AMAP POPs assessment (2009) and by Houde *et al. (*2011).

According to Butt *et al. (*2010) "*The bulk of the monitoring efforts in biological samples have focused on the perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs), although there are very few measurements of PFC precursors. The marine food web has been well studied, particularly the top predators. In contrast, freshwater and terrestrial ecosystems have been poorly studied. Studies from show that in wildlife perfluorooctane sulfonate (PFOS) is generally measured in the highest concentration, followed by either perfluorononanoate (PFNA) or perfluoroundecanoate*

(PFUnA). However, some whale species show relatively high levels of perfluorooctane sulfonamide (PFOSA) and seabirds are typically characterized by high proportions of the C11–C15 PFCAs. PFOA is generally infrequently detected and is present in low concentrations in Arctic biota. Food web studies show high bioaccumulation in the upper trophic-level animals, although the mechanism of PFC biomagnification is not understood. Spatial trend studies show some differences between populations, although there are inconsistencies between PFC trends. The majority of temporal trend studies are from the Northern American Arctic and Greenland. Studies show generally increa sing levels of PFCs from the 1970s, although some studies from the Canadian Arctic show recent declines in PFOS levels. In contrast, ringed seals and polar bears from Greenland continue to show increasing PFOS concentrations. The inconsistent temporal trends between regions may be representative of differences in emissions from source regions."

Houde *et al. (*2011) notes in a review of monitoring of PFCs in aquatic biota, that the most notable observation made was the preponderance of long-chain PFCAs found in organisms, particularly from East Asia and northern latitudes. PFCs detected in livers of tuna collected from the Pacific rim were predominantly PFOS and PFUnA, whereas PFDA and perfluorododecanoate (PFDoA) were also commonly identified (please find original references in the review). The predominance of PFUnA was also observed in livers of dolphins and porpoises, fish, and water bird eggs from several sites in Asia. In addition to Asian sites, the long-chain PFCA profile was also observed in Arctic regions. High proportion of C11-C15 PFCAs were found in Arctic seabirds and PFCA concentrations in polar bear liver were composed largely of C9- C11 with much lesser amounts of PFOA, PFDoA, and perfluorotridecanoate (PFTrA). The contamination profile may suggest specific sources of emission in East Asia dominated by long-chainPFCAs followed by long-range transport via ocean and atmospheric pathways to Northern regions of the globe, according to the authors. The overall observations made in aquatic wildlife worldwide seem to indicate that PFCA levels may surpass those of PFSAs in the future. However, this prediction also depends on trends in use and emissions (Houde *et al.,* 2011).

A recent study supported by the Nordic Council of Ministers analysed 18 PFASs in tissues of different marine mammals from the Arctic (Dam *et al.,* 2011). PFOS was generally found in the highest concentrations. A significant decrease in PFOS was found in hooded seals (1990–2007). On the other hand, increasing trends of one or more PFASs were found in samples of ringed seals, in pilot whales, white-sided dolphins and harbour porpoises. For PFUnA, a significantly increasing trend was found for ringed seals, pilot whales and white-sided dolphins, indicating that levels of the longer-chained PFASs are still increasing. The results are in accordance with the other results reviewed by Houde *et al. (*2011) and mentioned above.

7.1.5 PFOS and other polyfluorinated substances in point sources

In point sources such as wastewater treatment plants, industrial plants and landfills, significant differences in concentration levels have been observed among the different facilities.

The most recent monitoring data are shown in Table 22.

The available data suggests that wastewater treatment plants may be local sources of PFOS substances, as these substances were found not only in inlet water and sludge, but also in outlet water (Strand *et al.,* 2007). By far the highest concentrations of PFOS were found in the outlet water from an industrial facility. However, it was concluded in the study that the concentrations of PFAS in the outlet water were below the critical value where a risk to aquatic organisms is presented.

For data on effluents from landfills please see section 4.2.1.

TABLE 22
MOST RECENT MONITORING DATA FOR PFOS AND OTHER POLYFLUORINATED SUBSTANCES IN THE ENVIRONMENT FROM THE NATIONAL NOVANA PROGRAMME

Substance	Point source	Number of samples	Median (maximum) concentration, mg/kg dw	Year	Source of information
PFOS	Water WWT outlet	11 (13)	8,3 (18,1)	2006	Strand J. *et al.*, 2007
PFOS	WWT sludge	7 (7)	21,7 (74,1)	2006	-"-
PFHxS	Water WWT outlet	7 (13)	1,4 (2,7)	2006	-"-
PFHxS	WWT sludge	7 (7)	3,8 (10,7)	2006	-"-
PFOSA	Water WWT outlet	4 (13)	1,6 (2,1)	2006	-"-
PFOSA	WWT sludge	1 (7)	3,6 (3,6)	2006	-"-
PFOA	Water WWT outlet	12 (13)	15,1 (24,4)	2006	-"-
PFOA	WWT sludge	7 (7)	4,2 (19,7)	2006	-"-
PFNA	Water WWT outlet	10 (13)	2,4 (3,1)	2006	-"-
PFNA	WWT sludge	7 (7)	1,7 (8)	2006	-"-
PFDA	Water WWT outlet	2 (13)	3,1 (3,6)	2006	-"-
PFDA	WWT sludge	7 (7)	8,7 (10,5)	2006	-"-
PFUnA	Water WWT outlet	0 (13)	<2,2	2006	-"-
PFUnA	WWT sludge	3 (7)	2,2 (4,4)	2006	-"-

As part of the COHIBA project, running from 2009 to 2012 and co-financed by European Union within the Baltic Sea Region Programme, PFOS and PFOA sources of emissions of PFOS and PFOA to the Baltic Sea were identified and measures for emission reduction evaluated (COHIBA, 2011a,b). The following paragraph is extracted from the report on emission reduction measures.

Within the project, sources of emissions of PFOS and PFOA to the Baltic Sea were assessed on the basis of substance flow analyses (SFA) and review of the literature. Total input of PFOS/PFOA to all environmental compartments in the Baltic Sea catchment was estimated at 300-600 kg/year (around year 2010). Approximately 40% of the total load was emitted to water. The contribution of emissions from municipal waste water treatment plants to the total load was estimated to be in the range of 30% for PFOS and 40% for PFOA. These amounts included direct emissions to water via treatment plant effluent, as well as emissions to (agricultural) land via sewage sludge. The load in municipal waste water originated from urban stock (products), as well as from indirect dischargers, for example metal plating facilities. PFOA releases due to transformation of fluorotelomer were estimated to account for 30% of all releases. The largest contribution to the total load of PFOS/PFOA came from the use of fire fighting foam containing PFOS (and PFOA as impurity). It was estimated that the fire-fighting foams accounted for 70% of the total emissions, while accounting for 20% of the emissions of PFOA. This emission estimate was subject to high uncertainty, since the load emitted to the environment (mainly to land) depends on the incidence of fires and the fate of used fire fighting foam. This use of PFOS has been banned in the EU since 2008; the remaining stocks had to be used or destroyed by mid 2011 (see Chapter 4). Therefore, emissions from this source would currently be expected to decline sharply.

7.1.6 FFASs in groundwater

PFASs are not monitored in groundwater in Denmark.

A pan-European survey of the occurrence of other selected polar organic persistent pollutants in groundwater from 2011 presents data for PFOS, PFOA and PFHxS, PFHpA. The survey includes groundwater samples from Denmark and 22 other EU Member States from a total of 164 locations, but the data are not presented by country.

The maximum and average concentrations of PFOS were higher than the concentration of the three other substances, whereas the median concentration is highest for PFOA. Median concentrations are presented without decimals which make the data difficult to interpret.

TABLE 23
OCCURENCE OF PFOS, PFOA AND PFHXS, PFHPA IN GROUNDWATER ACROSS THE EU (LOOS *ET AL.*, 2010)

Chemical	Limit of detection, ng/L	Freq. of detection (%), ng/L	Max ng/L	Average ng/L	Median ng/L	90th per-centile
PFOS	0.4	48.2	135	4	0	11
PFOA	0.4	65.9	39	3	1	6
PFHxS	0.4	34.8	19	1	0	5
PFHpA	0.4	29.9	21	1	0	1

7.1.7 Environmental risk limits

The National Institute for Public Health (RIVM) in the Netherlands have developed environmental risk limits for PFOS and proposed water quality standards in accordance with the Water Framework Directive (RIVM, 2010).

TABLE 24
DERIVED MPC, MAC_{ECO}, NC, AND SRC_{ECO} VALUES FOR PFOS (RIVM, 2010)

ERL	MPC		MAC_{eco}	NC		SRC_{eco}
	µg/L	ng/L	µg/L	µg/L	ng/L	µg/L
Freshwater	6.5×10^{-4}	0.65	36	6.5×10^{-6}	0.0065	930
Surface water intended for drinking water abstraction	0.53	530	n.a.	n.a.	n.a.	n.a.
Marine water	5.3×10^{-4}	0.53	7.2	5.3×10^{-6}	0.0053	930

n.a. = not applicable

7.2 Human exposure and biomonitoring

Human exposure to PFASs was reviewed in the 2008 survey of fluorinated substances in impregnated consumer products and impregnating agents (Poulsen et al. 2008). The following review focuses on newer findings.

7.2.1 PFAS in food and dietary exposure

EU

In 2010, the European food safety authority EFSA issued a call for data on PFASs in food with a closing date of 31 January 2012. Thirteen countries have submitted 56,862 analytical results on 27

PFASs in food covering the sampling period 1998 to 2012. In addition, data on PFASs in food from a three-year EU research project (PERFOOD 8) were submitted to EFSA.

EFSA has summarised the information on the occurrence of perfluoroalkylated substances in food and estimated dietary exposure (EFSA, 2012). The following has been extracted from the report. Table 6 lists PFASs for which data were reported and to what extent quantified results were reported. For eleven of the substances, all analytical results were below the limit of detection or limit of quantification. A total of 54,195 analytical results were included in the assessment.

Most results were available for PFOS and PFOA, while results for PFPeDA, 8:2 FTOH, 8:2 monoPAP, 8:2 diPAP, EtFOSA, EtFOSE and FC-807 were very low. Across food groups, the highest number of data were available for 'Fish and other seafood' (n = 25,328) and 'Meat and meat products (including edible offal)' (n = 13,780).

Across food groups, PFASs were reported more frequently in fish and other seafood, in meat and meat products and to a lesser extent in other food groups. The highest concentrations for the different PFASs were found in edible offal and in particular in liver. Individually quantified values ranged from a low of 0.00034 µg/kg for drinking water to a high of 3480 µg/kg for wild boar liver. However, generally food with the highest concentrations does not have the greatest impact on exposure because the quantities consumed are low (e.g. liver from wild animals). Fish from fresh water were more highly contaminated than marine fish and diadromous fish (fish living in both salt and fresh water).

TABLE 25
LIST OF PFASS FOR WHICH DATA ON THE SUBSTANCES IN FOOD WERE REPORTED (EFSA, 2012)

PFAS family/substance	Acronyms	C atoms	Number of observations	Frequency quantified
Perfluoroalkyl carboxylic acids	PFCAs			
Perfluorobutanoic acid	PFBA	C4	1628	not detected
Perfluoropentanoic acid	PFPA	C5	2307	3%
Perfluorohexanoic acid	PFHxA	C6	3355	4%
Perfluoroheptanoic acid	PFHpA	C7	2486	2%
Perfluorooctanoic acid	PFOA	C8	7536	9%
Perfluorononanoic acid	PFNA	C9	3814	5%
Perfluorodecanoic acid	PFDA	C10	3715	6%
Perfluoroundecanoic acid	PFUnA	C11	2680	7%
Perfluorododecanoic acid	PFDoDA	C12	2693	6%
Perfluorotridecanoic acid	PFTrDA	C13	1495	6%
Perfluorotetradecanoic acid	PFTeDA	C14	1855	0.6%
Perfluoropentadecanoic acid	PFPeDA	C15	3	not detected
Perfluorohexadecanoic acid	PFHxDA	C16	968	not detected
Perfluorooctadecanoic acid	PFODA	C17	947	not detected
Perfluoroalkane sulfonic acids	PFSAs			
Perfluorobutane sulfonic acid	PFBS	C4	3197	2%
Perfluorohexane sulfonic acid	PFHxS	C6	3222	2%
Perfluoroheptane sulfonic acid	PFHpS	C7	761	0.1%
Perfluorooctane sulfonic acid	PFOS	C8	7523	29%
Perfluorodecane sulfonic acid	PFDS	C10	1851	0.7%
Perfluoroalkane sulfinic acids	PFSIAs			
Perfluorooctane sulfinic acid	PFOSI	C8	136	not detected
(n:2) Fluorotelomer alcohols	(n:2) FTOHs			
8:2 Fluorotelomer alcohol	8:2 FTOH	C8	18	not detected
Polyfluoroalkyl phosphoric acid esters	PAPs			
8:2 Fluorotelomer phosphate monoester	8:2 monoPAP	C8	13	not detected
8:2 Fluorotelomer phosphate diesters	8:2 diPAP	C8	3	not detected
Perfluoroalkane sulfonamides	FASAs			
Perfluorooctane sulfonamide	PFOSA	C8	1930	7%
N-ethyl perfluoroalkane sulfonamides	EtFASAs			
N-ethylperfluorooctane sulfonamide	EtFOSA	C8	28	not detected
N-Ethyl perfluoroalkane sulfonamidoethanol	EtFASEs			
N-Ethyl perfluorooctane sulfonamidoethanol	EtFOSE	C8	28	not detected
Perfluoroalkyl phosphate	FC-807	C8	3	not detected

The contributions from the different food groups to the total dietary exposure varied among the substances. The figures below show the contributions from different food groups to the total dietary exposure for PFOS and PFOA respectively.

The highest contributors to dietary PFOS exposure across all age classes were “Fish and other seafood”, whereas for PFOA, the exposure was more evenly distributed between food groups.

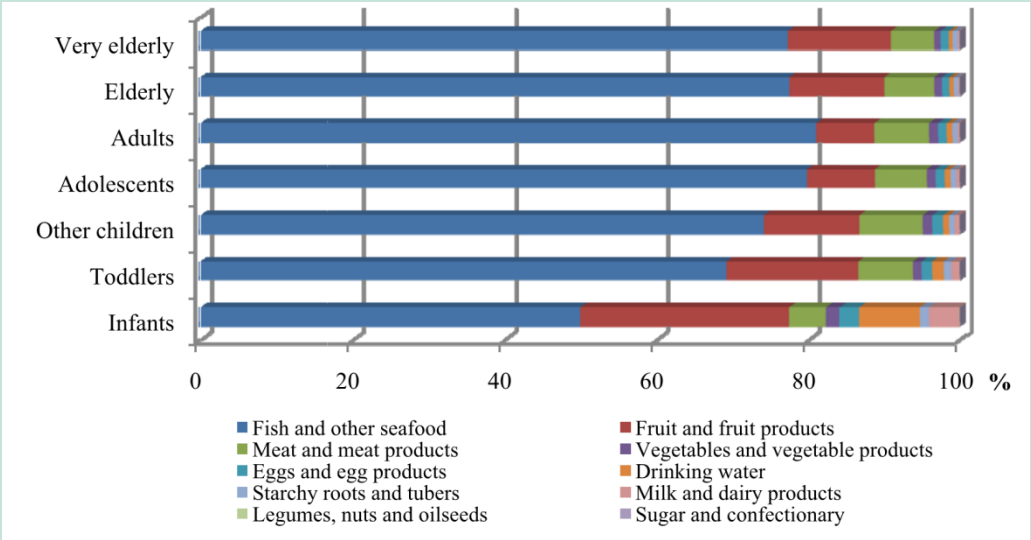


FIGURE 7
AVERAGE CONTRIBUTION (IN PERCENTAGE) OF BROAD FOOD GROUPS TO OVERALL LOWER BOUND MEAN PFOS EXPOSURE BY AGE GROUP (EFSA, 2012)

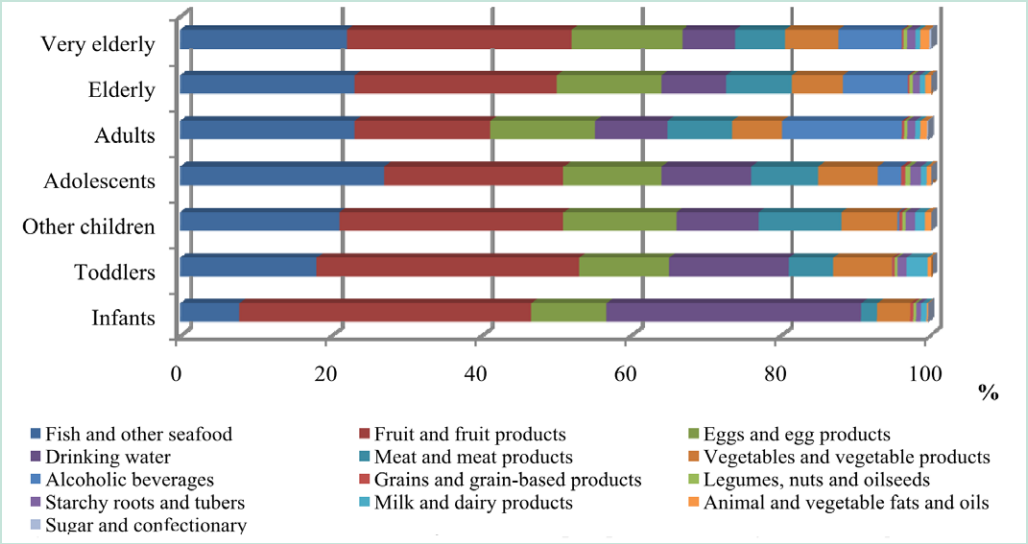


FIGURE 8
AVERAGE CONTRIBUTION (IN PERCENTAGE) OF BROAD FOOD GROUPS TO OVERALL LOWER BOUND MEAN PFOA EXPOSURE BY AGE GROUP (EFSA, 2012)

Based on the available occurrence data for 16 PFASs in fish, a comparison of the lower-boundary mean concentrations found in fresh water fish, marine fish and diadromous fish was performed

(Figure 9). The results showed consistently higher mean concentrations in fish from fresh water. Diadromous fish had mean concentrations slightly higher or similar to the marine fish. PFOS had a markedly higher mean concentration in all three fish categories than the other PFASs, whereas the concentration of PFOA was in the same range as most of the other PFAS.

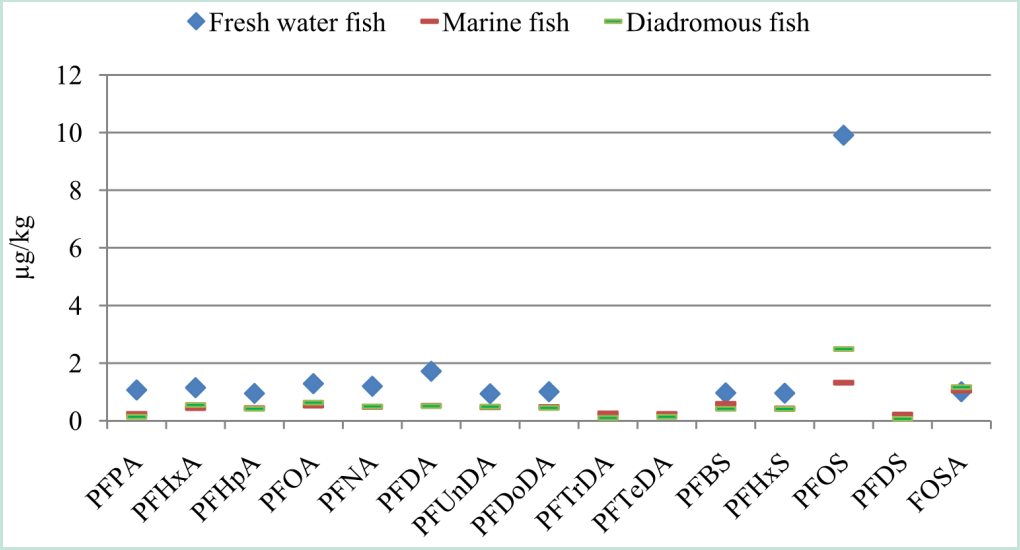


FIGURE 9
COMPARISON OF PFASS LOWER BOUND MEAN CONCENTRATIONS IN FISH IN RELATION TO THEIR AQUATIC ENVIRONMENT. NO DATA ON FRESH WATER FISH WERE AVAILABLE FOR PFTrDA, PFTeDA AND PFDS (EFSA,2012)

Dietary exposure was calculated using the overall European lower and upper boundary mean occurrence of PFASs. The low proportion of quantified results prevented calculation of a more realistic dietary exposure. The upper boundary results are highly overestimated, but still the exposure estimates in all age classes and for both the mean and the 95th percentile consumers were well below the TDIs for PFOS (150 ng/kg bw per day) and PFOA (1500 ng/kg bw per day) set by the EFSA Scientific Panel on Contaminants in the Food Chain (EFSA, 2008).

The TDI is based on animal studies and is discussed in Chapter 0.

For PFOS, the highest upper boundary mean exposure estimate for the adult population (5.2 ng/kg bw per day) represented 3.5 % of the TDI while the highest 95th percentile estimate (10 ng/kg bw per day) represented 6.7 % of the TDI. In toddlers, the age class having the highest exposure, the same parameters represented 9.3 % and 19 % of the TDI, respectively.

The highest contributors to dietary PFOS exposure across all age classes were 'Fish and other seafood' (50 to 80 %) followed by 'Fruits and fruit products' (8 to 27 %) and 'Meat and meat products' (5 to 8 %).

For PFOA, the chronic dietary exposure (long-term exposure over the entire lifetime.) in all age classes and for both average and high consumers was also far below the TDI. For adults, the highest upper boundary mean estimate (4.3 ng/kg bw per day) represented 0.3 % of the TDI while the highest 95th percentile estimate (7.7 ng/kg bw per day) represented 0.5 % of the TDI. In toddlers, the age class having the highest exposure, the highest mean and 95th percentile estimates would represent 1.1 % and 2.1 % of the TDI, respectively. The most important contributors to PFOA exposure in all age classes were 'Fruits and fruit products' (18 to 39 %) and 'Fish and other seafood' (7.6 to 27 %) but high variations were observed in relation to dietary habits.

For children younger than 1 year, EFSA notes that the uncertainty is particular high due to a lack of dietary surveys reporting consumption data for this age group.

Based on the available data with a low proportion of quantified results, the chronic dietary exposure to the other 25 single PFASs is expected to be in the low ng/kg bw per day range or even lower. Since no TDIs are available for these PFASs, it was not possible to evaluate the relevance of the dietary exposure for human health.

EFSA concludes that, based on further results from toxicological evaluations, the relevance of various PFASs to human health could be better established, thus allowing for the definition of a set of priority PFASs for future monitoring. The use of analytical methods with improved sensitivity would be required to monitor such priority PFASs in order to increase the proportion of quantified results and thereby the reliability of exposure assessments.

Denmark

The chronic dietary exposure to PFOS and PFOA in Denmark as compared to the EU average is shown in the table below. The exposures are calculated with relatively high uncertainties and the available data did not indicate significant differences between the exposure in Denmark and the EU average. Estimates of dietary exposure to other PFASs in Denmark are not available.

TABLE 26
MEAN AND 95 TH PERCENTILE (P95) CHRONIC DIETARY EXPOSURE TO PFOS (ng/kg BW PER DAY) FOR TOTAL POPULATION IN LOWER-BOUNDARY AND UPPER-BOUNDARY SCENARIO (EFSA, 2008)

Substance		Other children *1		Adolescents		Adults		Elderly		Very elderly	
		Mean	P95	Mean	P95	Mean	P95	Mean	P95	Mean	P95
PFOS	Denmark	1.8-7.2	5-14	0.8-3.9	2.4-7.3	0.8-3.0	2.1-5.6	1.0-3.7	2.2-6.5	1.2-4.1	*2
PFOS	EU, median	1.5-7.1	5.5-14	0.8-4.0	3.3-7.7	0.8-3.0	3.1-6.8	1.0-3.2	3.7-6.5	0.9-3.1	3.2-5.7
PFOA	Denmark	0.3-8.3	0.5-14	0.1-4.7	0.3-8.0	0.2-3.4	0.3-5.7	0.2-3.7	0.3-6.2	0.2-4.1	*2
PFOA	EU, median	0.2-6.8	0.4-11	0.1-3.8	0.3-7.0	0.1-3.2	0.3-5.4	0.2-3.0	0.3-5.0	0.1-3.0	0.3-4.9

*1 The report include data for infants, toddlers and "other children"; for Denmark only data for "other children" is calculated.

*2 P95 estimates for dietary surveys/age classes with less than 60 observations are not statistically robust and therefore not presented in the table.

Until 2011, analyses of PFOS in food were not included in the Danish monitoring programme for organic pollutants in food from environment and industrial processes.

In 2011, the Danish Veterinary and Food Administration (DVFA, 2012) has analysed for PFOS and PFOA in 43 samples, of which eight were samples of farmed fish (four from land-based trout farms, and four from marine trout farms) and 35 were other samples of animal origin (four beef, three chicken and 28 pork). No concentrations of PFOS or PFOA above the detection limit of 0.5 ng/g wet weight were found in the 35 samples of animal meat (DVFA, 2012a). PFOS was found in a concentration of 0.53 ng/g wet weight (just above the detection limit) in one sample of farmed trout (from a marine fish farm); however, the other samples from fish did not reveal any PFOS contents. Samples were also taken from wild fish, where PFOS was detected in all samples at mean concentrations of 1.3-3.3 ng/g (2012b.) PFOA was not detected in any of the samples.

7.2.2 PFASs in drinking water

PFASs are not covered by any monitoring programmes for groundwater or drinking water in Denmark.

PFASs in drinking water have recently been reviewed by Fromme *et al. (*2009) and D'Hollander *et al. (*2010). Data from Japan, Germany, Spain and Italy varies considerably. Particularly high levels are reported from contaminated areas in Germany.

TABLE 27
OBSERVED RANGE OF PERFLUORINATED CHEMICALS IN DRINKING WATER, ng/L (D'HOLLANDER *ET AL.,* 2010)

Sampling sites (*n*) Country, sampling date	**PFHxA***	PFHpA	**PFOA**	**PFBS**	PFHxS	**PFOS**	PFNA	PFDA	PFUnA	PFDoA	References **
Tokyo, Kyoto Japan, not given						0.1-51					Harada *et al.* (2003)
Osaka and Tohoku, Area, Japan 2003			0.7-50			<0.1-12					Saito *et al.* (2004)
Rhine, Ruhr Moehne area, Germany 2006	<1-56	<1-23	<1-519	<1-26		<1-22					Skutlarek *et al.* (2006)[a]
Area of Lake Maggiore (n = 6) Italy 2007		0.3-0.8	1.0-2.9			6.2-9.7	0.3-0.7	0.1-0.3	0.1-0.4	0.1-2.8	Loos *et al.* (2007)
Catalonia (n = 4) Spain 2007	<0.9	<0.6-3.0	0.3-6.3	<0.3	<0.2-0.3	0.4-0.9	<0.4-0.5	<0.8	<0.4	<0.3	Ericson *et al.* (2008b)[b]
Catalonia (n = 4)[c] Spain 2007	<0.9	<0.6-0.4	0.2-0.7	<0.3	<0.2	<0.24	<0.4-0.2	<0.8-0.6	<0.4	<0.3	Ericson *et al.* (2008b)[b]
Osaka (n = 14) Japan 2006-2007			2.3-84			<0.1-22					Takagi *et al.* (2008)

*PFHxA: perfluorohexanoic acid; PFHpA: perfluoroheptanoic acid; PFOA: perfluorooctanoic acid; PFBS: perfluorobutane sulfonate; PFHxS: perfluorohexane sulfonate; PFOS: perfluorooctane sulfonate; PFNA: perfluorononanoic acid; PFDA: perfluorodecanoic acid; PFUnA: perfluoroundecanoic acid; PFDoA: perfluorododecanoic acid
aSkutlarek *et al. (*2006) measured also PFBA (perfluorobutanoic acid, <1-11); PFPeA (perfluoropentanoic acid, <1-77)
bEricson et al. (2008b) measured also PFBS (<0.3); THPFOS (1,1,2,2,-tetrahydro perfluorooctanoic acid, <1.0); PFOSA (<0.19); PFDS (perfluorodecane sulfonate, <1.0), and PFTdA (perfluorotetradecanoid acid, <0.9)
cBottled water
** see original source for full references

Guidelines for PFOS and PFOA in drinking water have been issued by the authorities in several EU Member States. The Health Protection Agency (HPA) in the UK, for example, advises that the maximum acceptable concentration of perfluorooctane sulfonate (PFOS) in drinking water is 0.3 µg/L, and that the maximum acceptable concentration of perfluorooctanoic acid (PFOA) in drinking water is 10 µg/L (Health Protection Agency, 2012). These concentratins are well above the maximum concentration of PFOS found in ground water in Table 23.

7.2.3 Consumer products as sources of PFASs

Releases of PFASs from consumer products may be a source of exposure to PFASs in the home.

In order to make an estimation of exposure, Washburn *et al. (*2005) determined concentrations of PFOA in the consumer articles from extraction tests and product formulation information. Potential exposures during consumer use of the articles were quantified based on an assessment of behaviour patterns and regulatory guidance. For each of the population groups addressed, exposures were quantified for mill-treated carpeting, solution-treated carpeting (including home application of carpet-care solution), apparel (treated with fluorotelomer-based product, sometimes containing a fluoropolymer membrane), treated nonwoven medical garments, non-stick cookware, and thread seal tape. For the Reasonable Maximum Exposure (RME) Scenarios the treated carpeting accounted for the highest contribution to the hypothetical annual average intake. The RME value for infants due to exposure to PFOS in the carpeting was one to two orders of magnitude higher than the RME values for adult residents.

Guo *et al. (*2009) analysed the PFCA content of 116 consumer products ("articles of commerce") and estimated the quantities which could be present in a "typical" American home. Given the quantities of articles found in typical homes, it was concluded that professional carpet-care liquids, pretreated carpeting, treated floor waxes and sealants, and treated home textile products and upholstery are likely to be the most important PFCA sources in non-occupational indoor environments. According to the study, limited data suggest that the PFCA content in consumer products has shown a downward trend overall; however, definitive confirmation of such a trend will require long-term monitoring.

Food packaging and cookware as sources of PFASs in the food

A report from EFSA with results of the monitoring of PFASs in food in the period 2000 – 2009 (EFSA, 2011) includes a brief discussion of the significance of packaging and cookware as a source of the substances in the food. According to the report, Jogsten *et al.* (2009, as cited by EFSA, 2011) evaluated the exposure to PFASs from consumption of various raw and cooked foodstuffs, including packaged food. It was not sufficiently clear as to whether cooking with non-stick cookware or packaged foods, could contribute to a higher human exposure to PFASs. Nelson *et al. (*2010, as cited by EFSA, 2011) found a positive association between the serum concentration of PFOA and PFNA and fast food consumption. The authors suggest that PFASs may enter the food chain both through bioaccumulation and contact with packaging.

The French Food Safety Agency evaluated the potential human health risks related to the residual presence of PFOA in non-stick coatings for cookware in 2009 (AFSSA, 2009 as cited by EFSA, 2011). It has been concluded that the consumer health risk related to residues of PFOA in non-stick coating for cookware is negligible.

A study by the Norwegian Institute of Public Health (2007, as cited by Posner *et al.,* 2007) examined the significance of exposure to PFOA from PTPE cookware. The study showed that in a worst case scenario an adult human would be exposed to 66 ng PFOA /kg bw, when drinking 100 ml of water cooked in a PTFE-coated pan. It was concluded that, even at an assumption of 100% uptake of PFOA, these low levels would not constitute an essential intake route for humans (Posner *et al.,* 2007).

Stahl *et al. (*2012), on the basis of a review of the existing literature, reach the conclusion that given the present state of knowledge, it is not possible to say whether the use of nonstick-coated cooking utensils or packaging materials with PFC-based coating lead to a significant increase in dietary intake.

PFASs in packaging on the Danish market and migration from the packaging are described in section 3.3.2. The significance of the migration as regards the human exposure was not estimated.

Clothing as a source of PFAS exposure

According to the German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) it has not been shown that consumers are significantly exposed to PFOA and FTOH from clothing fabrics (Umweltbundesamt, 2009). The BfR estimates that the maximum quantity amounts to 20 ng/kg gram of body weight. A recently published report came to the conclusion that less than one per cent of the daily uptake of PFOS and PFOA occurs through the skin (Kudo *et al.,* 2002 as cited by Umweltbundesamt, 2009).

7.2.4 Total human exposure

The total human exposure to PFOS and PFOA was reviewed in a Scientific Opinion of the Panel on Contaminants in the Food Chain in 2008 (EFSA, 2008). The EFSA Scientific reached the conclusion that for PFOA, the total contribution from the non-food sources, mainly indoor exposure, could be as high as 50% of the estimated average dietary exposure to PFOA (EFSA, 2008).

Fromme *et al. (*2009) and Trudel *et al. (*2008) have reviewed the current knowledge of PFAS monitoring data in environmental media relevant for human exposure. In this context, PFAS concentrations in indoor and ambient air, house dust, drinking water and food were outlined. Furthermore, the papers summarized human biomonitoring data of PFAS levels in blood, breast milk, and human tissues.

The estimated adult daily intake of PFOS, PFOA, ∑FTOH and ∑FOSE/FOSA for the general population is shown in Table 28 (Fromme et al., 2009).

As seen from the table, dietary exposure is the dominant intake pathway for PFOS and PFOA ∑ FOSE/FOSA, responsible for 91% and 99%, respectively, of the total intake of the general adult population using mean intake data. Using high daily intake data, house dust may be a significant source of PFOA exposure. A scoring by the authors using a simple one-compartment toxicokinetic model showed that the dietary intake corresponds well with the blood plasma level of the same population. The total estimated intake of PFOS and PFOA were well below the TDI values recommended by the EFSA Scientific Panel on Contaminants in the Food Chain of 150 ng/kg body weight for PFOS and 1500 ng/kg bw per day for PFOA.

For ∑FTOH and ∑FOSE/FOSA, in the mean exposure scenario, house dust is the the main source of exposure while in the high exposure scenario the diet may be the major exposure source for ∑ FOSE/FOSA.

The study did not specifically estimate the exposure of children. According to the Fromme *et al. (*2009), it is obvious from biomonitoring data that the internal exposure of children is comparable to that of adults, but the exposure situation of children is not well understood, and therefore the authors do not make any statements on the risks of children's exposure to PFAS using the data available. Trudel *et al. (*2008) notes that children tend to experience higher total uptake doses (on a body weight basis) than teenagers and adults because of higher relative uptake via food consumption and hand-to-mouth transfer of chemical from treated carpets and ingestion of dust.

Furthermore the authors conclude that besides this background exposure of the general population, a specific additional exposure may occur which causes an increased PFAS body burden. This has been observed in populations living near PFAS production facilities or in areas with environmental contamination of PFASs. The consumption of highly contaminated fish products may also cause an increase in PFAS body burdens.

In accordance with the results of Fromme *et al. (*2009), Trudel *et al. (*2008) concludes that the greatest portion of the chronic exposure to PFOS and PFOA is likely to result from the intake of contaminated foods, including drinking water. Consumer products cause a minor portion of the consumer exposure to PFOS and PFOA. Of these, it is mainly impregnation sprays, treated carpets in homes, and coated food contact materials that may lead to consumer exposure to PFOS and PFOA.

Haug et al. (2011) estimated individual PFC intakes from multiple exposure sources for a study group of 41 Norwegian women using measured PFC concentrations in indoor air and house dust as well as information from food frequency questionnaires and PFC concentrations in Norwegian food. Food was generally the major exposure source, representing 67-84% of the median total intake for PFOA and 88-99% for PFOS using different dust ingestion rates and biotransformation factors of 'precursor' compounds. However, on an individual basis, the indoor environment accounted for up to 50% of the total intake for several women. Significant positive associations between concentrations of PFCs in house dust and the corresponding serum concentrations underline the importance

of indoor environment as an exposure pathway for PFCs. For breast-fed infants, breast milk was calculated to be the single most important source to PFCs by far (Haug et al., 2011).

Several authors have emphasized that there may be additional sources of human exposure to PFOS and PFOA from precursor compounds including fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (PFOSAs) and amido alcohols (PFOSEs) that are metabolized to form PFOA and PFOS, respectively. Considering the potential routes of human exposure, Fromme *et al. (*2009) estimated the overall mean and high daily intake for a non-occupationally exposed adult population to two groups of potential precursors of PFCAs and PFAS: ∑FTOH, AND ∑FOSE/FOSA (Table 28).

Using some rough estimates regarding the percentage of the precursors converted in the human body to PFOS and PFOA, the authors conclude that FTOHs have only a negligible contribution (<1%) to the total mean and high intake PFOA exposures of adults. Moreover, the contribution of the converted ∑FOSAs/FOSEs to total PFOS exposure of the general population was estimated to reach only 10%.

TABLE 28
ESTIMATED ADULT DAILY INTAKE OF PFOS, PFOA, ∑FTOH, AND ∑FOSE/FOSA FOR THE GENERAL POPULATION. MEAN INTAKE BASED ON MEAN OR MEDIAN CONCENTRATIONS; HIGH INTAKE BASED ON UPPER PERCENTILE OR MAXIMUM CONCENTRATIONS (FROMME *ET AL.*, 2009)

Source	Daily intake pg/kg bw							
	PFOS		PFOA		∑FTOH		∑FOSE/FOSA	
	Mean	High	Mean	High	Mean	High	Mean	High
Indoor air	0.9	0.9	4.7	4.7	38.0	105.0	460.0	2,050.0
Outdoor air	1.3	12.0	0.1	1.0	3.0	3.2	1.1	11.5
House dust	16.4	1,028.3	31.7	4216.7	102.5	1,016.7	9,83.3	2,033.3
Diet	2,816.7	11,483.3	1,500.0	4,483.3	-	-	216.7	6,866.7
Drinking water	21.7	86.7	23.3	130.0	-	-	-	-
Overall intake	2,857	12,611	1,560	8,836	144	1,125	1,661	10,962

Vestergren *et al. (*2008) estimated the relative importance of precursor-based doses of PFOS and PFOA to be 2–5% and 2–8% in an intermediate scenario and 60–80% and 28–55% in a high-exposure scenario. Compared to the data of Fromme *et al. (*2009) the results of Vestergren *et al. (*2008) indicate that subgroups of the population may receive a substantial part of the PFOS and PFOA doses from precursor compounds, even though they are of low importance for the general population.

7.2.5 Human biomonitoring data

PFAS concentrations in the serum of exposed workers have been a subject of study since 1993, whereas data on serum concentrations in the general population have only been available since 1998 (Stahl *et al.,* 2011). Since then PFOS and PFOA in particular have been measured in human blood (including cord blood) and in human milk in many countries, while measurements in other specimen types are few. The data have been reviewed by several authors (e.g. Jensen *et al.,* 2008; Fromme *et al.,* 2009, Stahl *et al.,* 2011). Data up to 2008 were reviewed in the previous Danish survey of PFCs (Jensen *et al.,* 2008). The following focuses on the overall trend, in particular the temporal trends and the levels of other PFCs as compared with PFOS and PFOA, as well as data from Denmark.

Human blood

Poulsen *et al. (*2008) reviewed existing information on PFOS and PFOA in blood. As mentioned in the review, in blood the perfluorinated chemicals are mainly bound to serum proteins, especially albumin. In most studies blood serum is analysed but other studies analyse whole blood or blood plasma. When comparing such studies it is important to take into account that results will depend on what medium is analysed. The levels in serum or plasma are approximately two to three times the levels in whole blood. A summary of the PFOS and PFOA levels in serum/plasma samples across the world showed a wide range in concentration, with PFOS typically three to ten times higher than the concentration of PFOA (Figure 10). In a similar figure summarising the data on whole blood samples, the difference between PFOS and PFOA was less distinctive.

The levels shown are well in accordance with an overview prepared by OECD (2002) of PFOS and PFOA levels in human blood sampled in various countries from 1998-2000. The average levels ranged from 17 to 53 ng/mL for PFOS and 3 to 17 ng/mL for PFOA (OECD, 2002, as cited by Jensen *et al.,* 2008).

Mean and median concentrations for some PFASs, such as PFOS, from North American populations appear to be slightly higher than European, Asian, and Australian populations studied (Fromme *et al.,* 2009). Another commonly found substance that appeared to vary amongst populations was PFHxS. Concentrations reported were <0.4–40.0 mg/L for Europe, 0.1–20.9 mg/L for Asia and 00.4–712 mg/L for North America (Fromme *et al.,* 2009).

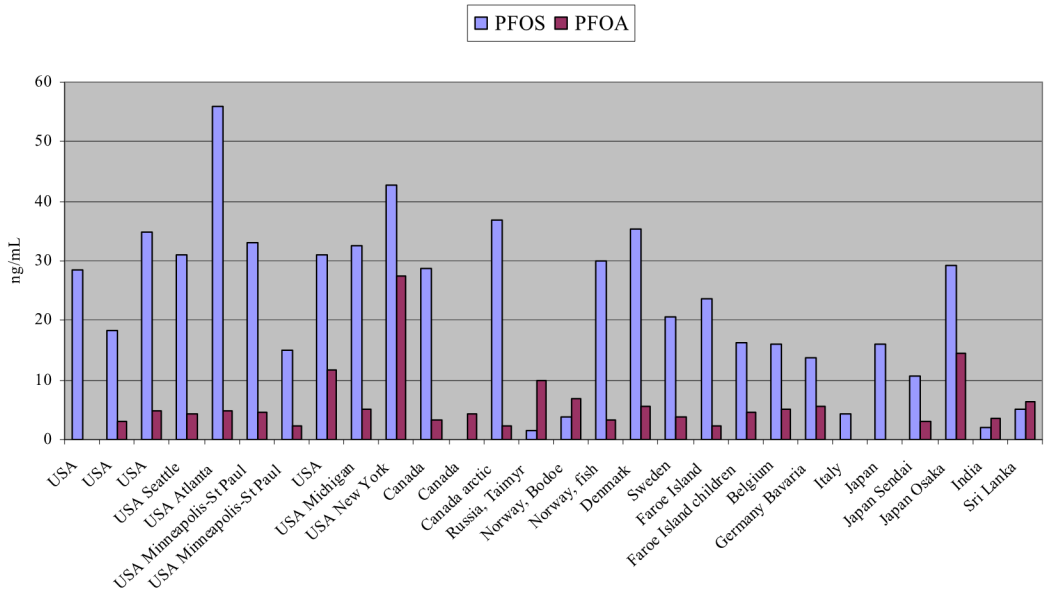


FIGURE 10
AVERAGE CONCENTRATIONS OF PFOS AND PFOA IN HUMAN BLOOD SERUM/PLASMA FROM VARIOUS COUNTRIES (POULSEN *ET AL.*,2008)

Vestergren and Cousins (2009) have reviewed a wide range of studies of PFOA in human blood sera from all over the world. The data show that the background-exposed population in the industrialized countries worldwide exhibits a narrow concentration range; arithmetic means of published studies range between 2 and 8 µg/L PFOA, with the exception of a few outlier studies. Significantly higher concentrations were found in ammonium perfluorooctanoate (APFO) production workers and elevated serum concentrations of PFOA (mean 27.4-423 µg/L) in non-occupationally exposed populations have been reported from areas where use of contaminated soil conditioner and a fluoropolymer production site, respectively, were identified as sources of contamination. The authors conclude that food intake is the major contemporary exposure pathway for the background popula-

tion, whereas drinking water exposure is dominant for populations near sources of contaminated drinking water.

Compared to the PFOS, PFOA and PFHxS, less information is available on other PFASs. In some recent studies, mean PFNA concentrations of 0.3–1.1 µg/L have been estimated, as summarised by Fromme *et al. (*2009). Other PFASs, such as PFDA or PFUnA, were found at only very low concentrations, if at all.

EFSA (2008) concludes that most studies did not find clear gender or age related differences in the concentrations of PFOS in blood, but also quotes data from the USA demonstration significantly higher levels in males than in females. Fromme *et al.* (2009) state, contrary to the conclusion of EFSA, that in the majority of the studies, differences in blood levels of PFOS between sexes have been observed with higher levels in male donors.

Since PFASs are highly persistent contaminants that do not undergo metabolism, it might be expected that PFAS body levels would increase with age. However, most studies that have examined the association of age with PFAS concentrations in blood (including plasma and serum) have not observed significant age effects (Fromme *et al.,* 2009).

Denmark
As reported in Jensen *et al. (*2008), a study by Fei *et al. (*2007) reports the results of PFOS and PFOA in 1399 blood plasma samples collected during March 1996 - November 2002 among a cohort of pregnant women in Denmark. The average levels of PFOS and PFOA were 35.3 ng/mL (range: 6.4-106.7 ng/mL) and 5.6 ng/mL (range: <1.0-41.5 ng/mL), respectively.

Surveys of the 1,076 Danish pregnant women published in 2008 (as part of studies into the effect of PFOS and PFOA on the foetus) showed an average mean concentration of PFOS in blood plasma, at the start of the pregnancy, of 35 ng/mL (Halldorsson *et al.,* 2008). The level of PFOS in the blood was relatively stable throughout the pregnancy and correlated positively with the intake of red meat, animal fats, and snacks (e.g. popcorn and crisps), whereas the level correlated negatively with the intake of vegetables and poultry. This suggests that intake from food, at least in the past, has been a significant source of PFOS intake in Denmark.

A study from 2011 of 652 Danish males addressng the connection between exposure to PFOS and PFOA and the risk of cancer, found only intake of eggs to correlate positively with the level of PFOS in the blood plasma (Eriksen *et al.,* 2011). However, in overall terms, these results did not suggest that diet is the primary source of exposure in Denmark. The results also suggested a geographical variation in the source of exposure in Denmark, in that people residing in Aarhus had significantly higher levels of PFOS in their blood plasma than people residing in Copenhagen. The paper gave no explanation for that difference.

As reported in Jensen *et al. (*2008), serum concentrations of 9 perfluorinated compounds (PFOS, PFOA, PFOSA, MeFOSA-AcOH, EtFOSA-AcOH, PFHxS, PFNA, PFDA and PFDoA) have been measured in two groups of Faroe Island residents (Kato *et al.,* 2007). The first group included 12 mothers sampled in 2000 and their 5 year old children sampled in 2005. The median concentrations for PFOS were 23.7 and 16.3 ng/mL respectively. The children had the lower levels. Levels of the other contaminants were much lower: 2.4 and 4.5 ng/mL, respectively, for PFOA. The second group consisted of 103 children of 7 years of age with samples collected in 1993-1994. The median concentration for PFOS was 29 ng/mL and for PFOA 5.5 ng/mL.

Sweden – temporal trends
Glynn *et al. (*2012) have recently investigated temporal trends of blood serum levels of 13 perfluorinated alkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in primiparous women (N =

413) from Uppsala County, Sweden, sampled 3 weeks after delivery 1996-2010. Levels of the short-chain perfluorobutane sulfonate (PFBS) and the long-chain perfluorohexane sulfonate (PFHxS) increased 11%/y and 8.3%/y, respectively, during the period and levels of the long-chain perfluorononanoate (PFNA) and perfluorodecanoate (PFDA) increased 4.3%/y and 3.8%/y, respectively. Concomitantly, levels of FOSA (22%/y), perfluorooctane sulfonate (PFOS, 8.4%/y), perfluorodecane sulfonate (PFDS, 10%/y), and perfluorooctanoate (PFOA, 3.1%/y) decreased. Therefore, one or several sources of exposure to the latter compounds have been reduced or eliminated, whereas exposure to the former compounds has recently increased. PFAA levels in maternal serum sampled during pregnancy and the nursing period as well as in cord blood were strongly correlated. The strongest correlations between cord blood levels and maternal levels were observed for maternal serum sampled shortly before or after the delivery.

Norway – temporal trends
Fifty-seven pooled archived human serum samples were analyzed to assess the time trends in the period 1976 to 2007 as well as the influence of age and gender of 19 PFCs in Norwegian residents (Haug *et al*., 2009). A 9-fold increase in the serum concentrations of PFOS, PFOA, and PFHpS was measured for men (40-50 years) from 1977 to the mid 1990s where the concentrations reached a plateau before starting to decrease around year 2000. A similar trend was also seen for PFHxS, PFNA, PFDA and PFUnA, but no clear decline was observed for these PFCs in recent years. The highest concentrations were found for PFOS and PFOA, with levels around 30 ng/mL and 5 ng/mL, when the concentrations peaked around year 2000 for men of the age group 40-50 years. In 2006 the concentrations in pooled serum samples from men, age 40-50 years were in decreasing order: PFOS (12 ng/mL), PFOA (2.7 ng/mL), PFHxS (1.4 ng/mL), PFNA (0.55 ng/mL), PFDA (0.22 ng/mL), PFPeDA (0.11), PFHpA (0.078 ng/mL), ng/mL), PFTrDA (0.071 ng/mL), and PFHpS (0.055 ng/mL). Other analysed PFCs were below the detection level.

Germany - temporal trends
From the PFC-affected area in the Sauerland, Germany time trend analysis of PFOS and PFOA samples of young adults (20–31 years old) indicated a slight, but not significant, increase in concentrations from 1977 to about 1990, which was then followed by a decreasing tendency of the concentration (Wilhelm *et al.,* 2008 as cited by Fromme *et al*., 2009). The sampling time period covered 1977–2004. In contrast, there was a clear linear increase of PFHxS plasma concentrations up to 2004.

USA – temporal trends
Based on 7876 serum samples collected from a representative sample of the general U.S. population 12 years of age during NHANES (National Health and Nutrition Examination Survey) 1999-2008, Kato *et al. (*2011) concluded that PFOS concentrations in the USA showed a significant downward trend, because of discontinuing industrial production of PFOS, but PFNA concentrations showed a significant upward trend. PFOA concentrations during 1999-2000 were significantly higher than during any other time period examined, but PFOA concentrations have remained essentially unchanged during 2003-2008. PFHxS concentrations showed a downward trend from 1999 to 2006, but concentrations increased during 2007-2008.

Olsen *et al. (*2012) analysed eleven PFASs in plasma from a total of 600 American Red Cross adult blood donors from six locations in 2010. Findings were compared to results from different donor samples analyzed at the same locations collected in 2000-2001 (N = 645 serum samples) and 2006 (N = 600 plasma samples). Most measurements in 2010 were below the lower limit of quantification for PFBS, PFPA, PFHxA, and PFDoA. For the remaining analytes, the geometric mean concentrations are shown in Table 29.

The decline in PFOS suggested a population half-life of 4.3 years. According to the authors this estimate is comparable to the geometric mean serum elimination half-life of 4.8 years reported in

individuals. This similarity supports the conclusion that the dominant PFOS-related exposures to humans in the United States were greatly mitigated during the phase-out period.

The concentration of PFOS in the blood was significantly higher than the concentration of any other of the analysed PFASs, with PFOA and PFHxA ranking second and third.

TABLE 29
GEOMETRIC MEAN CONCENTRATIONS OF PFASs IN BLOOD PLASMA FROM AMERICAN BLOOD DONORS (OLSEN *ET AL.*, 2012)

Analyte	Geometric mean concentrations, ng/mL			Decline, %
	2000/2001	2006	2010	
PFOS	34.9	14.5	8.3	76
PFOA	4.7	3.4	2.4	48
PFHxS	2.25	1.52	1.34	40
PFNA	0.57	0.97	0.83	45
PFDA	0.16	0.34	0.27	68
PFHpA	0.13	0.09	0.05	61
PFUnA	0.10	0.18	0.14	40

PFAS in breast milk
No Danish data on PFASs in breast milk have been obtained.

EFSA (2008) states that few data are available for PFAS in human milk. The results of local measurements in Sweden and China found that PFOS was present at similar concentrations in the milk from either country: 0.060– 0.470 (mean, 0.201) ng/mL in Sweden and 0.045–0.360 (mean, 0.121) ng/mL in China.

Based on the results of German samples, Vörkel *et al. (*2008) estimated an intake of 0.10 mg PFOS/day (using median) or 0.27 PFOS g/day (using maximum value) via breast milk for an infant of 5 kg body weight. The concentration ranged between 28 and 309 pg/mL (median:119 pg/mL). The data suggested that fully breastfed infants are unlikely to exceed the recommended tolerable daily intake of PFOS and PFOA, according to the authors.

More recently, based on data on the concentrations of PFOS, PFHxS, and PFOA in pooled human milk samples obtained in Sweden between 1972 and 2008 (a period representing the most significant period of PFAS production) Sundström *et al. (*2011) investigated whether the time trend of these substances in human milk parallels that indicated in human serum. PFOS was the predominant analyte present in the breast milk and all three analytes showed statistically significant increasing trends from 1972 to 2000, with concentrations reaching a plateau in the 1990s. In the last part of the 1990s, the measured concentrations of PFOS, PFHxS, and PFOA were at 212-237 pg/mL, 16-28 pg/mL, and 120-139 pg/mL, respectively. PFOA and PFOS showed statistically significant decreasing trends during 2001–2008. At the end of the study, in 2008, the measured concentrations of PFOS, PFHxS, and PFOA in pooled human milk were 75 pg/mL, 14 pg/mL, and 74 pg/mL, respectively. The temporal concentration trends of PFOS, PFHxS, and PFOA observed in human milk are parallel to those reported in the general population serum concentrations.

7.3 Summary on monitoring and exposure

Environmental monitoring and exposure

Seven PFASs are included in the NOVANA monitoring programme for point sources while only PFOS is included in the programme for marine animals. PFOS and PFOA are generally the predominant components of the measured PFASs in both effluent from point sources and in the aquatic environment in Denmark. An assessment from the Danish NOVANA programme and a HELCOM assessment concluded that the level of PFOS in fish may represent an environmental risk, especially to fish-eating birds and mammals at the highest tropic levels of the food chain, as most of the fish samples exceed the PNEC value. No conclusion was drawn for the other analysed FPASs. Data from EFSA demonstrates that the concentration of PFOS in freshwater fish is typically about 10 times higher than the concentration of each of the fourteen other analysed PFASs.

The risks and threats of PFOA to the Baltic marine environment are currently difficult to estimate due to the lack of ecotoxicological information according to a HELCOM assessment (i.e. PNEC value has not been comprehensively assessed). The assessment does not include other PFASs.

In a recent study of sediment from the German Bight and western Baltic Sea, PFOS had the highest concentrations followed by PFOA. The levels of seven other analysed PFASs were five to ten times lower.

In a study of 18 PFASs in tissues of different marine mammals from the Arctic, PFOS was generally found in the highest concentrations. A significant decrease in PFOS was found in hooded seals (1990–2007). Increasing trends of one or more PFASs were found in samples of ringed seals, in pilot whales, white-sided dolphins and harbour porpoises. For PFUnDA a significantly increasing trend was found for ringed seals, pilot whales and white-sided dolphins, indicating that levels of the larger PFASs are still increasing.

The maximum and average concentrations of PFOS in groundwater across the EU were higher than the concentration of the three other analysed substances (PFOA, PFHxS and PFHpA).

In all environmental compartments the concentration of PFOS exceeds the concentration of other PFASs. As expected, a decreasing trend has been demonstrated for PFOS while the concentration of other PFASs increase, although the concentrations are still well below the concentration of PFOS. The data confirm that the PFOS and PFOA are of the highest concern, but it would still be relevant to follow the trend of other PFASs and more specifically assess the potential risk of some of the newer PFASs.

Human biomonitoring and exposure

The dietary intake of PFOS and PFOA in the EU seems to be well below the established tolerable daily intake (TDI). According to a recent EFSA assessment for PFOS, the highest upper boundary mean exposure estimate for the adult population (5.2 ng/kg bw per day) represented 3.5 % of the TDI while the 95th percentile estimate (10 ng/kg bw per day) represented 6.7 % of the TDI. In toddlers, the age class having the highest exposure, the same parameters represented 9.3 % and 19 % of the TDI, respectively. For PFOA, the chronic dietary exposure in all age classes and for both average and high intake consumers was also far below the TDI. Based on the available data with a very low proportion of quantified results, EFSA expects the chronic dietary exposure to 25 other single PFASs to be in the low ng/kg bw per day range or even lower. Since no TDIs are available for these PFASs, it was not possible for EFSA to evaluate the relevance of the dietary exposure for human health.

EFSA concludes that the relevance of various PFASs to human health could be better established on the basis of further results from toxicological evaluations, thus allowing for the definition of a set of priority PFASs for future monitoring. The use of analytical methods with improved sensitivity

would be required to monitor such priority PFASs in order to increase the proportion of quantified results and thereby the reliability of exposure assessments.

The French Food Safety Agency and the Norwegian Institute of Public Health have evaluated the potential human health risks related to the residual presence of PFOA in non-stick coatings for cookware and concluded that the consumer health risk related to residues of PFOA in non-stick coating for cookware is negligible. According to the German Federal Institute for Risk Assessment, it has not been shown that consumers are significantly exposed to PFOA and FTOH from clothing fabrics. However, some authors conclude that given the present state of knowledge, it is not possible to say whether the use of nonstick-coated cooking utensils or packaging materials with PFC-based coating lead to a significant increase in dietary internal PFC contamination in humans.

The EFSA Scientific Panel on Contaminants in the Food Chain reached the conclusion that for PFOA, the total contribution from the non-food sources, mainly indoor exposure, could be as high as 50% compared to the estimated average dietary exposure to PFOA (EFSA, 2008). For the adult population, reviews show that dietary exposure is the dominant intake pathway, responsible for 91% (PFOS) and 99% (PFOA) of the total intake of the general adult population, when mean intake data are used for the estimate. Using high-intake data (based on maximum concentrations), the intake with house dust may be of the same size as dietary exposure as reported by the EFSA Scientific Panel. The total estimated intake of PFOS and PFOA were still when using high-intake data below the TDI values recommended by EFSA. Biomonitoring data indicate that the internal exposure of children is comparable to that of adults, but the exposure situation of children is not well understood, and therefore the authors do not make any statements on the risks of children's exposure to PFAS using the data available.

On the basis of reviews of the literature of the potential direct exposure from precursors, it has been concluded that FTOHs have only a negligible contribution (<1%) to the total mean and high intake PFOA exposure of adults. Moreover, the contribution of the converted ∑FOSAs/FOSEs to total PFOS exposure of the general population was estimated to reach only 10%.

A wealth of data on PFOS, PFOA and PFHxS in human blood exists from all over the world demonstrating elevated concentrations in workers with occupational exposure and populations in contaminated areas. Compared to the PFOS, PFOA and PFHxS, less information is available on other PFASs. The available data demonstrate that the concentration of PFOS, even though it has decreased in recent years, is significantly higher than the concentration of the other PFASs.

The general change from PFOS and PFOA substances to other PFASs is reflected in changes in human blood levels. Investigations of temporal trends of blood serum levels of PFAS in Sweden have demonstrated that the levels of the short-chain PFBS and levels of the long-chain PFHxS, PFNA and PFDA increased increased over the period 1996-2010. Concomitantly, levels of FOSA, PFOS, PFDS, and PFOA decreased. Similar trends have been demonstrated in Norway

A decreasing trend in the concentrations of PFOS and PFOA has also been demonstrated in the USA, but one study from the USA also indicates a decline in the concentration of PFHpA, PFNA, PFDA, and PFUnA, while other studies indicate increases for some substances. However, even though the concentration of PFOS has decreased from 34.9 ng/mL in 2000 to 8.3 ng/mL in 2010, the mean PFOS concentration was still significantly higher than the concentration of the other analysed PFASs.

The concentration in breast milk has also been demonstrated to follow the trend in the use of the substances. Analysis of breast milk in Sweden showed statistically significant increasing trends in the concentration of PFOS, PFHxS, and PFOA from 1972 to 2000, with concentrations reaching a plateau in the 1990s. PFOA and PFOS showed statistically significant decreasing trends during

2001–2008. In 2008 the concentration of PFOS and PFOA were both around 75 pg/mL, while the concentration of PFHxS was 14 pg/mL.

8. Information on alternatives

Three extensive reports are available on alternatives to PFOS for the different traditional application areas:

- Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications. Prepared for the Persistent Organic Pollutants Review Committee, Eighth meeting, Geneva, 15–19 October 2012 (UNEP, 2012);
- Guidance on alternatives to perfluorooctane sulfonate and its derivatives. Prepared for the Persistent Organic Pollutants Review Committee Sixth meeting, Geneva, 11–15. October 2010. (UNEP, 2010), and
- More environmentally friendly alternatives to PFOS-compounds and PFOA (Poulsen *et al.,* 2005).

Furthermore, a few reports are available on more specific applications; among these, a recent report on alternatives to PFOS in non-decorative hard crome plating (Poulsen *et al.,* 2011) is available (see section 3.3.2).

The US EPA is reviewing substitutes for PFOA, PFOS and other long-chain perfluorinated substances as part of its review process for new chemicals under EPA's New Chemicals Program. Over 150 alternatives of various types have been received and reviewed by EPA. It has not been possible to identify any public assessments or reviews on these substances.

As part of the data collection FluoroCouncil has been contacted and the Council has forwarded some comments prepared by the Council to the first draft of the technical paper on the identification and assessment of alternatives to the use of PFOS in open applications (UNEP, 2012). No further information was received.

8.1 Main alternatives to PFOS and PFOS-related substances

An overview of the status of the use of PFOS-related substances and the main alternatives is shown in Table 30 from the guidance on alternatives to perfluorooctane sulfonate and its derivatives from 2010, prepared under the auspices of the Stockholm Convention.

TABLE 30
STATUS OF SUBSTITUTION OF PFOS AND PFOS-RELATED SUBSTANCES FOR THE DIFFERENT APPLICATION AREAS *1

Use area	Use status for PFOS-related substances	Alternatives used	Remarks
Aviation hydraulic oils	PFOS-related compounds may still be used.	Other fluorinated substances and non-fluorinated phosphate compounds other fluorinated substances and non-fluorinaed phosphate compounds could be use after considering hazards/risk characteristics	Considerable information gaps though there are several products established on the market for years.
Fire-fighting foams	The use of PFOS-related substances in new products has been phased out in most OECD countries. Stocks are still being used up.	C6– fluorotelomers are used as substitutes in new products; fluorine-free alternatives are used for training exercises and possibly in other settings than offshore.	Alternatives to PFOS are widely used and easily accessible on several markets in North America, Europe and Asia (China). Costs for the alternatives are assessed as equal to PFOS with the exception of China that states that the alternative is slightly more expensive than PFOS.
Pesticides	Sulfluoramid is used in some countries as an active substance and surfactant in pesticide products for termites, cockroaches and other insects. Other fluorosurfactants may be used as “inert” surfactants in other pesticide products.	Synthetic insecticides such as S-Methoprene, Pyriproxyfen, Fipronil, Imidacloprid, Chlorpyrifos, Cypermethrin, Deltamethrin, Fenitrothion, Abamectin (commercial mixture) and their mixtures are alternative active substances, sometimes used in combination. Alternative surfactants may exist. There are also a number of alternative nonchemical methods, mainly biological controls	Some or all chemical alternatives to PFOS are easily available in South America (Argentina, Brazil) and Asia (China). These substances are mostly systemic insecticides that are in the range from highly toxic to humans and environment to less toxic to humans” and moderately or highly toxic to environment. Some of the alternatives are considered as less effective than PFOS by Brazil. Biological control agents are available in a number of countries including South America, USA, and China (Taiwan).
Metal plating	PFOS-compounds are still used in hard chrome plating. Cr-III has replaced Cr-VI in decorative chrome plating.	Some non-fluorinated alternatives are marketed but they are not considered equally effective in hard chrome plating. A C6-fluortelomer is used as a substitute and may be effective. PFBS derivatives may also be used. Physical barriers may also apply.	Only Canada and China report that alternatives to PFOS are used for years with success. They are easily available on their markets. There is little or no health environmental data available for the chemical alternatives from the parties. Costs for the alternatives are slightly higher than PFOS.
Electrical and electronic parts	PFOS-based chemicals are or have been used in the manufacturing of digital cameras, mobile phones, printers, scanners, satellite communication and radar systems, etc.	For most of these uses, alternatives are available or are under development.	Considerable information gaps

Use area	Use status for PFOS-related substances	Alternatives used	Remarks
Chemically driven oil production (Oil production and mining)	PFOS derivatives may occasionally be used as surfactants in the oil and mining industries.	PFBS, telomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids and thioether	Considerable information gaps.
Carpets, leather and apparel, textiles and upholstery (Impregnation of textiles, leather and carpets)	PFOS-related substances have been phased out in most OECD countries.	Other fluorinated compounds, like C6-fluorotelomers and PFBS, silicone-based products, stearamidomethyl pyridine chloride, perfluorobutane sulfonate for leather. Dendrimers.	Both USA and China describe short chain alternatives used on their markets on a regular basis as alternatives to PFOS. Perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives, which are not feasible alternatives to PFOS and related substances, exist on the Chinese market and are commercialized with a production volume of 20 tons per year. The Chinese full production capacity of perfluorohexane sulfonyl fluoride (PFhxSF) and its derivatives is up to 50 tons per year that is in line with production of PFOS. Perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives used as textile finishing agents with waterproof, antifouling effect equals with that of PFOS, but its grease-proof is lower than that of PFOS. There are concerns over the persistence of C6 compounds and the increased ability of C6 and C4 compounds to contaminate water. Dendrimers are used as non-fluorine alternatives to PFOS as water proofing agents on textiles and leather. There are considerations concerning health since cytotoxicity studies have shown dendrimers able to cross cell membranes, disrupt platelet function, and cause hemolysis.
Paper and packaging (Impregnation of paper and cardboard)	PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances and phosphates, mechanical processes	Considerable information gaps.
Coatings and coating additives (Surface coatings, paint and varnish)	PFOS-related substances have been phased out in most OECD countries	Telomer-based compounds, fluorinated polyethers, PFBS, propylated aromatics, silicone surfactants, sulfosuccinates, polypropylene glycol ethers. Dendrimers.	Considerable information gaps. PFOS-related substances are no longer used on coatings and coating additives, although such articles may still be imported.
Photographic industry *2	A shift to digital techniques has reduced the use drastically.	Telomer-based surfactants products, hydrocarbon surfactants, silicone products, C_3-C4-fluorinated chemicals	-

Use area	Use status for PFOS-related substances	Alternatives used	Remarks
Semiconductor industry *2	PFOS is still used but in lower concentrations.	No substitutes with comparable effectiveness have been identified, and doing so may take up to 5 years, according to the industry. It should be possible to use PFBS, fluorinated polyethers or telomers.	-
Medical devices *2	Old video endoscopes at hospitals contain a CCD colour filter that contains a small amount of PFOS. PFOS is also used as an effective dispersant for contrast agents in radio-opaque catheters.	Repairing such video endoscopes requires a CCD colour filter containing PFOS. New CCD filters are PFOS-free. For radio-opaque ethylene tetrafluoroethylene, PFBS can replace PFOS.	-
Others (Cleaning agents, waxes and polishes for cars and floors)	PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances, fluorinated polyethers, C4-perfluorinated compounds	Note that these applications are banned.

*1 The majority of table is derived from UNEP, 2012. Applications marked with *2 are derived from UNEP, 2010.

8.2 Non-fluoro or low-fluoro alternatives to long-chain PFAA substances

The technological best alternatives to the long-chain (≥ C8) fluorinated chemicals are most often other less hazardous fluorinated chemicals with a fluorinated alkyl chain length of ≤ C6 or fluoropolymers. Most of these substances have been discussed above.

The others, which are fluoroalkyl polyether, fluorinated ethers, ketones etc., will be discussed in the following paragraphs together with some non-fluorinated alternatives, such as silicone polymers, siloxanes, propylated aromatics, sulfosuccinates, etc.

Where PFOS derivatives had very broad application areas, many of the non-fluorinated alternatives only can be used to specific applications. The following review of substitutes to long-chain polyfluorinated chemicals not already discussed in the paper is based on the “Draft Guidance document on Alternatives to perfluorooctane sulfonic acid (PFOS) and its derivatives” as drafted by Allan Astrup Jensen for the Stockholm Convention in 2010 (UNEP, 2010).

TABLE 31
MAIN ALTERNATIVES TO LONG-CHAIN POLYFLUORINATED COMPOUNDS (UNEP, 2010)

Alternative compound	Product trade name	Company	Used in / used for
Perfluorobutane sulfonate (PFBS) or based on different C4-perfluorocompounds	Novec ™	3M	Paint and coatings industry, electronic coating; industrial and commercial cleaning; stain protectors for carpets, leather, furniture, automotive, hard surfaces and other apparels
C6 fluorotelomer sulfonamide compounds (80%)		DuPont	Fire-fighting foam
C4-C6 Fluorotelomer alcohols and esters	Scotchgard™	DuPont	Surfactant, coating, printing, textile and chemical industries
Fluorinated co-polymers.	FORAFAC™ 1157; 1183	DuPont	Impregnation of leather and indoor car upholstery
CF_3 or C_2F_5 fluoroalkyl polyethers	Zonyl®	OMNOVA Solutions Inc.	Surfactant and flow-, level-, and wetting additive for coating formulations, floor polish.
Dodecafluoro-2-methylpentane-3-one	Capstone®	3M	Fire-fighting foam
Perfluorobutyl methyl ethers	Foraperle 225 etc.	3M	Industrial cleaning
Propylated naphthalenes or biphenyls	Ruetasolv™	Rütgers Kureha Solvents Gmbh	Water repelling agents for rust protection systems, marine paints, coatings, etc.
Fatty alcohol polyglycol ether sulfate	Emulphor™	BASF	Levelling and wetting agents
Silicone polymers	WorléeAdd™	Worlée-Chemie	Wetting agents in the paint and ink industry
Sulfosuccinate	Lutensit™	BASF	Levelling and wetting agents
	EDAPLAN™ LA 451	Münzing Chemie	Paint and coating industry: Wetting and dispersing agents for water based applications e.g. wood primers
	HYDROPALAT™ 875	Cognis	

Fluorinated ethers and ketones

The fluorinated ethers and ketones are used for industrial cleaning and fire-fighting foams, respectively. There is no available information about the properties of these chemicals. Among the polyfluorodialkyl ether sulfonates, FC-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate) and FC-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate) are used in hard chrome plating in China[7]. The structure of FC-53 is an analogue of PFOS with a CF_2-group substituted by oxygen.

[7] Jun HUANG, Tsinghua University. Presentation at the International Workshop on new POPs, Beijing, 1-2 July, 2010.

Fluorinated polyethers

The company OMNOVA Solutions Inc. produces a family of short-chain fluorosurfactants based on fluorinated polyethers with a molecular weight greater than 1,000 and with C_2F_5- or CF_3- perfluoroalkyl side chain structures, under the trade name PolyFoxTM. The PolyFox product line includes anionic and non-ionic surfactants, UV-radiation curable acrylic monomer derivatives and polyols. It seems that these surfactants have a moderate surface tension, which is not quite as low as the conventional fluorinated surfactants. The new surfactants are claimed to have a broad processing window, where less interference with other compounds is experienced. Coating quality is improved as reduced foaming is achieved. The last item is an important factor in producing and processing water-based coatings. PolyFox fluorosurfactants have found use in aqueous and solvent-borne semiconductor coating formulations. In a number of examples, excellent wetting, flow and leveling properties have been afforded to semiconductor coatings. In addition, the poly(alkylene oxide) chain of all PolyFox materials has an inherently low refractive index compared to other commercial polymers such as acrylics. The presence of even very short (-CF_3, -C_2F_5) side chains additionally reduces the refractive index, and PolyFox materials are also used as antireflection layers in photoresist and LCD screen applications. The PolyFox formulation is currently being used as a surfactant in floor polish products in the USA, Europe and Asia.

The acute toxicities of PolyFox formulations are low (oral rat LD_{50} > 2 g/kg bw) but the fluorinated polyether may irritate skin and the respiratory system. Generally, there is a lack of data. Fluorinated polyethers do have a high molecular weight, making them less available for transport across biomembranes and therefore less biologically available. Furthermore, the polymer backbone linkage of the PolyFox molecules is an ether link, which is more environmentally stable than e.g. the ester/amide linkages of PFOS and telomer-based fluorosurfactants. This makes the PolyFox molecule more resistant to degradation to lower molecular carboxylic acids. PolyFox has low acute toxicity to aquatic organisms and will not bioaccumulate. PolyFox products seem to have reduced environmental impacts versus most other fluorosurfactants commercially available.

Siloxanes

Siloxanes are chemical substances containing units with the general formula R_2SiO, where "R" represents either hydrogen or a hydrocarbon group. They may be straight-chain or cyclic compounds and vary in weight from a few hundred to several hundred thousand g/mol for the polymers. Siloxanes are building blocks for silicone products. The siloxanes of main interest from an environmental perspective are the volatile methyl siloxanes, having a short SiO backbone, in particular the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes, MM (or HMDS), MDM, MD2M and MD3M. Out of these commercially used siloxanes, D4, D5, and MM are chemicals of high production volume within the European Union. The first two are the most commonly used siloxanes in the Nordic countries (Kaj *et al.,* 2005).[8] Recent activities within the Nordic area have focused on investigating the environmental occurrence of the above-mentioned siloxanes, which are used in a large number of industrial and consumer products such as sealants, fuel, car polish, cleaners, anti- foaming agents, car waxes, personal care and biomedical products (Lassen C *et al.* 2005).[9] The widespread use of siloxanes, their broad application, high volatility and potential for toxic effects have raised concerns about these compounds within various disciplines of environmental science. Recent studies indicate that they may be widespread in the environment (Cousins AP *et al.* 2009).[10]

Silicone polyethers are another class of silicone derivatives which have special surfactant properties. The leading manufacturers are Bluestar, Dow Corning, Evonik-Goldschmidt, Momentive and Wacker. Other companies sell specially formulated mixtures for specific applications. The company

[8] Kaj L, Schlabach M, Andersson J, Cousins AP, Schmidbauer N, Brorström-Lundén E. Siloxanes in the Nordic Environment. TemaNord 2005:593.
[9] Lassen C, Hansen CL, Mikkelsen SH, Maag J. Siloxanes - Consumption, Toxicity and Alternatives. Environmental Project No. 1031. Copenhagen: DEPA, 2005.
[10] Cousins AP, Kaj L, Broström-Lundén E. Siloxanes in the Nordic environment. Norman Bulletin no. 1, December 2009

"Bluestar Silicones" markets some PFOS alternatives based on silicone for textile applications with the trade name Advantex™.

Worlée-Chemie produces silicone polymers, which in the paint and ink industry can be used as alternative wetting agents to fluorosurfactants in several cases. WorléeAdd® 340 is a low viscosity, non-ionic special modified silicone polyether (contains 3-(polyoxyethylene) propylheptamethyl trisiloxane, CAS no. 67674-67-3) which can improve surface wetting of aqueous systems on difficult substrates like polyethylene and polypropylene or contaminated substrates. It has a low surface tension and is claimed to be highly efficient in improving wetting, spreading and leveling of water-borne coatings and eliminating surface defects without foam stabilizing. It is further claimed that the compound normally has no negative effect on recoating. Another product, WorléeAdd® 345, is a mixture of a silicone polyether (10-15%) and a dioctyl sulfosuccinate (50-55%) in ethanol and water. This surfactant can be used to improve wetting properties of aqueous coatings for different substrates, where the penetration into absorbing surfaces also is improved.

A study carried out by the National Food Institute at the Technical University of Denmark investigated the toxic effects of siloxanes as a group in order to set a health-based quality criterion for ambient air (Greve K *et al.,* 2008).[11] Toxic effects of D3, D4, D5, D6, and HMDS were studied using a 'read-across' method, which is based on structural similarity and its relation to toxicity. The linear siloxane HMDS appeared to have lower potential for liver toxicity, but higher potential for lung toxicity, than the cyclic substances. Decreasing toxicity with increasing chain length was also indicated. An ambient quality criterion of 0.01 mg/m^3 was derived, based on lung toxicity, and including a safety factor of 250. The silicone industry disagrees with the conclusions of this study.

Low molecular weight polydimethylsiloxanes have been studied extensively by industry to define their safety profile. These studies demonstrated that the polydimethylsiloxanes studied all possess a very low potential for toxicity (ECETOC, 1994).[12] However, other studies of siloxanes indicate that these substances may be harmful by inhalation, and that exposure may induce serious damage to eyes. Prolonged and frequent skin contact to WorléeAdd 340 may cause skin irritation. Thus, knowledge on the toxicity of siloxanes is still incomplete.

The Scientific Committee for Consumer Products in the EU has published an Opinion on D4 in which the safety of D4's use as a cosmetic ingredient has not been questioned. In the United States, the Cosmetic Ingredients Review panel is about to publish its final assessment of the safety of cyclomethicone, D3, D4, D5, D6 and D7. The panel has concluded that D4, D5, D6 and D7 are safe for use in cosmetics. D3 will be taken off the INCI list of cosmetic ingredients, because D3 is not a commercial product.

Perfluoroalkyl derivatives of siloxanes also exist, e.g. 1*H,1H,2H,2H*-perfluoroalkyl-triethoxysilane, which is effective for glass and surface treatment. A particular compound, polyfluorooctyl triethoxysilane (*1H,1H,2H,2H*-perfluorooctyl triethoxysilane), has been banned in Denmark, because of lung damage in experimental mice (Nørgaard *et al.* 2010

Siloxanes are widely distributed in the Nordic environment and diffuse sources via the dominant emission pathway of the sewage system to the aquatic environment are the dominant emission pathways. In general, the siloxanes are highly stable and persistent compounds without degradation in the environment. The cyclic- and short-chained linear siloxanes are bioconcentrated in aquatic organisms. These siloxanes may be toxic to aquatic organisms and are bioaccumulative; however, there are still gaps in our knowledge.

[11] Greve K, Nielsen E, Ladefoged O. Toxic effects of siloxanes: Group evaluation of D3, D4, D5, D6 and HMDS in order to set a health based quality criterion in ambient air. Toxicology Letters 2008; 180: S67.
[12] ECETOC - JACC 026 - Linear Polydimethylsiloxanes (CAS No.63148-62-9), September 1994.

In a MSDS the silicone polymer in WorléeAddTM 340 was classified as environmentally dangerous with the R-phrases R51/53 ("Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment"). The R-phrase R53 indicates that the substance is bioaccumulative. Canada has identified decamethyl cyclopentasiloxane (D5) and octamethyl cyclotetrasiloxane (D4) as "inherently toxic to wildlife". The cyclic siloxanes D4, D5 and D6 have been subjected to an environmental risk assessment by the United Kingdom Environment Agency applying the EU Technical Guidance. In 2009 the silicone industry submitted extensive monitoring data to the UK as the EU Rapporteur demonstrating that none of these substances biomagnifies in the environment.

Propylated aromatics

The company "Rütgers Kureha Solvents" produces different aromatic surfactants with the trade name Ruetasolv®, based on propylated naphthalenes and biphenyls, which can be used as water repelling agents for different applications, such as corrosion protection systems, marine paints, resins, printing inks, coatings, electrical, electronically and mechanical applications. They may also act as plasticizers and film forming aids in emulsion paints and adhesives. The various isopropyl naphthalenes and isopropyl biphenyls are highly hydrophobic substances that are compatible with almost all raw materials as follows: Epoxy resins, polyurethane resins, resin esters, hydrocarbon resins, polystyrene, elastomers, dispersions, emulsions, styrene-acrylate-copolymers, vinyl acetate and ethylene vinyl acetate polymers, mineral oils, bitumen, etc.

The propylated aromatic products are all colourless liquids with a boiling point of about 300˚C and have a very low solubility in water. The substances *p*-isopropyl-1,1'-biphenyl (Ruetasolv BP 4103,) and *p,p'*-diisopropyl-1,1'-biphenyl (Ruetasolv BP 4201,) can cause skin sensitization or dermatitis at repeated skin contact, and long-term exposures cause irritation of the eyes, nose, throat, mucous membranes and the respiratory tract. *p*-Isopropyl-1,1'-biphenyl has a very low acute toxicity with an oral LD_{50} value for rats of > 4 g/kg. Central nervous system (CNS) damage, liver and kidney damage have, however, been reported as chronic effects of this chemical in animals. The isopropylated naphthalenes are also irritating substances. The acute toxicity of diisopropyl naphthalene (Ruetasolv DI) is very low with an oral rat LD_{50} of 3900 mg/kg.

The biphenyls and the naphthalenes have high octanol/water partition coefficients (log K_{OW}) and the bioconcentration factor (BCF) for the substances is greater than 100. Therefore, these chemicals are potentially bioaccumulative. The biphenyl moiety appears to be easily biodegradable, whereas the naphthalene moiety only slowly biodegrades. The sparse information available suggests that the biphenyls are acutely toxic to aquatic organisms, whereas the naphthalenes have no acute toxic effects in the investigated fish species.

Sulfosuccinates

Several companies produce surfactants based on 50-75% of the sodium salt of di(2-ethylhexyl) sulfosuccinate, which can be used as a wetting agent for aqueous systems of detergents, cleaners, paints and coatings. It is also used in pesticides. In a product from BASF (Lutensit®A-BO) the sulfosuccinate is mixed with water and ethanol, and in a product from Cognis (Hydropalat® 875) the sulfosuccinate is mixed with water and 2,2-dimethylpropane-1,3-diol. The product from Cognis can be used as a wetting agent in aqueous coating systems and is particularly suitable for difficult-to-wet substrates like plastics, metal, cellulose film, silicone treated papers and glass. This surfactant may also be used as an emulsifier for emulsion polymerization. Another area where it can be used as an alternative to fluorinated surfactants is in optimizing the color acceptance of aqueous pigment concentrates in different coatings. The product has a medium foam formation. Münzing Chemie produces a surfactant (Edaplan® LA 451) based on a sulfosuccinate derivative in ethanol and water, which also can be used as a wetting agent for aqueous paints and coatings. The identity of the sulfosuccinate was not disclosed. The product is claimed to have good wetting properties, no increase in foam and good re-coatability. The surface tension is moderate. Application areas are decorative

paint, wood and furniture coatings, automotive and repair coating, industrial coatings, printing inks and overprint varnishes.

Toxicological information is scarce. Sulfosuccinates are irritants to eyes, skin and the respiratory system, especially for prolonged or repeated contact. Dermatitis has been observed as a long-term effect as well as CNS depression and injury to heart, liver and blood-forming organs. The substance di(2-ethylhexyl) sulfosuccinate has low acute toxicity if swallowed (LD_{50} (oral, rat) = 1.9 g/kg). Information found in the HSDB database suggests that di(2-ethylhexyl) sulfosuccinate is mildly toxic (by ingestion) to humans with a probable oral lethal dose (human) of 0.5-5 g/kg. A possible metabolite is the branched 2-ethylhexanol, which may have reproductive effects. Di(2-ethylhexyl) sulfosuccinate is easily biodegradable and not likely to bioaccumulate; however, a $^{96h}LC_{50}$ value of 10-100 mg/l for *Leuciscus idus* (small fresh-water cyprinoid fish) shows that this sulfosuccinate may be harmful to aquatic organisms.

Stearamidomethyl pyridine chloride

A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, earlier marketed by ICI as Velan PF. The substance is reacted with cellulose at elevated temperatures to form a durable water-repellent finish on cotton. It was later found that the reaction was restricted to the surface of the fibers and the high cure temperature weakened the fabric. Sodium acetate had to be added to prevent the decomposition of the cellulose by the hydrogen chloride formed. Also, the pyridine liberated during the reaction has an unpleasant odour, and the fabric had to be scoured after the cure. The toxicological properties of pyridine ended its use in the 1970s when government regulations on such substances were introduced. It may be evaluated differently at present. Further information about properties is lacking. There is a lack of public data on this chemical.

Polypropylene glycol ether, amines, and sulfates

Possible replacements of fluorosurfactants in some applications are anionic surfactants based on aliphatic alcohols. The BASF product Emulphor® FAS 30 is the sodium salt of fatty alcohol polyglycol ether sulfate, which are preferentially used in the emulsion polymerization of acrylate and methacrylate esters, styrene and vinyl esters. These anionic emulsifiers are also combined with non-ionic Emulan® grades in order to achieve the desired properties such as particle size or emulsion stability (BASF). Because of its foaming properties, it is also used in cosmetics and fire-fighting foams. A fatty alcohol polyglycol ether sulfate has the general formula:

$$R1\text{-}O\text{--}(CH_2CH_2O)_n\ SO_3X$$

wherein R1 represents a linear or branched alkyl and/or alkenyl group having e.g. 12 to 16 carbon atoms, n represents a number usually from 2 to 4, and X represents a cation selected from the group consisting of Na^+, ammonium, or substituted ammonium.

A related non-fluorosurfactant is Enthone® (ethoxylated oleyl amine, CAS no. 26635-93-8) used in decorative chrome plating but also in many other applications. Its general formula is:

$$R\text{-}N(CH_2CH_2O)H_m(CH_2CH_2O)H_n.$$

The Emulphor FAS 30 has low acute toxicity by ingestion (oral LD_{50} > 2 g/kg bw) and it is not considered to be irritating. There is a lack of data on this chemical. Enthone and other polyethylene glycol amines are non-toxic and non-irritating, non-ionic emulsifiers. The Emulphor FAS 30 is readily biodegradable (>70% elimination according to OECD 301E) and does not seem to be acutely toxic to aquatic organisms as the reported $^{96h}LC_{50}$ value for fish (*Leuciscus idus*) is > 100 mg/L. Enthone is readily degradable with low toxicity. There is, however, a lack of data on these chemicals.

8.3 Summary on alternatives

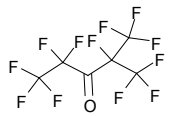
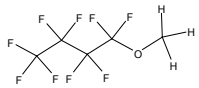
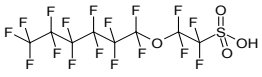
There are alternatives to long-chain fluorinated chemicals for most applications. The technologically best alternatives to hazardous fluorinated chemicals are short-chain and less hazardous fluorinated chemicals with a fluorochain length of ≤C6 or fluoropolymers. In addition some non-fluorinated alternatives, such as siloxanes, propylated aromatics, and sulfosuccinates, can be used for specific applications.

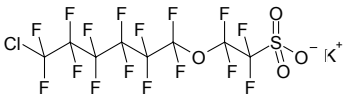
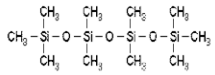
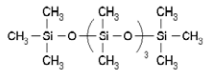
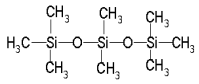
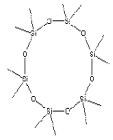
The fluorinated alternatives are still rather persistent but much less bioaccumulative and toxic than the long-chain homologues.

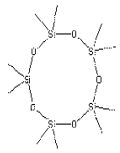
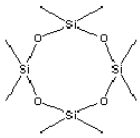
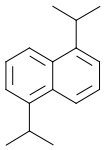
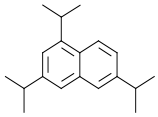
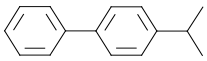
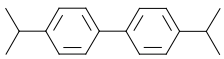
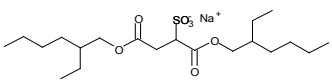
The non-fluorinated alternatives are not very persistent and bioaccumulative, but some of the substances are more toxic. In general, there is a lack of public data on the properties of the alternatives, which often are protected by commercial secrecy, and because most academic research has been on the polyfluorinated chemicals.

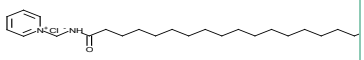
In TABLE 32 an overview is shown of the properties of the discussed alternatives based on the screening system developed by US EPA in their "Design for the Environment Programme" (http://www.epa.gov/dfe/alternative_assessments.html).

TABLE 32
OVERVIEW OF THE PROPERTIES OF THE DISCUSSED ALTERNATIVES

Chemical	CAS No	Persistance	Degradion products of concern	Bioaccumulation	Animal toxicity	Degradate Aquatic toxicity	Application	Other infor
Fluorinated ethers and ketones								
Dodecafluoro-2-methylpentan-3-one 	756-13-8	*H*	*H*	*VL*	*n.d.*	*n.d.*	Fire-fighting foam	Novec™ 1230
Methyl nonafluorobutyl ether 	163702-07-6	*H*	*M*	*VL*	*n.d.*	*n.d.*	Commercial and industrial cleaning	Novec™
Methyl nonafluoro isobutyl ether	163702-08-7	*H*	*M*	*VL*	*n.d.*	*n.d.*	Commercial and industrial cleaning	Novec™
Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy) ethane sulfonate 	not available	*VH*	*H*	*H*	*n.d.*	*n.d.*	Hard chrome plating	FC-53
Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate)	not available	*VH*	*VH*	*H*	*n.d.*	*n.d.*	Hard chrome plating	FC-53B

Chemical	CAS No	Persistance	Degradion products of concern	Bioaccumula-tion	Animal toxicity	Degradate Aquatic toxicity	Application	Other infor
								
Fluorinated polymers								
2-Methyl-2-propenoic acid dodecyl ester, co-polymer with 10-15% α-fluoro-ω-[2-[(2-methyl-1-oxo-2-propenyl)oxy]-ethyl poly(difluoro-methylene)	65605-58-5	***M***	***M***	***VL***	***n.d.***	***n.d.***	Fabric protector	Zonyl® G
Dodecyl methacrylate polymer with α-fluoro-ω-[2-[(1-oxo-octadecyl)-oxy]ethyl]-poly(difluoro-methylene)	65530-65-6	***M***	***M***	***VL***	***VL***	***VL***	Finishing and protection of leathers and car upholstery	Foraperle®
Fluoroalkyl polyethers 	not available	***M***	***M***	***VL***	***n.d.***	***n.d.***	Surfactant, semiconductor coating formula-tions, antireflec-tion layers, floor polish	PolyFox™ 656
Siloxanes and silicone polymers								
Hexamethyl disiloxane 	107-46-0	***H***	***M***	***M***	***H***	***H***	Industrial and consumer prod-ucts such as sealants, fuel, car polish, cleaners, anti-foaming agents, car waxes, personal care and biomedical products	MM
Octamethyl trisiloxane 	107-51-7	***H***	***M***	***M***	***H***	***H***		MDM
Decamethyl tetrasiloxane 	141-62-8	***H***	***M***	***M***	***H***	***H***		MD2M
Dodecamethyl cyclohexasilox-ane 	540-97-6	***H***	***M***	***M***	***H***	***VH***		D6
Decamethyl cyclopentasiloxane	541-02-6	***H***	***M***	***M***	***H***	***H***		D5

Chemical	CAS No	Persistance	Degradion products of concern	Bioaccumula-tion	Animal toxicity	Degradate Aquatic toxicity	Application	Other infor
								
Octamethyl cyclotetrasiloxane 	556-67-2	***H***	***M***	***M***	***H***	***H***		D4
3-(Polyoxyethylene) propyl heptamethyl trisiloxane	67674-67-3	***H***	***H***	***M***	***H***	***H***		WorléeAdd® 340
Propylated aromatics								
Bis(1-ethylethyl)-naphthalene, 	38640-62-9	***M***	***n.d.***	***M***	***M***	***n.d.***	Corrosion protection, marine paints, resins, printing inks, coatings, electrical, electronically and mechanical applications	Ruetasolv DI
Tris(1-methylethyl)-naphthalene, 	35860-37-8	***M***	***n.d.***	***M***	***M***	**n.d.**		Ruetasolv TTPN
Bis(1-methylethyl) 1,1'-biphenyl 	69009-90-1	***M***	***n.d.***	***M***	***M***	**n.d.**		Ruetasolv BP 4201
(1-methylethyl)-1,1'-biphenyl 	25640-78-2	***M***	***n.d.***	***M***	***M***	**n.d.**		Ruetasolv BP 4103
Sulfosuccinates etc								
Di(2-ethylhexyl) sulfosuccinate 	577-11-7	***VL***	***VL***	***VL***	***L***	***H***	Wetting agent for aqueous systems of detergents, cleaners, paints and coatings, pesticides.	Lutensit® A-BO
Stearamidomethyl pyridine chloride	4261-72-7	***VL*** .	**n.d.**	**n.d.**	**n.d.**	**n.d.**	Textile surfactant	Velan PF

Chemical	CAS No	Persistance	Degradion products of concern	Bioaccumula-tion	Animal toxicity	Degradate Aquatic toxicity	Application	Other infor
								
Polypropylene glycol ether, amines, and sulfates								
Sodium salt of fatty alcohol polyglycol ether sulfate R-O-$(CH_2CH_2O)_n$-SO_3X	not available	***VL***	***VL***	***VL***	***L***	***L***	Anionic emulsi-fiers, cosmetics and fire-fighting foams.	Emulphor FAS 30
Ethoxylated oleyl amine R-N$(CH_2CH_2O)H_m$-$(CH_2CH_2O)H_n$.	26635-93-8	***VL***	***VL***	***VL***	***L***	***M***	Decorative chrome plating	Enthone

VL = Very low hazard **L** = Low hazard **M** = Moderate hazard **H** = High hazard **VH** = Very high hazard - Endpoints in colored text (**VL**, **L**, **M**, **H**, and **VH**) were assigned based on experimental data.
Endpoints in black italics (***VL, L, M, H,*** and ***VH***) were assigned using estimated values and professional judgment (Structure Activity Relationships). Y=Yes…N=No; n.d = no data

9. Overall conclusions

9.1 Main issues

PFOS and other long-chain perfluoroalkyl sulfonates

The use of PFOS and substances that may degrade to PFOS is today restricted by the EU POPs regulation. The main issues concern management of PFOS-containing waste (solid waste and sewage sludge), remaining exempted uses of the PFOS and PFOS-contaminated soil. These issues are addressed by the action plan for reduction of PFOS is Denmark.

PFOA and other long-chain perfluoroalkyl carboxylic acids

PFOA, precursor chemicals and higher homologue chemicals are addressed by the US EPA PFOA Stewardship Program and the major global manufacturers (representing more than 90% of the global production) have agreed to work toward eliminating emissions and product content of these chemicals by 2015. Expectedly this will result in significantly lower environmental concentrations and human exposure to these chemicals in the future, even some manufactures e.g. in China are not participating in the stewardship program. Human biomonitoring studies have demonstrated a decrease in concentration of PFOA in blood and breast milk for the period 2000-2010.

Annex XV dossiers have been prepared for APFO and three longer chained PFCAs and an Annex XV dossier for PFOA is on its way. The dossiers do not address possible precursors. The pathways and substance flows that lead to the presence of PFOA and longer homologues in the environment and human exposure is, however still not fully understood and it is not clear to what extent precursors are present in articles produced in the EU or imported from countries outside the EU.

Short-chain perfluoroalkyl acids

According to information from the industry the current trend is to replace the long-chain PFASs with short-chain homologues. The short-chain homologues have a better toxicological profile and do not bioaccumulate to the same extent as the long-chain substance as they are excreted more rapidly from both humans and organisms in the environment, but they are still persistent in the environment. The short-chain homologues and their precursors (e.g. fluorotelomers base on short-chain fluorochemistry) generally seems to have a better human health and environmental profile than the substances based on long-chain fluorochemistry, but it is difficult on the current knowledge to assess to what extent non-fluorinated substances could be alternatives of less concern to the long-chain PFASs for some applications.

Fluorotelomers and side-chain-fluorinated polymers

Fluorotelomers and fluorotelomer-based side-chain-fluorinated polymers account for the major part of the use of PFCs. The formation of hazardous transformation products has traditionally been a major concern related to these substances.

The side-chain fluorinated polymers are exempt from registration under REACH and do not appear to have been pre-registered. The status of these polymers under REACH and particularly side-chain-fluorinated polymers imported from countries outside the EU is not clear. More information on how the use of these substances can be assessed and regulated under REACH would be advantageous.

It has been demonstrated in many studies that a wide range of perfluorinated substances at low concentrations can be extracted from e.g. textiles and packaging treated with side-chain-fluorinated polymers. The releases of substances from the different parts of the life cycle of the substances and the significance of the exposure of humans and the environment from substances released from articles treated with the side-chain-fluorinated polymers is still not fully understood and again, more information would be of advantage.

Exposure across substance groups
Recently published data from EFSA indicates that the total dietary intake of PFOS and PFOA is well below the established TDI. On the other hand have population studies discovered positive associations between a number of adverse effects at commonly prevalent exposures.

9.2 Data gaps

The PFCs is a large and diverse group of substances and for most of the substances limited information on their use, fate and possible effects exists. The main data gaps indentified in this report are summarised below.

The action plan for reduction of PFOS in Denmark addresses some data gaps for PFOS and PFOS-related substances:

- Limited information is available on the possible sources of contamination of soil and groundwater with PFOA/PFOS, and it is not clear whether contamination of soil and groundwater in connection with fire drill sites is a generally occurring phenomenon.
- Limited data are available on the destruction efficiency of PFOS under the actual conditions in the municipal solid waste incinerators, and more studies are necessary to clarify whether it would be necessary to dispose of PFOS-containing waste to hazardous waste incinerators in order to comply with the requirements of the Stockholm Convention

For substances other than PFOS and PFOA, the link between the use of the substances and the environmental and human exposure is poorly understood. It is not clear to what extent perfluorinated side-chains of the side-chain-fluorinated polymers are released from the articles and at what stage of the lifecycle of the substances releases occur. Analysis of e.g. packaging and textiles demonstrates that a range of substances can be extracted at low levels from the articles, but the significance of this as regards possible human exposure and releases to the environment is not known.

Long-chain homologues to PFOA (C9-C12 or longer) are found in relatively high concentrations in the environment, but hardly any information on the use of these substances and their possible precursors is available.

Public available data on the ecotoxicity of the short-chain PFASs is very limited. The short-chain PFASs (e.g. butane-based) appear to be persistent but not to bioaccumulate to the same extent as the long-chain homologues, as they are excreted rapidly from the organisms studied. The ecotoxicity may not be a critical issue, but data are not available.

A recent Danish risk evaluation of perfluorinated compounds in sewage concludes that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems where the sludge is applied and that more information on the fate and effects of PFASs is needed.

The risks and threats of PFOA and long-chain homologues to the marine environment are currently difficult to estimate due to the lack of ecotoxicological information e.g. PNEC value has not been comprehensively assessed.

In general the knowledge about the human toxicology of most perfluorinated compounds is rather sparse, and it will take some years and much effort, before sufficient information for evaluation of

the full impact of the present levels in humans is available. EFSA concludes that, based on further results from toxicological evaluations, the relevance of various PFASs to human health could be better established, thus allowing for the definition of a set of priority PFASs for future monitoring. The use of analytical methods with improved sensitivity would be required to monitor such priority PFASs in order to increase the proportion of quantified results and thereby the reliability of exposure assessments.

Population studies have discovered positive associations between a number of adverse effects at commonly prevalent exposures to the PFCs. More knowlegde on adverse effects at actual exposure leves and a better understanding og which substance contribute to the effects is needed.

Many of the non-fluorinated alternatives are not very persistent and bioaccumulative, but are some of them are more toxic than the PFCs. However, there is a lack of public data on the properties of the non-fluorine alternatives to the PFCs, which often are protected by commercial secrecy, and because most academic research has been on the polyfluorinated chemicals.

10. Abbreviations and acronyms

10:2 monoPAP	10:2 Fluorotelomer phosphate monoester
4:2 FTOH	4:2 Fluorotelomer alcohol
6:2 FTAC	6:2 Fluorotelomer acrylate
6:2 FTMAC	6:2 Fluorotelomer methacrylate
6:2 FTO	6:2 Fluorotelomer olefin
6:2 FTS	6:2 Fluorotelomer sulfonate
6:2 FTSA	6:2 Fluorotelomer sulfonic acid ()
8:2 diPAP	8:2 Fluorotelomer phosphate diesters
8:2 FTAL	8:2 Fluorotelomer aldehyde
8:2 FTCA	8:2 Fluorotelomer carboxylic acid
8:2 FTI	8:2 Fluorotelomer iodide
8:2 FTOH	8:2 Fluorotelomer alcohol
8:2 FTUOH	8:2 Unsaturated fluorotelomer alcohol
8:2 monoPAP	8:2 Fluorotelomer phosphate monoester
AMAP	Arctic Monitoring and Assessment Programme
APFN	Ammonium perfluorononanoate
APFO	Ammonium perfluorooctanoate
BAT	Best available techniques
BCF	Bioconcentration factor
BMF	Biomagnification factor
BEP	Best environmental practice
BSAF	Biota-to-soil accumulation factor
BfR	German Federal Institute for Risk Assessment
BuFASAs	N-butyl perfluoroalkane sulfonamides
C4-PFSAs	Perfluoroalkyl sulfonic acids with a chain length of four
C6/C6-PFPIA	Bis(perfluorohexyl) phosphinic acid
C6-PFSAs	Perfluoroalkyl sulfonic acids with a chain length of six
C8-PFPA	Perfluorooctyl phosphonic acid
CKD	Chronic kidney Disease
CLP	Classification, Labelling and Packaging (Regulation)
C&L	Classification and Labelling
CMR	Carcinogenic, mutagenic or toxic to reproduction
CN	Combined nomenclature
DDD	Dichlorodiphenyldichloroethane
diPAPS	polyfluoroalkyl-diester phosphates
d.l.	Detection limite
d.w.	dry weight
EC_n	Effect concentration where n % of the species tested show the effect
ECF	Electrochemical fluorination
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
ESWI	European Scientific Working group on Influenza

EtFASAs	N-ethyl perfluoroalkane sulfonamides
EtFASEs	N-Ethyl perfluoroalkane sulfonamidoethanol
EtFBSE	N-Ethyl perfluoro-butane sulfonamidoethanol
EtFBSE	N-Ethyl perfluoro-butane sulfonamidoethanol
EtFOSA	N-ethylperfluorooctane sulfonamide
EtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid
EtFOSAC	N-Ethyl perfluoro-octane sulfonamidoethyl acrylate
EtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol
EUSES	European Union System for the Evaluation of Substances
FASAAs	Perfluoroalkane sulfonamidoaceticacids
FASAs	Perfluoroalkane sulfonamides
FASEs	Perfluoroalkane sulfonamidoethanols
FC-807	Perfluoroalkyl phosphate
FOSA	Perfluorooctane sulfonamide
FTBP	Fluorotelomer based polymer
FTCA	Fluorotelomer carboxylates
PTO	Fluorotelomer olefin
FTOH	Fluorotelomer alcohols
FTS	Fluorotelomer sulfonates
FTUCA	Fluorotelomer unsaturated carboxylic acids
GJIC	Gap junction intercellular communication
HCB	Hexachlorobenzene
HFP	Hexafluoropropylene
HMDS	Hexamethyldisiloxane
HPA	Health Protection Agency
ICCM	International Conference on Chemicals Management
MeFASA	N-methyl perfluoroalkane sulfonamides
MPC	Maximum permissible concentration
KPFO	PFOA potassium salt
Kd	Soil/water distribution coefficient
LC	Lethal effect concentration
L-FABP	Liver-fatty acid binding protein
LOAEL	Lowest observable adverse effect level
LOUS	List of Undesirable Substances
MACeco:	Maximum Acceptable Concentration for ecosystems
monoPAPS	polyfluoroalkyl-mono phosphates
NHANES	National Health and Nutrition Examination Survey (in the USA)
NOAEL	No observable adverse effect level
NOEC	No observable effect concentration
NOVANA	Danish national surveillance programme for the aquatic environment
MCF-7	Michigan Cancer Foundation – 7 breast cancer cell line
MSWI	Municipal solid waste incinerator
MTBE	Methyl tertiary butyl ether
MWWTP	Municipal waste water treatment plant
n:2 FTIs	n:2 Fluorotelomer iodides
n:2 FTOHs	n:2 Fluorotelomer alcohols
NC	Negligible Concentration
NCP	New Chemicals Program
NEt4-PFOS	Tetraethylammonium perfluorooctane sulfonate
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PAFs	Perfluoroalkanoyl fluorides

PAPs	Polyfluoroalkyl phosphoric acid esters
PASFs	Perfluoroalkane sulfonyl fluorides
PBSF	Perfluorobutane sulfonyl fluoride
PBT	Persistent, bioaccumulative and toxic (in the environment)
PCBs	Polychlorinated biphenyls
PFAA	Perfluoroalkyl acids
PFAIs	Perfluoroalkyl iodides
$PFALH_2Os$	Perfluoroalkyl aldehyde hydrates
PFALs	Perfluoroalkyl aldehydes
PFASs	entire group of perfluoroalkyl and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCAs	Perfluoroalkyl carboxylic acids
PFCAs	Perfluoroalkyl carboxylates
PFCs	Collective designation of perfluoroalkyl substances, polyfluoroalkyl substances and side-chain fluorinated polymers
PFDA	Perfluorodecanoic acid
PFDoDA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptane sulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxDA	Perfluorohexadecanoic acid
PFHxI	Perfluorohexyl iodide
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid
PFNAL	Perfluorononanal
PFOA	Perfluorooctanoic acid
PFODA	Perfluorooctadecanoic acid
PFOS	Perfluorooctane sulfonate
PFOS	Perfluorooctane sulfonic acid
PFOSA	Perfluorooctane sulphonamide
PFOSF	Perfluorooctane sulfonyl fluoride
PFOSI	Perfluorooctane sulfinic acid
PFOSI	Perfluorooctane sulfinic acid
PFPA	Perfluoropentanoic acid
PFPAs	Perfluoroalkyl phosphonic acids
PFPeDA	Perfluoropentadecanoic acid
PFPEs	Perfluoropolyethers
PFPIAs	Perfluoroalkyl phosphinic acids
PFSAs	Perfluoroalkyl sulfonic acids
PFSAs	Perfluoroalkane sulfonates
PFSAs	Perfluoroalkane sulfonic acids
PFSIAs	Perfluoroalkane sulfinic acids
PFTE	Polytetrafluoroethylene
PFTeDA	Perfluorotetradecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFUnDA	Perfluoroundecanoic acid = PFUnA
PNEC	Predicted No Effect Concentration
POF	Perfluorooctanoyl fluoride
POPs	Persistent organic pollutants
POSF	Perfluorooctane sulfonyl fluoride
PPARα	Peroxisome proliferator-activated receptor-α

PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
PVF	Polyvinylfluoride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals ((Regulation (EC) No 1907/2006)
RME	Reasonable Maximum Exposure
ROS	Reactive oxygen species
SAICM	Strategic Approach to International Chemicals Management
SRC_{eco}	Serious Risk Concentration for ecosystems
SFAenes	Semifluorinated n-alkenes
SFAs	Semifluorinated n-alkanes
SVHC	Substances of Very High Concern
TDI	Tolerable daily intake
TDS	Testicular dysgenesis syndrome
TFE	Copolymers of tetrafluoroethylene
TSCA	Toxic Substances Control Act
UNEP	The United Nations Environment Programme
UNIDO	The United Nations Industrial Development Organization
USEPA	United States Environmental Protection Agency
vPvB	Very persistent and very bioaccumulative
w.w.	Wet weight
WWTP	Waste water treatment plant

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Annex 1: List of specific substance abbreviations used in the report

Abb.	Chemical name	CAS No	Chain length	Group name	Group abb.
10:2 monoPAP	10:2 Fluorotelomer phosphate monoester	57678-05-4	C10	n:2 Polyfluoroalkyl phosphoric acid esters	PAPs
4:2 FTOH	4:2 Fluorotelomer alcohol	2043-47-2	C4	n:2 Fluorotelomer alcohols	n:2 FTOHs
6:2 FTAC	6:2 Fluorotelomer acrylate	65104-64-5	C6	n:2 Fluorotelomer acrylates	n:2 FTACs
6:2 FTMAC	6:2 Fluorotelomer methacrylate	2144-53-8	C6	(n:2) Fluorotelomer methacrylates	n:2 FTMACs
6:2 FTOH	6:2 Fluorotelomer alcohol	647-42-7	C6	n:2 fluorotelomer alcohols	n:2 FTOHs
6:2 FTS	6:2 Fluorotelomer sulfonate	29420-49-3	C4	n:2 Fluorotelomer sulfonic salts	n:2 FTSAs
6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	C6	6:2 Fluorotelomer sulfonic acid	n:2 FTSAs
6:2FTO	6:2 Fluorotelomer olefin	25291-17-2	C6	n:2 Fluorotelomer olefins	n:2 FTOs
8:2 diPAP	8:2 Fluorotelomer phosphate diesters	678-41-1 8	C8	Polyfluoroalkyl phosphoric acid diesters	diPAPs
8:2 FTAL	8:2 Fluorotelomer aldehyde	135984-68-8	C8	(n:2) Fluorotelomer (saturated) aldehydes	n:2 FTALs
8:2 FTCA	8:2 Fluorotelomer carboxylic acid	27854-31-5	C8	(n:2) Fluorotelomer (saturated) carboxylic acids	n:2 FTCAs
8:2 FTI	8:2 Fluorotelomer iodide	2043-53-0	C8	n:2 Fluorotelomer iodides	n:2 FTIs
8:2 FTOH	8:2 Fluorotelomer alcohol	678-39-7	C8	(n:2) Fluorotelomer alcohols	n:2 FTOHs
8:2 FTUOH	8:2 Unsaturated fluorotelomer alcohol	-	C8	(n:2) Fluorotelomer (unsaturated) alcohols	n:2 FTuOHs
8:2 monoPAP	8:2 Fluorotelomer phosphate monoester	57678-03-2	C8	PAPs: Polyfluoroalkyl phosphoric acid esters	PAPs
APFN	Ammonium perfluorononano-ate	4149-60-4	C9	Perfluoroalkyl carboxylic acids	PFCAs
APFO	Ammonium perfluorooctanoate	3825-26-1	C8	Perfluoroalkyl carboxylic acids	PFCAs
C6/C6-PFPIA	Bis(perfluorohexyl) phosphinic acid	40143-77-9	C6	Perfluoroalkyl phosphonic acids	PFPIAs
C8-PFPA	Perfluorooctyl phosphonic acid	40143-78-0	C8	Perfluoroalkyl phosphonic acids	PFPAs
EtFBSE	N-Ethyl perfluorobutane sul-fonamidoethanol	34449-89-3	C4	Perfluoroalkane sulfonamidoeth-anols	FASEs
EtFOSA	N-ethylperfluorooctane sulfon-amide	4151-50-2	C8	N-ethyl perfluoroalkane sulfona-mides	EtFASAs
EtFOSAC	N-Ethyl perfluorooctane sulfon-amidoethyl acrylate	423-82-5	C8	N-Ethyl perfluoroalkane sulfonamidoethyl acrylates	EtFAS(M)ACs
EtFOSE	N-Ethyl perfluorooctane sulfon-amidoethanol	1691-99-2	C8	N-Ethyl perfluoroalkane sulfon-amidoethanol	EtFASEs

Abb.	Chemical name	CAS No	Chain length	Group name	Group abb.
EtFOSAA	N-Ethyl perfluorooctane sulfon-amidoacetic acid	2991-50-6	C8	N-Methyl perfluoroalkane sulfonamidoethyl acrylates	MeFAS(M)ACs
FC-807	Perfluoroalkyl phosphate	-	C8	Perfluoroalkyl phosphates	-
FOSA	Perfluorooctane sulfonamide	754-91-6	C8	Perfluoroalkane sulfonamides	FASAs
KPFO	PFOA potassium salt	-	C8	Perfluoroalkyl carboxylales	PFCAs
Na-PFOA	Sodium perfluorooctanoate	335-95-5	C8	Perfluoroalkyl carboxylic acids	PFCAs
NEt4-PFOS	Tetraethylammonium perfluo-rooctane sulfonate	56773-42-3	C8	Perfluoroalkane sulfonic acids	PFSAs
PBSF	Perfluorobutane sulfonyl fluo-ride	375-72-4	C4	Perfluoroalkane sulfonyl fluorides	PASFs
PFBA	Perfluorobutanoic acid	375-22-4	C4	Perfluoroalkyl carboxylic acids	PFCAs
PFBS	Perfluorobutane sulfonic acid	375-73-5	C4	Perfluoroalkane sulfonic acids	PFSAs
PFDA	Perfluorodecanoic acid	335-76-2	C10	Perfluoroalkyl carboxylic acids	PFCAs
PFDoDA	Perfluorododecanoic acid	307-55-1	C12	Perfluoroalkyl carboxylic acids	PFCAs
PFDS	Perfluorodecane sulfonic acid	335-77-3	C10	Perfluoroalkane sulfonic acids	PFSAs
PFHpA	Perfluoroheptanoic acid	375-85-9	C7	Perfluoroalkyl carboxylic acids	PFCAs
PFHpS	Perfluoroheptane sulfonic acid	-	C7	Perfluoroalkane sulfonic acids	PFSAs
PFHxA	Perfluorohexanoic acid	307-24-4	C6	Perfluoroalkyl carboxylic acids	PFCAs
PFHxDA	Perfluorohexadecanoic acid	67905-19-5	C16	Perfluoroalkyl carboxylic acids	PFCAs
PFHxI	Perfluorohexyl iodide	355-43-1	C6	Perfluoroalkyl iodides (Telomer A)	PFAIs
PFHxS	Perfluorohexane sulfonic acid	355-46-4	C6	Perfluoroalkane sulfonic acids	PFSAs
PFNA	Perfluorononanoic acid	375-95-1	C9	Perfluoroalkyl carboxylic acids	PFCAs
PFNAL	Perfluorononanal	63967-40-8	C8	Perfluoroalkyl aldehydes	-
PFOA	Perfluorooctanoic acid	335-67-1	C8	perfluoroalkyl carboxylic acids and salts	PFCAs
PFODA	Perfluorooctadecanoic acid	16517-11-6	C17	Perfluoroalkyl carboxylic acids	PFCAs
PFOS	Perfluorooctane sulfonic acid	1763-23-1	C8	Perfluoroalkane sulfonic acids	PFSAs
PFOSA	Perfluorooctane sulfonamide	754-91-6	C8	Perfluoroalkane sulfonamides	FASAs
PFOSI	Perfluorooctane sulfinic acid	-	C8	Perfluoroalkane sulfinic acids	PFSIAs
PFPA	Perfluoropentanoic acid	2706-90-3	C5	Perfluoroalkyl carboxylic acids	PFCAs
PFPeDA	Perfluoropentadecanoic acid	141074-63-7	C15	Perfluoroalkyl carboxylic acids	PFCAs
PFTeDA	Perfluorotetradecanoic acid	376-06-7	C14	Perfluoroalkyl carboxylic acids	PFCAs
PFTrDA	Perfluorotridecanoic acid	72629-94-8	C13	Perfluoroalkyl carboxylic acids	PFCAs
PFUnA	Perfluoroundecanoic acid	4234-23-5	C11	Perfluoroalkyl carboxylic acids	PFCAs

Abb.	Chemical name	CAS No	Chain length	Group name	Group abb.
PFUnDA	Perfluoroundecanoic acid = PFUnA	4234-23-5	C11	Perfluoroalkyl carboxylic acids	PFCAs
POF	Perfluorooctanoyl fluoride	335-66-0	C8	Perfluoroalkanoyl fluorides	PAFs
POSF	Perfluorooctane sulfonyl fluoride	307-35-7	C8	Perfluoroalkane sulfonyl fluorides	PASFs

Annex 2: OECD 2007 substance groups

Grouping of PFCs used in the OECD surveys (OECD, 2007). Annex 1, 2 and 3 include substances that may be potentially degrade to PFOS, other PFASs and PFOA, respectively.

Annex 1	Perfluorooctane sulfonate (PFOS) and related compounds.
Annex 2	Perfluoroalkyl sulfonate (PFAS) and related compounds (other than the substances included in Annex 1)
Annex 3	List of perfluorooctanoic acid (PFOA) and related compounds.
Annex 4 Fluorinated chemicals that potentially degrade to PFCA	P1: Perfluoro alcohol compounds
	P2: Perfluoro amine compounds
	P3: Perfluoro carboxylic compounds (some overlap with annex 3)
	P4: Perfluoro ester compounds
	P5: Perfluoro ether compounds
	P6: Perfluoro iodide compounds
	P7: Perfluoro phosphonic/phosphinic compounds
	P8: Partial perfluoro & miscellaneous perfluoro compounds
	F1: Fluoro alcohol compounds
	F2: Fluoro ammonium compounds
	F3: Fluoro amine compounds
	F4: Fluoro carboxylic compounds
	F5: Fluoro ester compounds
	F6: Fluoro ether compounds
	F7: Fluoro iodide compounds
	F8: Fluoro phosphate compounds
	F9: Fluoro sulfate compounds
	F10: Fluoroalkyl silicate compounds
	F11: Fluoro sulfonate/sulfonamide/sulfonyl compounds
	F12: Fluoro siloxane/silicone/silane compounds
	F13: Fluoro thiols compounds
	F14: Fluoro thioether compounds
	F15: Fluoro thioester compounds
	F16: Fluoro urethane compounds
	F17: Partial fluoro & miscellaneous fluoro compounds

Annex 3: Data from the Danish Product Register

The PFAFs and fluorinated polymer substances identified by the data retreivals from the Danish Product Register in 2006 (Jensen *et al.,* 2008), and 2012 are listed in the table below. The substances are ranked by quantity in 2012.

For the 2006 data for confidentiality reasons no exact figures are given, but the amounts are instead listed as uses over 5 tonnes in total, below 1 tonne, below 0.1 tonne and as 0.00/0.000 tonne which indicate that no amount have been reported to the Danish Product Register. The 2012 data are indicated sligtly differently in accordance with the current confidentiality policy. Total quantities and total number of products are considered confidential if the substance is registered by less than 3 companies. For the majority of substances, the quantity is confidential.

For substances not on the 2006 list chemical names from preregistrations are indicated; for substances not preresistered the name used in the Product Register is indicated.

The 2012 data include:

- Substances on the OECD 2007 list
- Substances from the 2006 list of substances registered in the Product Register, but not on the OECD list (10 substances)
- Additionel substances identified by Poulsen *et al. (*2008) (3 substances).
- Substances in the database of registred substances or the list of 2013 intentions which are not on the OECD 2007 list (xx substances). However, none of these substances were registered in the Product Register.

Three substances indentified in the 2006 survey were included in the data retreival, but turned out to be mixtures based in fluoropolymers which are beyond the scope of this study;

- Tetrafluorethen polymer (CAS No 9002-84-0), constituent of PFTE polymer-based waxes. This substances was registered in 168 products with a total of 12 tonnes.
- Poly[oxy[trifluoro(trifluoromethyl)-1,2-ethanediyl]], α-(1,1,2,2,2-pentafluoroethyl)-ω-[tetrafluoro(trifluoromethyl)ethoxy]- (CAS No 60164-51-4) is a FPPE polymer. Data confidential.
- Poly(difluoromethylene), .alpha.-fluoro-.omega.-(2-iodoethyl) (CAS No 71215-70-8). Fluoropolymer. Data confidential.

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of preparations
				2006	2012	
26655-00-5	Propane, 1,1,1,2,2,3,3-heptafluoro-3-[(trifluoroethenyl)oxy]-, polymer with tetrafluoroethene	None / miscellaneous perfluoroalkyl	5	> 5	confidential	-
65545-80-4	Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, ether with α-fluoro-ω-(2-hydroxyethyl) poly(difluoromethylene) (1:1) (TSCA, DSL, AICS)	Fluoro ether (F6)	n	> 1	0.9	10
143372-54-7	Siloxanes and silicones, (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy Me, hydroxy Me, Me, octyl, ethers with polyethylene glycol mono-Me ether (TSCA, NDSL)	Fluorosiloxane/silicone/silanes (F12)	8	> 1	0.6	84

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of preparations
				2006	2012	
24448-09-7	1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6, 7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-N-methyl- (TSCA, DSL, AICS) (MeFOSE)	PFOS	8	> 1	0.4	21
65530-70-3	Poly(difluoromethylene), α, α'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[ω-fluoro-, ammonium salt (TSCA, DSL)	Fluoro phosphate (F8)	n	< 1	0.3	19
68298-62-4	2-Propenoic acid, 2- [butyl [(heptadecafluorooctyl)sulfonyl]amino]ethyl ester, telomer with 2-[butyl[(pentadecafluoroheptyl) sulfonyl]amino]ethyl 2-propenoate, methyloxirane polymer with oxirane di-2-propenoate, methyloxirane polymer with oxirane mono-2-propenoate and 1-octanethiol (TSCA, DSL, AICS)	PFOS, PFAS	7-8	< 0.1	0.03	32
65530-74-7	Ethanol, 2,2'-iminobis-, compd. With α -fluoro-ω-[2-(phosphonooxy)ethyl] poly(difluoromethylene) (1:1) (TSCA, DSL)	Fluoro phosphate (F8)	n	< 0.1	0.003	8
65530-69-0	Poly(difluoromethylene), α -[2-[(2-carboxyethyl)thio]ethyl]- ω-fluoro-, lithium salt (TSCA, DSL, AICS)	Fluoro thioether (F14)	n	< 0.1	0.1	17
68391-08-2	Alcohols, C8-14, g-ω-perfluoro (TSCA, DSL, EINECS, AICS)	Fluoro alcohols (F1)	6-12	< 0.1	0.02	8
68391-08-2	Alcohols, C8-14, γ-ω-perfluoro	Fluoro alcohols (F1)	8-14	n.i.	0.02	8
65530-72-5	Poly(difluoromethylene), α-fluoro-ω-[2-(phosphonooxy)ethyl]-, diammonium salt (TSCA,DSL)	Fluoro phosphate	n	< 1	0.01	19
2991-51-7	Glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)	PFOS	8	< 0.1	0.01	11
65530-71-4	Poly(difluoromethylene), α -fluoro-ω-[2-(phosphonooxy)ethyl]-, monoammonium salt (TSCA, DSL)	Fluoro phosphate (F8)	n	< 0.1	0.004	18
65530-74-7	Ethanol, 2,2'-iminobis-, compd. With α -fluoro-ω-[2-(phosphonooxy)ethyl] poly(difluoromethylene) (1:1) (TSCA, DSL)	Fluoro phosphate (F8)	n	< 0.1	0.003	8
54950-05-9	Butanedioic acid, sulfo-, 1,4-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) ester, sodium salt (TSCA, NDSL, AICS)	Fluoro ester (F5)	6	< 0.1	0.003	11
65530-63-4	Ethanol, 2,2'-iminobis-, compd. With α -fluoro-ω-[2-(phosphonooxy)ethyl] poly (difluoromethylene) (2:1) (TSCA, DSL)	Fluoro phosphate (F8)	n	< 0.1	0.001	7
65530-64-5	Ethanol, 2,2'-iminobis-, compd. With α, α'-[phosphinicobis(oxy-2,1-ethanediyl)] bis[ω-fluoropoly(difluoromethylene)] (1:1) (TSCA, DSL)	Fluoro phosphate (F8)	n	< 0.1	0.001	7
65530-63-4	Ethanol, 2,2'-iminobis-, compd. With α -fluoro-ω-[2-(phosphonooxy)ethyl] poly (difluoromethylene) (2:1) (TSCA, DSL)	Fluoro phosphate (F8)	n	< 0.1	0.001	7

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of preparations
				2006	2012	
65530-64-5	Ethanol, 2,2'-iminobis-, compd. With α, α'-[phosphinicobis(oxy-2,1-ethanediyl)] bis[ω-fluoropoly(difluoromethylene)] (1:1) (TSCA, DSL)	Fluoro phosphate (F8)	n	< 0.1	0.001	7
67584-51-4	Glycine, N-ethyl-N-[(nonafluorobutyl)sulfonyl]-, potassium salt (TSCA, DSL, AICS)	PFAS	4	< 0.1	0.001	7
67584-62-7	Glycine, N-ethyl-N- [(pentadecafluoroheptyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)	PFAS	7	< 0.1	0.001	7
67584-53-6	Glycine, N-ethyl-N-[(tridecafluorohexyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)	PFAS	6	< 0.1	0.001	11
65530-83-8	Poly(difluoromethylene), α -[2-[(2-carboxyethyl)thio]ethyl]- ω-fluoro- (TSCA, DSL, AICS)	Fluoro thioether (F14)	n	0.00	<0.000	13
67584-52-5	Glycine, N-ethyl-N-[(undecafluoropentyl)sulfonyl]-, potassium salt (TSCA, DSL, AICS)	PFAS	5	0.000	<0.000	7
68412-68-0	Phosphonic acid, perfluoro-C6-12-alkyl derivatives (TSCA, DSL, EINECS)	Perfluoro phosphonic/phosphinic (P7)	6-12	> 1	conf.	-
68412-69-1	Phosphinic acid, bis(perfluoro-C6-12-alkyl) derivatives (TSCA, DSL, EINECS)	Perfluoro phosphonic/phosphinic (P7)	6-12	> 1	conf.	-
56773-42-3	Ethanaminium, N,N,N-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1) (TSCA, DSL, AICS, SWISS)	PFOS	8	< 1	conf.	-
69991-67-9	1-Propene, 1,1,2,3,3,3-hexafluoro-, oxidized, polymerized	None / miscellaneous perfluoroalkyl	5	< 1	conf.	-
68555-92-0	2-Propenoic acid, 2-methyl-, 2-[[(heptadecafluorooctyl)sulfonyl]methylamino] ethyl ester, polymer with 2- [methyl[(nonafluorobutyl)sulfonyl]amino]ethyl 2- methyl-2-propenoate, 2- [methyl[(pentadecafluoroheptyl)sulfonyl]amino]eth yl 2-methyl-2-propenoate, 2-[methyl[(tridecafluorohexyl)sulfonyl]amino]ethyl 2-methyl-2-propenoate, 2-[methyl[(undecafluoropentyl)sulfonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-methyl-2- propenoate (TSCA, DSL, AICS)	PFOS, PFAS	4-8	< 0.1	conf.	-
174125-96-3	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with d-wperfluoro-C10-16-alkyl acrylate and vinyl acetate (TSCA, NDSL, AICS)	Fluoro ester (F5)	7-13	< 0.1	conf.	

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of prepara-tions
				2006	2012	
17741-60-5	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl ester (TSCA, DSL, ENCS)	Fluoro ester (F5)	10	< 0.1	conf.	-
27905-45-9	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl ester (TSCA, DSL, ENCS)	Fluoro ester (F5)	8	< 0.1	conf.	-
2795-39-3	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt (TSCA, DSL, AICS)	PFOS	8	< 0.1	conf.	-
1652-63-7	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulfonyl]amino]-N,N,Ntrimethyl-, iodide (TSCA, DSL, AICS)	PFOS	8	< 0.1	conf.	
647-42-7	1-Octanol, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro- (TSCA, DSL, ENCS, AICS) 6:2 FTOH	Fluoro alcohols (F1)	6	< 0.1	conf.	
79070-11-4	Poly(difluoromethylene), .alpha.-chloro-.omega.- (2,2-dichloro-1,1,2-trifluoroethyl)-	None (PFAS)	8	< 0.1	conf.	-
3825-26-1	Ammonium pentadecafluorooctanoate (EINECS)	PFOA	7	< 0.1	conf.	-
72276-08-5	2-Propenoic acid, 2-[methyl[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13, 14,14,15,15,16,16,17,17,18,18,18-tritriacontafluorooctadecyl)sulfonyl] amino]ethyl ester (TSCA, NDSL)	Fluoro sulfonate/sulfonamide/ sulfonyl (F11)	16	0.00	conf.	
91032-01-8	Fatty acids, C7-19, perfluoro (EINECS)	PFOA, Perfluoro carboxylics (P3)	6-18	0.00	conf.	-
678-39-7	heptadecafluoro- (TSCA, DSL, AICS) 8:2 FTOH	Fluoro alcohols (F1)	8	0.000	conf.	-
65530-66-7	Poly(difluoromethylene), α -fluoro-ω-[2-[(2-methyl- 1-oxo-2-propenyl)oxy]ethyl]- (TSCA, DSL)	Fluoro ester (F5)	n	0.000	conf.	-
865-86-1	1-Dodecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluoro- (TSCA, DSL, AICS) !0:2 FTOH	Fluoro alcohols (F1)	10	0.000	conf.	-
67584-58-1	1-Propanaminium, N,N,N-trimethyl-3-[[(pentadecafluoroheptyl)sulfonyl]amino]-, iodide (TSCA, DSL, ENCS, AICS)	PFAS	7	0.000	conf..	-
67939-95-1	1-Propanaminium, N,N,N-trimethyl-3-[[(nonafluorobutyl)sulfonyl]amino]-, iodide (TSCA, DSL, AICS)	PFAS	4	0.000	conf.	-
68957-57-3	1-Propanaminium, N,N,N-trimethyl-3-[[(undecafluoropentyl)sulfonyl]amino]-, iodide (TSCA, DSL, AICS)	PFAS	5	0.000	conf.	-
68957-58-4	1-Propanaminium, N,N,N-trimethyl-3-[[(tridecafluorohexyl)sulfonyl]amino]-, iodide (TSCA, DSL, ENCS, AICS)	PFAS	6	0.000	conf..	-

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of preparations
				2006	2012	
27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctanesulfonic acid	Fluoro sulfonate/sulfonamide/sulfonyl compounds (F11)	6	n.i.	conf	-
70969-47-0	Thiols, C8-20, .gamma.-.omega.-perfluoro, telomers with acrylamide	Fluoro amine compounds (F3)	6-18	n.i.	conf	-
203743-03-7	2-Propenoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, .gamma.-.omega.-perfluoro-C10-16-alkyl acrylate and stearyl methacrylate	Fluoro ester compounds (F5)	8-14	n.i.	conf	-
196316-34-4	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with .gamma.-.omega.-perfluoro-C10-16-alkyl acrylate and vinyl acetate, acetates	Fluoro ester compounds (F5)	8-14	n.i.	conf	-
68187-47-3	1-Propanesulfonic acid, 2-methyl-, 2-[[1-oxo-3-[(γ-ω-perfluoro-C4-16-alkyl)thio]propyl]amino] derivs., sodium salts	Fluoro amine compounds (F3)	2-14	n.i.	conf	-
142636-88-2	Octadecylmethacrylat/2-propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl ester/2-propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl ester/2-propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,1	Fluoro carboxylic compounds (F4)	8, 10 & 12	n.i.	conf	-
70983-60-7	1-Propanaminium, 2-hydroxy-N,N,N-trimethyl-, 3-[(γ-ω-perfluoro-C6-20-alkyl)thio] derivs., chlorides	Fluoro thioether compounds (F14)	4-18	n.i.	conf	-
70969-47-0	Thiols, C8-20, .gamma.-.omega.-perfluoro, telomers with acrylamide	Fluoro amine compounds (F3)	6-18	n.i.	conf	-
39239-77-5	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Pentacosafluorotetradecanol	Fluoro alcohol compounds (F1)	12	n.i.	conf	-
60699-51-6	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Nonacosafluorohexadecanol	Fluoro alcohol compounds (F1)	14	n.i.	conf	-
65104-67-8	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Tritriacontafluorooctadecanol	Fluoro alcohol compounds (F1)	16	n.i.	conf	-
65530-66-7	Poly(difluoromethylene),.alpha.-fluoro-.omega.-(2-((2-methyl-1-oxooctadecy)ethyl)-	Fluoro ester compounds (F5)	n	n.i.	conf	-
1652-63-7	[3-[[(heptadecafluorooctyl)sulfonyl] amino]propyl]trimethylammonium iodide	PFOS	8	n.i.	conf	-

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of prepara-tions
				2006	2012	
14650-24-9	2-Propenoic acid, 2-methyl-, 2-(((Heptadeca-fluorooctyl)sulfonyl)methylamino)-ethyl ester	None (PFAS precursors)	15	< 0.1	conf	-
119973-85-2	2-Propenoic acid, 2-methyl-, 3-chloro-2-hydroxypropyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-propenoate, N-(hydroxymethyl)-2-propenamide, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-nonacosafluoro-hexadecyl 2-propenoate, octadecyl 2-propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,11,11,12,12,13,13,14,14,14-pentacosa-fluorotetradecyl 2-propenoate (AICS)	Fluoro ester (F5)	8-14	< 1	n.r.	-
163702-08-7	Propane, 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoro- (approximately 70% by weight of mix-ture)	Perfluoro ethers (P5)	4	< 0.1	n.r.	-
34455-29-3	1-Propanaminium, N-(carboxymethyl)-N,Ndimethyl-3-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, inner salt (TSCA)	Fluoro sul-fonate/sulfona mide/ sulfonyl (F11)	6	< 0.1	n.r.	-
67584-42-3	Cyclohexanesulfonic acid, decafluoro(pentafluoroethyl)-, potassium salt	None (PFAS)	8	< 0.1	n.r.	-
65530-85-0	Poly(difluoromethylene), alpha-(cyclohexylmethyl)-omega-hydro-	None (miscel-laneous perfluoroalkyl)	n	< 0.1	n.r.	-
34395-24-9	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafluorotetradecyl ester (TSCA, NDSL, ENCS)	Fluoro ester (F5)	12	< 0.1	n.r.	-
163702-07-6	Butane, 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy- (TSCA, DSL, SWISS)	Perfluoro ethers (P5)	4	< 0.1	n.r.	-
29420-49-3	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFBS)	PFAS	4	< 0.1	n.r.	-
3871-99-6	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFHxS)	PFAS	6	< 0.1	n.r.	-
60270-55-5	1-Heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFHpS)	PFAS	7	< 0.1	n.r.	-
68156-07-0	Cyclohexanesulfonic acid, decafluoro(trifluoromethyl)-, potassium salt (TSCA, DSL, AICS)	PFAS	7	< 0.1	n.r.	-

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of prepara-tions
				2006	2012	
67584-61-6	2-Propenoic acid, 2-methyl-, 2-[methyl[(tridecafluorohexyl)sulfonyl]amino] ethyl ester (TSCA, NDSL)	PFAS	6	0.00	n.r.	-
90622-43-8	Alcohols, C7-22, ε-ω-perfluoro-, β-δ-fluoro (EINECS)	Fluoro alcohols (F1)	3-18	0.00	n.r.	-
150135-57-2	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with Bu acrylate, g-w-perfluoro-C8-14-alkyl acrylate and polyethylene glycol monomethacrylate, 2,2'-azobis[2,4-dimethylpentanenitrile]-initiated (TSCA, NDSL)	Fluoro ester (F5)	6-12	0.00	n.r.	-
34362-49-7	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14, 15,15,16,16,16-nonacosafluorohexadecyl ester (TSCA, NDSL, ENCS)	Fluoro ester (F5)	14	0.00	n.r.	
65605-70-1	Poly(difluoromethylene), α -fluoro-ω-[2-[(1-oxo-2-propenyl)oxy]ethyl]- (DSL)	Fluoro ester (F5)	n	0.000	n.r.	-
2043-53-0	Decane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodo- (TSCA, NDSL) 8:2 FTI	Fluoro iodide (F7)	8	0.00	n.r.	-
2043-54-1	Dodecane, 1,1,1,2,2,3,3,4,4,5,5, 6,6,7,7,8,8,9,9,10,10-heneicosafluoro-12-iodo- (TSCA, NDSL) 10:2 FTI	Fluoro iodide (F7)	10	0.00	n.r.	-
78560-44-8	Silane, trichloro (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)- (TSCA, NDSL)	Fluoro silox-ane/silicone /silanes (F12)	8	0.00	n.r	-
68140-18-1	Thiols, C4-10, γ-ω-perfluoro (TSCA, NDSL, EINECS)	Fluoro thiols (F13)	2-8	0.00	n.r.	-
68140-19-2	Thiols, C4-10, γ-ω-perfluoro (TSCA, NDSL, EINECS)	Fluoro thiols (F13)	2-18	0.00	n.r.	-
68140-20-5	Thiols, C6-12, γ-ω-perfluoro (TSCA, NDSL, EINECS)	Fluoro thiols (F13)	4-10	0.00	n.r.	-
68140-21-6	Thiols, C10-20, γ-ω-perfluoro (TSCA, NDSL, EINECS)	Fluoro thiols (F13)	8-18	0.00	n.r.	-
376-14-7	2-Propenoic acid, 2-methyl-, 2-(ethyl((heptadecafluorooctyl)sulfonyl)amino)ethyl ester	None (PFAS precursors)	16	0.00	n.r.	-
9011-17-0	1,1-Difluorethen/hexafluorpropen polymer	None (miscel-laneous perfluoroalkyl)	n	0.00	n.r	-
376-18-1	1-Nonanol, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro- (TSCA, NDSL)	Partial fluoro & miscellaneous fluoro (F17)	8	0.00	n.r	-

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of prepara-tions
				2006	2012	
86508-42-1	Perfluoro compounds, C5-18 (TSCA, DSL, AICS)	Partial perfluo-ro & miscellaneous perfluoro (P8)	5-18	0.00	n.r.	-
17202-41-4	1-Nonanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-nonadecafluoro-, ammonium salt (TSCA, DSL, AICS) (PFNS)	PFAS	9	0.000	n.r.	-
3872-25-1	1-Pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFPeS)	PFAS	5	0.000	n.r.	-
56372-23-7	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(tridecafluorohexyl)sulfonyl]amino]ethyl]- ω-hydroxy- (TSCA, DSL, AICS)	PFAS	6	0.000	n.r.	-
67584-59-2	2-Propenoic acid, 2-methyl-, 2-[methyl[(nonafluorobutyl)sulfonyl]amino]ethyl ester (TSCA, NDSL)	PFAS	4	0.00	n.r.	-
67584-60-5	2-Propenoic acid, 2-methyl-, 2-[methyl[(undecafluoropentyl)sulfonyl]amino] ethyl ester (TSCA, NDSL	PFAS	5	0.00	n.r.	-
67906-42-7	1-Decanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heneicosafluoro-, ammonium salt (TSCA, DSL, AICS) (PFDS)	PFAS	10	0.000	n.r.	-
67939-96-2	2-Propenoic acid, 2-methyl-, 2-[methyl[(pentadecafluoroheptyl)sulfonyl] amino]ethyl ester (TSCA, NDSL	PFAS	7	0.00	n.r.	-
68298-79-3	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(nonafluorobutyl)sulfonyl]amino]ethyl]- ω-hydroxy- (TSCA, DSL, AICS)	PFAS	4	0.000	n.r.	-
68298-80-6	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(undecafluoropentyl)sulfonyl]amino]ethyl]- ω-hydroxy- (TSCA, DSL, AICS)	PFAS	5	0.000	n.r.	-
68298-81-7	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(pentadecafluoroheptyl)sulfonyl]amino] ethyl]- ω-hydroxy- (TSCA, DSL, AICS)	PFAS	7	0.000	n.r.	-
68957-62-0	1-Heptanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro- (TSCA, DSL) (EtFHpSA)	PFAS	7	0.000	n.r.	-
68958-60-1	Poly(oxy-1,2-ethanediyl), a-[2-[ethyl[(pentadecafluoroheptyl)sulfonyl] amino]ethyl]- ω-methoxy- (TSCA, DSL, AICS)	PFAS	7	0.000	n.r.	-
70225-15-9	1-Heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)	PFAS	7	0.000	n.r.	-

CAS No.	Substance name	OECD class	Chain length	Total amount in tonnes		Number of prepara-tions
				2006	2012	
70225-16-0	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)	PFAS	6	0.000	n.r.	-
70225-17-1	1-Pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)	PFAS	5	0.000	n.r.	-
70225-18-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)	PFAS	4	0.000	n.r.	-
29117-08-6	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(heptadecafluorooctyl)sulfonyl] amino]ethyl]-ω-hydroxy- (TSCA, DSL, ENCS, AICS)	PFOS	8	0.000	n.r.	-
4151-50-2	1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (TSCA, DSL) (EtFOSA)	PFOS	8	0.000	n.r.	-
76752-82-4	Heptadecafluorooctane-1-sulfonamide, compound with triethylamine (1:1) (EINECS)	PFOS	8	0.00	n.r.	-
68958-61-2	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(heptadecafluorooctyl)sulfonyl] amino]ethyl]-ω-methoxy- (TSCA, DSL, AICS)	PFOS	8	0.000	n.r.	-
70225-14-8	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compd. With 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)	PFOS	8	0.000	n.r.	-
68081-83-4	Carbamic acid, (4-methyl-1,3-phenylene)bis-, bis[2-[ethyl[(perfluoro-C4-8-alkyl) sulfonyl]amino]ethyl] ester (TSCA, DSL, EINECS, AICS)	PFOS, PFAS	4-8	0.000	n.r.	-

Annex 4: Background information to chapter 3 on legal framework

[vi er ikke sikre på at dette skal med, men valgte at lave en differentiering på denne måde så den mindre vidende læser kunne få ekstra information vedrørende kapitel 3]

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 3.

EU and Danish legislation
Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvre as to the form and means of implementation. However, there are great differences in the room for manoeuvre between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include still valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving member state representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.

- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulate to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation

REACH and CLP

The REACH Regulation[13] and the CLP Regulation[14] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration

All manufacturers and importers of chemical substance > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered dead-lines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

Evaluation

A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation

Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given dead-line (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction

The 'safety net'. If the authorities assess that that risks to be addressed at the EU level are still in place despite the above mechanisms, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling

The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two lassification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of

[13] Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

[14] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.
2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publish the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

Ongoing activities - pipeline
In addition to listing substance already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)
The EU member states have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV
Before a substance is included in REACH Annex XIV and thus being subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list[15]
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions
When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction

this is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intensions in relation to Annex XV dossiers divided into:
- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

[15] It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

for the three types of Annex XV dossiers.

International agreements

OSPAR Convention
OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out.
- guidelines or guidance setting out the way that any programme or measure should be implemented
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties

HELCOM - Helsinki Convention
The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

Stockholm Convention on Persistent Organic Pollutants (POPs)
The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention
The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention
The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

Eco-labels
Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower
The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

Nordic Swan
The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is

hosted by Ecolabelling Denmark "Miljømærkning Danmark" (http://www.ecolabel.dk/). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).

Blue Angel (Blauer Engel)
The Blue Angel is a national German eco-label. More information can be found on: http://www.blauer-engel.de/en.

Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances
This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The report define the substances groups and present information on the use and occurrence of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, waste management and information regarding ongoing activities under REACH, among others.

Kortlægning af PFOS, PFOA og andre perfluoralkyl- and polyfluoralkylforbindelser
Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Rapporten definerer stofgrupperne og indeholder blandt andet en beskrivelse af brugen og forekomsten af PFOS, PFOA og andre perfluoralkyl- and polyfluoralkylforbindelser, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, og viden om alternativer, eksisterende regulering, moniteringsdata, eksponering, affaldsbehandling og igangværende aktiviteter under REACH.

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CHEMSERVICE

POSITION PAPER

Fluoropolymers: an outlier in the PFAS class of substances

Final report

Date

18 July 2022

Executive Summary

Fluoropolymers are frequently confused with other chemicals that belong to the PFAS group of substances. While fluoropolymers meet the chemical and structural conditions set in the broad definition of PFAS, their properties and range of applications are very different not only from the short-chain or long-chain non-polymeric PFAS that have been cause of concern due to their toxic properties for human health or the environment, but they are also very different from other polymeric PFAS like perpolyfluoroethers or side-chain fluorinated polymers.

In addition to their clearly defined and differentiated structure, existing scientific data shows that fluoropolymers are biologically stable and chemically inert, negligibly soluble in water, non-bioavailable, non-bioaccumulative, and non-toxic. Furthermore, their range of applications is different from the other polymeric PFAS, since fluoropolymers are mainly used in industrial applications.

This report highlights the main differences between fluoropolymers, perfluoropolyethers and side-chain fluorinated polymers, highlighting how those differences justify considering fluoropolymers as chemicals posing no relevant risk for human health or the environment. While the first three Sections intend to explain such differences in a way that will be easy to understand for any reader, Section 4 goes slightly deeper in technical justifications of the contrast between these families of chemicals. Since one of the most critical differences, particularly between fluoropolymers and side-chain fluorinated polymers is the potential of degradation, both during normal conditions of use as well as under ambient conditions in the natural environment (which is negligible in the case of fluoropolymers) a technical Annex with data on information available for fluoropolymers has been added.

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1. Introduction

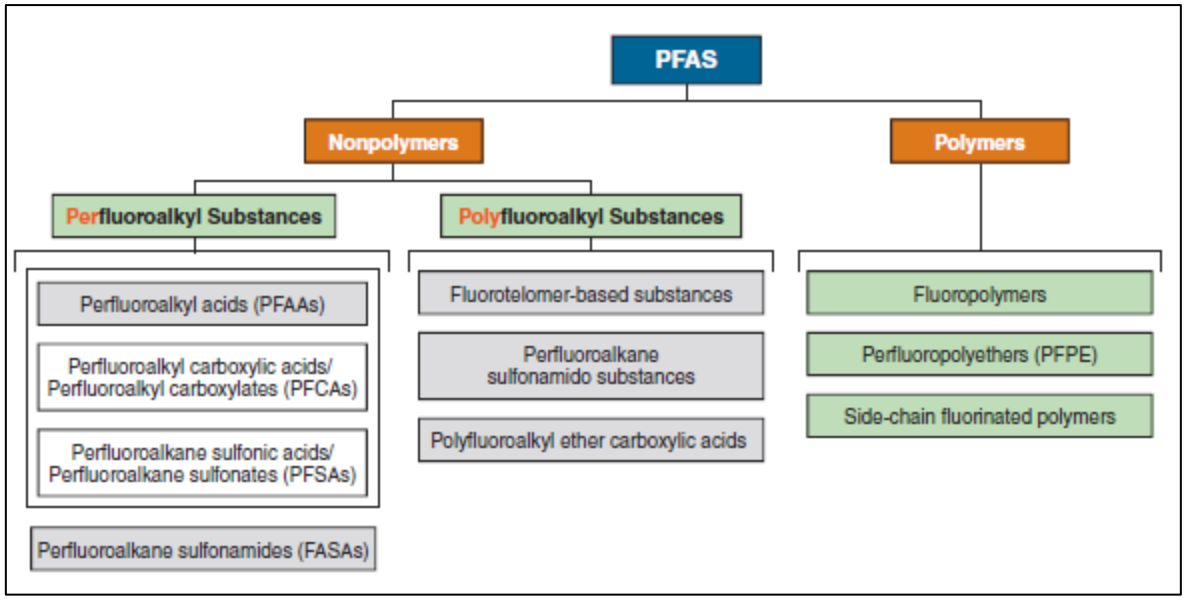
A restriction proposal under the REACH Regulation[1] on per-and polyfluoroalkyl substances (PFAS) is currently under development, in order to limit the risks to human health and the environment from their manufacture and use. Fluoropolymers (FPs), which are high molecular weight polymers with unique properties (Korzeniowski et al., 2022; Henry et al., 2018), are a separate family within the PFAS group, and could therefore be adversely impacted by this restriction even though the vast majority of FPs meet the condition of Polmers of Low Concern (PLC).

In this paper, the position of FPs inside the broad group of PFAS will be defined, and the difference between FPs and other types of polymeric PFAS, namely side-chain fluorinated polymers (SCFPs) and perfluoropolyethers (PFPEs), will be highlighted.

2. Where do fluoropolymers fit within the PFAS group?

PFAS are a group of 4,730 (OECD, 2018) different highly fluorinated synthetic (man-made) substances, both polymeric and non-polymeric, although other sources increase the number to approximately 9,000 chemicals (NIOSH, 2022). Due to the large number of chemicals pertaining to this group, and the wide variability of composition and properties, PFAS can be divided in different families. A summary of the structure of the PFAS group is displayed in **Figure *1*Error! Reference source not found.** (ITRC, 2020).

Figure 1. Structure of families in the PFAS group



[1] Regulation (EC) No 1907/2006

As seen in **Figure 1**, FPs are part of the PFAS group and, for this reason, they are candidates to be included in the scope of the restriction proposal. However, because of their different chemical structure and properties, they need to be considered as a separate family within the group, clearly distinct not only from the non-polymeric PFAS, but also from the other polymeric PFAS. These differences are relevant not only in terms of grouping, but more importantly also in relation to the risk for human health and the environment that will be derived from their manufacture and use.

3. Why should fluoropolymers be considered different from other PFAS?

FPs should be considered a separate class under the PFAS group, which can be differentiated from other PFAS on the basis of their nature, structure, uses and applications, as well as from the point of view of safety and environmental impacts.

The polymeric nature of FPs

The term polymer is derived from the Greek roots “poly” (many) and “mer” (part) and this popularly defines these substances as long-chain materials made up of many simple parts (Jensen, 2008). More scientifically, a polymer is defined as a molecule of high relative molecular mass (macromolecule), the structure of which essentially comprises the multiple repetitions of units derived from molecules of low relative molecular mass, known as monomers (IUPAC, 2022).

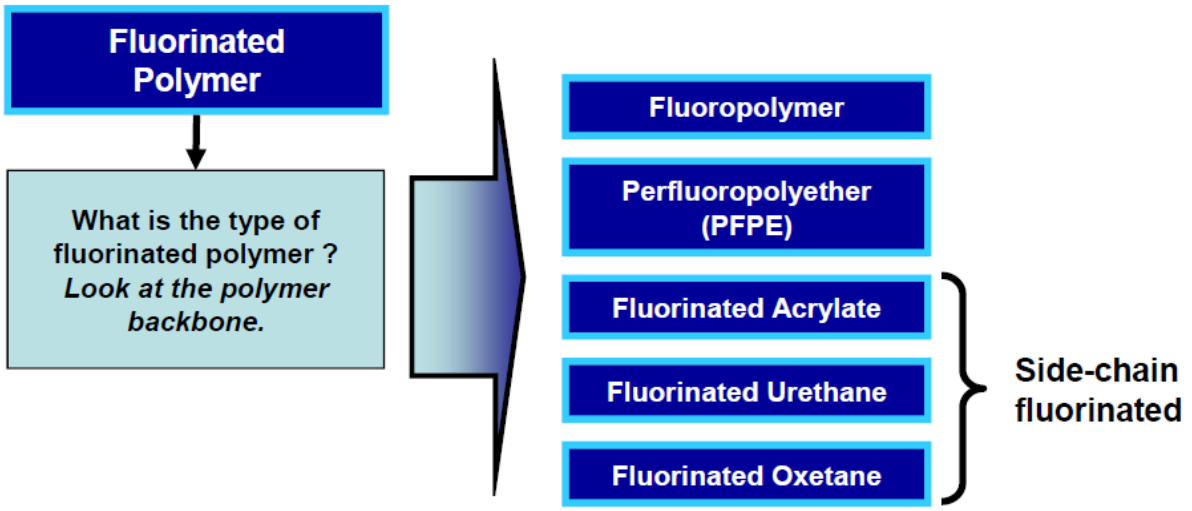
In the case of FPs, this macromolecule is a long chain (backbone) of thousands of connected carbon atoms (C) to which fluorine atoms (F) are bound (FPG, 2022).

For this reason, this family of synthetic polymers can be easily differentiated from the non-polymeric PFAS, which are also based on chains of C atoms, but which are much shorter than those of polymers (chain length between 2 and 13 C atoms).

The structure of FPs

FPs are the only polymeric PFAS in which F is directly attached to C in a carbon polymeric backbone. This fact differentiates FPs from the other polymeric PFAS, in which F is directly attached to C in another type of polymeric backbone (polyether), or F is directly attached to C in a side chain and not to the carbon polymeric backbone (SCFPs). This is displayed in **Figure 2** (Wahlström et al., 2021).

Figure 2. Types of polymeric PFAS based on their structure.



Use and applications.

FPs are mostly used in industrial applications due to their unique set of material properties. They are solid materials, and the main applications are the production of plastic and rubber elements which are later used in a wide variety of industrial sectors such as pharmaceutical and medical products and devices, renewable energy, telecommunications, electronics and semiconductors, automotive and aerospace, food and water processing, architecture and building, and chemical process industries (Glüge et al., 2020; Banerjee et al., 2017).



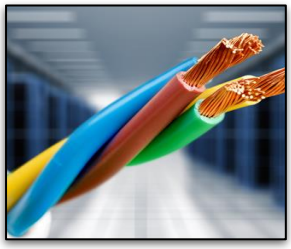
Pharmaceutical



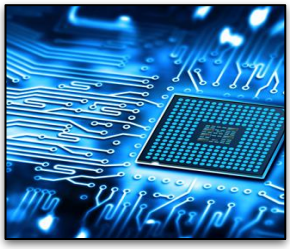
Medical devices



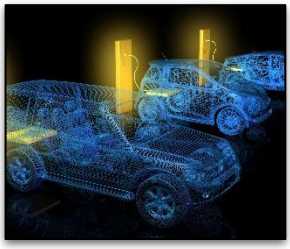
Renewable energy



Telecommunications



Electronic and semiconductors



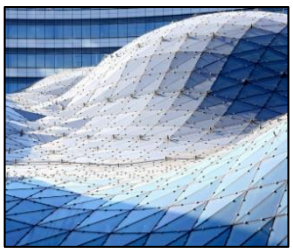
Automotive



Aerospace



Food and water processing



Architecture and building



Chemical processing

In contrast, the other polymeric PFAS such as SCFPs are focused predominantly on consumer applications due to their surface properties. The main application is the surface protection of textile, apparel, leather, carpets, and paper (Glüge et al., 2020). The Danish EPA (2013) highlighted that around 50% of the use of SCFPs is found in textile applications such as carpets and carpet care products. The main industrial sectors of use are cosmetics, nonwovens, carpets, textiles, food and packaging, and firefighting foams. In relation to PFPEs, while these are mainly used as lubricants in specific industrial sectors, certain consumer applications related to surface protection are also relevant (Fiedler et al., 2020). These differentiated polymeric PFAS can be liquids, greases, or dispersions in water.



Cosmetics



Nonwovens



Carpets



Textiles



Food packaging



Firefighting foams



Lubricants

Environmental considerations and degradation to small PFAS molecules.

FPs and PFPEs do not degrade to small PFAS molecules that may be mobile or bioaccumulative, under intended use conditions or under environmental conditions at the end-of-life phase of their applications. This is due to the strength of the C-F bond, the high molecular weight, and the lack of water solubility or volatility, (Fiedler et al., 2020; Danish EPA, 2013).

On the contrary, depending on the type of side chain included in the structure, the SCFPs can potentially lead to the formation of non-polymeric PFAS substances as a result of degradation under environmental conditions (Fiedler et al., 2020; Danish EPA, 2013).

Safety considerations.

The main FPs meet the conditions set out by the OECD (2009) to be regarded as Polymers of Low Concern (PLC) because they are biologically stable and chemically inert in presence of virtually any chemical, negligibly soluble in water, non-bioavailable, non-bioaccumulative, and non-toxic (Henry et al., 2018). While this original research was limited to four FPs, additional work has demonstrated that approximately 96% of the FPs available on the market meet the PLC criteria (Korzeniowski et al., 2022).

For other polymeric PFAS, their behaviour against the PLC criteria is currently unknown. Furthermore, the fact that they are mainly used in consumer applications could be linked to potential higher risk compared to the case of FPs, which are mainly used in industrial sectors.

4. Key differences between fluoropolymers and other polymeric PFAS

4.1. Structural comparison

Attending to the structure of the macromolecules, the polymeric PFAS can be grouped in the following three main categories (COM, 2020):

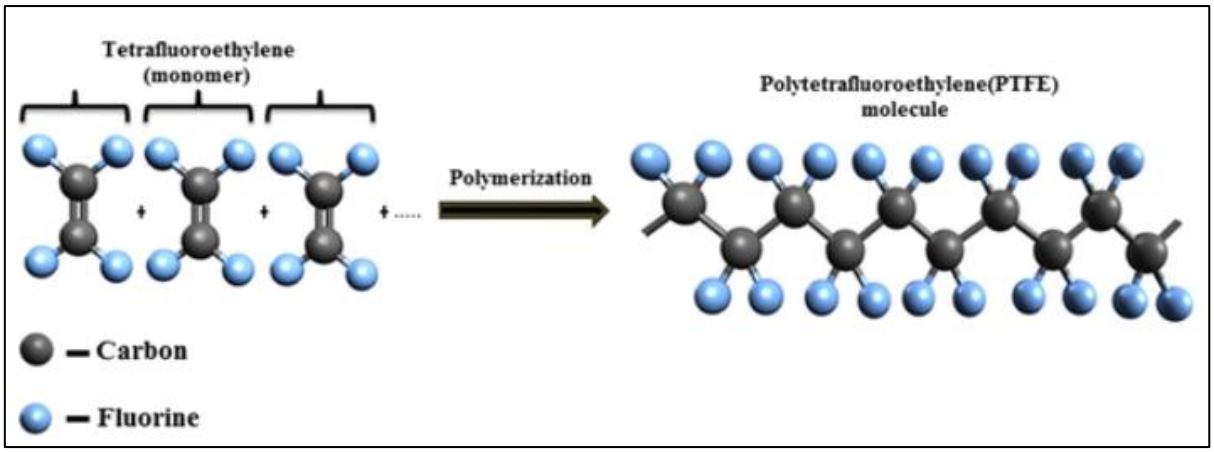
- FPs: have a carbon polymer backbone with F directly attached to C in the backbone.
- PFPEs: have a polyether polymer backbone, in which repeating monomer contains a carbon-oxygen (C-O) bond, with F directly attached to C in the backbone.
- SCFPs: have a carbon polymer backbone with fluorinated side chains directly attached to C in the backbone. In this case, F are not directly attached to C in the backbone.

Fluoropolymers

FPs are polymers with F directly attached to their carbon backbone that are manufactured by (co)polymerisation of olefinic monomers. In order to obtain a FP, it is necessary that at least one of these monomers contains a F bond to one or both of the olefinic C atoms, so that the carbon-only polymer backbone with F directly bonded to it can be generated (Henry et al., 2018). The exceptionally strength of the C-F bond in FPs generates their unique, high value properties (Banerjee et al., 2017).

Figure 3 (Dhanumalayan et al., 2018) shows the polymerization process and the final structure of polytetrafluoroethylene (PTFE), the most important FP in terms of production and use.

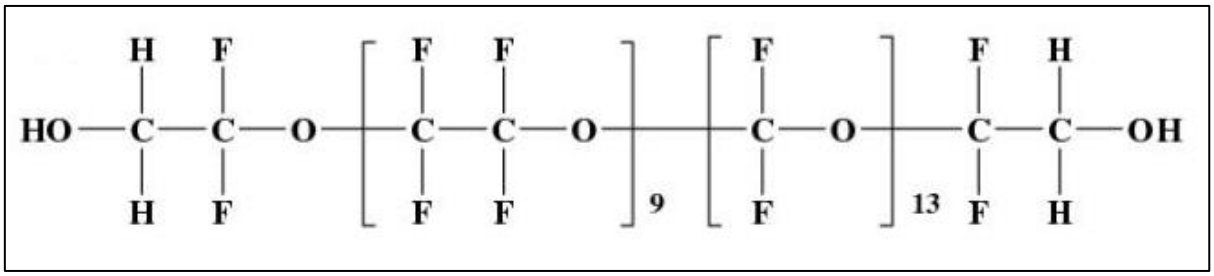
Figure 3. Chemical structure of PTFE.



Perfluoropolyethers

PFPEs are long-chain polymers that consist of a polyether polymer backbone composed of C, O, and F, in which F and O are strongly bonded to C. The chemical structure is shown in **Figure 4** (Lee et al., 2006).

Figure 4. Chemical structure of PFPE.

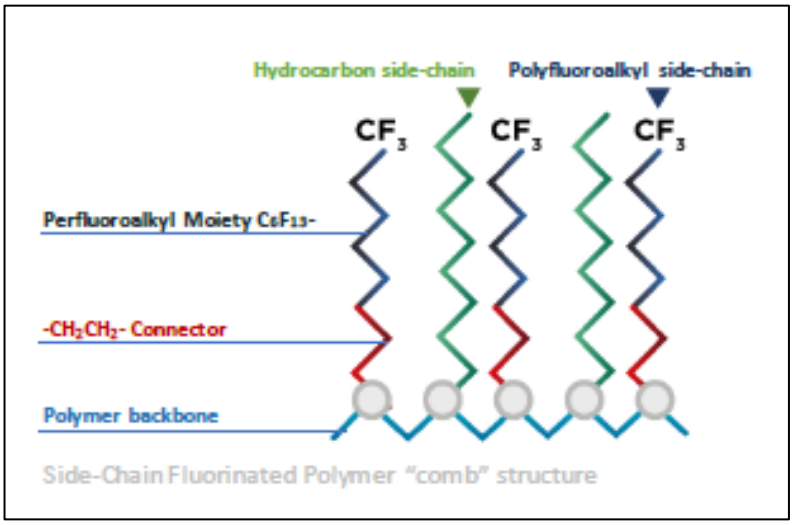


Side-chain fluorinated polymers

SCFPs constitute a diverse type of polymeric PFAS substances. They are fluorotelomer based products of polymeric nature, both long and short chain (FPG, 2017). The fluorinated side-chain moieties are produced by the telomerization or electrochemical fluorination process, in such a way that the fluorinated side chains are attached to the polymer backbone by a spacer moiety and a linking group (Fiedler et al., 2020). The final structure, which can be seen in **Figure 5** is a hydrocarbon polymer backbone with a polyfluoroalkyl side chain bound to the backbone that contains a perfluoroalkyl moiety as well as side chains that have no fluorinated

carbons. The polymer has a comb structure where some of the tines (aka teeth) are a side chain with the perfluoroalkyl moiety while other side chains contain hydrocarbon functionality, not fluorine (FPG, 2022).

Figure 5. Chemical structure of SCFP.



4.2. Safety considerations

Fluoropolymers

Due to their unique properties, initially four FPs have been classed as PLC according to the OECD criteria, given that they have been proven to be biologically stable and chemically inert in presence of virtually any chemical, negligibly soluble in water, non-bioavailable, non-bioaccumulative, non-toxic and resistant to degradation (Henry et al., 2018). The four FPs are:

- polytetrafluoroethylene (PTFE)
- fluorinated ethylene propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (PFA)

However, according to a recent study (Korzeniowski et al., 2022) the PLC classification can be extended to at least 96% of the commercial FPs available on the market worldwide, due to their physio-chemical, biological, toxicological, and ecotoxicological properties.

Furthermore, the main uses of FPs are related to industrial applications. Industrial use is considered per definition as non-dispersive as this use can take place at only a few numbers of sites and/or involve few users. Also, the safety & waste disposal requirements in the industrial environment are more stringent than in other uses, such as consumer uses.

Perfluoropolyethers

PFPEs are mainly used as lubricants in specific industrial sectors, however consumer applications related to surface protection are also relevant (Fiedler et al., 2020).

Side-chain fluorinated polymers

SCFPs are used as surface protectors in textile, apparel, leather, carpets, and paper. These are open and dispersive uses where many consumers come into contact with the SCFPs-containing products (Glüge et al., 2020).

4.3. Relevant uses of application

Fluoropolymers

According to the bibliography, out of the 4,730 substances included in the PFAS category (OECD, 2018), only 256 are commercially relevant (Buck et al., 2021). In the case of FPs, only 38 substances are currently available on the market, out of the 267 compounds that are currently identified. This means that commercial FPs only represent 0.8% of the PFAS universe, but they represent 14.8% of the PFAS with commercial relevance. This is due to the unique properties of these materials and their high performance.

FPs are extremely stable, solid specialty materials used in a wide range of sectors: transport, chemicals and power, cookware, electronics and semiconductors, food and pharma, textiles, architecture, medical applications, renewable energies, and consumer articles (FPG, 2017). Also, FPs play an important role in the development of new materials for advanced applications in aeronautics and aerospace, building industries, petrochemicals, automotive industries, Li-ion batteries, high performance membranes, textile treatment, wires and cables, and microelectronics (Banerjee et al., 2017).

It is relevant to note that FPs are used when other materials fail to satisfy minimum performance criteria as per global standards. As example, FPs have been used in the production of electrical cables for airplanes due to their unique combination of properties (high insulation, resistance to high voltages, flexibility at very low and high temperatures, fire retardancy, chemical resistance to specialty fuels, low weight), that ensure safety for passengers and crew during flight. Usually being a higher price option, FPs are only used when other materials fail to provide critical properties (or combination of properties) that are absolutely necessary under certain conditions (e.g., resistance at extreme temperature ranges and under very corrosive environments).

Perfluoropolyethers

8 of the polymeric substances that are currently in the market are PFPEs (Buck et al., 2021), which represents 0.2% of the PFAS universe and 3.1% of the PFAS with commercial relevance.

PFPEs are used as functional fluids, surfactants, and surface protection products (Buck et al., 2011). The main use of PFPEs is as lubricants in many industrial sectors, such as aerospace (Jones W.R., 1994), aviation, automotive, pharmaceutical and medical applications, process

equipment, semiconductors and electronics (Huskey 2005). Also, they are marketed as surface treatments for natural stone, metal, glass, plastic, textiles, leather, and paper and paperboard treatment for food-contact applications (Buck et al., 2011).

The main uses of PFPEs are industrial, but some consumer uses related to the surface protection have to be considered. PFPEs are available as liquids or greases (Fiedler et al., 2020).

Side-chain fluorinated polymers

In the case of the SCFPs, only 6 substances are commercially relevant (Buck et al., 2021). This represents 0.1% of the PFAS universe and 2.3% of the PFAS with commercial relevance. They are frequently marketed as polymer dispersions in water (FPG, 2022).

SCFPs have surface properties (FPG, 2022) and, for this reason, they are used as surface protectors to provide water, oil, and stain repellence to textiles, apparel, leather, carpets, nonwovens, and paper, and soil release properties (Glüge et al., 2020; FPG, 2017).

4.4. Key properties

Fluoropolymers

FPs have material properties, which include durability, mechanical strength, inertness, thermal stability in foreseeable use conditions, and resistance to chemical, biological, and physical degradation (Henry et al., 2018). Also, they are non-wetting, non-stick, and highly resistant to temperature, fire, and weather.

These properties are attributable to the very strong C-F bonds, the strongest bond between C and any other atom, making them highly stable. C atoms alone form the FP backbone, each surrounded by an envelope of F atoms.

The main properties of FPs are (Henry et al., 2018):

- very high molecular weight (>100 000 Da)
- high thermal, chemical, photochemical, oxidative, hydrolytic, and biological stability
- low flammability
- low dielectric constant
- resistance to degradation
- negligible residual monomers and low molecular weight oligomer content
- limited low molecular weight leachables
- no reactive functional groups of concern in the structure

Perfluoropolyethers

PFPEs are a special class of materials, mainly used as lubricants and functional fluids, which can be used in different applications because of their versatility. However, they show some different features compared with FPs, such as low surface tension and radiation resistance to gamma ray (Huskey, 2005).

Side-chain fluorinated polymers

SCFPs are mainly used as surface protector due to the high level of repellence to harmful chemicals, oils, blood and bodily fluids, etc. This behaviour is directly related to their surface properties, such as low surface tension and low surface free energy, and non-fouling behaviour (Honda et al., 2005).

4.5. Outcome from potential degradation processes

Fluoropolymers

FPs are substantially different from the other polymeric PFAS in terms of potential emissions due to degradation during intended use or under environmental conditions.

FPs generally display a high molecular weight, they show no degradation under their intended use nor under ambient conditions typically found in the natural environment, little to no water solubility or volatility, and therefore would not be expected to degrade to lower molecular weight PFAS (Fiedler et al., 2020; Danish EPA, 2013). Also, they do not lead to the formation of long-chain PFAS as a result of degradation (COM, 2020).

Perfluoropolyethers

Regarding degradation, according to literature sources, PFPEs exhibit a similar behaviour to FPs (COM, 2020; Fiedler et al., 2020; Danish EPA, 2013). Specifically, because the repeating units of the PFPEs contain only 2 or 3 perfluorinated C atoms per O atom, their degradation cannot lead to the formation of long-chain PFAS (Buck et al., 2011).

Side-chain fluorinated polymers

The linking group in the structure of the SCFPs can be susceptible to cleavage, depending on the structure of each material, resulting in loss of the fluoroalkyl side chain. Thus, SCFPs can ultimately be a source of perfluoroalkyl acids (PFAAs), such as PFOA, PFOS, perfluorobutanoic acid (PFBA), perfluorohexane sulfonic acid (PFHxS), or perfluorohexane carboxylic acid (PFHxA), and so forth, unless there is stability data to prove otherwise. It means that, under environmental conditions, SCFPs can degrade to these non-polymer PFAS (Fiedler et al., 2020; Danish EPA, 2013), which are well known due to their effects on human health and the environment.

Annex I at the end of this report provides further information on the fact that FPs do not degrade during normal use or under intended environmental conditions.

5. Conclusions

Fluoropolymers are a well-defined and distinct family of substances inside the PFAS group that show unique combination of properties, which are not shared by other members of these large group of chemicals. Although they pertain to the polymeric PFAS, they are clearly different from other fluorinated polymeric materials (specifically perfluoropolyethers and side-chain fluorinated polymers) due to:

- Unique combination of properties, which make them highly valuable in extremely demanding applications.
- No degradation potential, since they do not degrade to small PFAS molecules during the intended use or under ambient conditions in the natural environment.
- Safety considerations, since they are not toxic, not bioaccumulative, and have insignificant human health impact.
- Environmental considerations, as non-soluble, non-mobile substances with insignificant environmental impact.
- Main uses related to industrial applications.

Due to their chemical structure (carbon backbone with polyfluoroalkyl side chains bound to it), side-chain fluorinated polymers can degrade to hazardous non-polymeric PFAS during the intended use or under environmental conditions at the end-of-life phase of their applications. Moreover, these substances are used mainly at the consumer level, which is considered an open and dispersive use. Therefore, side-chain fluorinated polymers could develop effects on human health and the environment that would never be exhibited by fluoropolymers.

In the case of perfluoropolyethers, degradation potential during the use phase is limited and therefore, potential risks related to their use are expected to be limited.

On the other hand, the vast majority of fluoropolymers fulfil the criteria to be considered as Polymers of Low Concern: they are high molecular weight polymers, have narrow molecular weight distribution, and have negligible oligomer content and organic and inorganic leachables. Data show that fluoropolymers have thermal, chemical, photochemical, hydrolytic, and biological stability. However, the behaviour against the Polymer of Low Concern criteria of side-chain fluorinated polymers and perfluoropolyethers is currently unknown.

Based on these differentiating properties, mainly related to the specific chemical structure of fluoropolymers (carbon backbone with F atoms directly bonded to C atoms), it is possible to conclude that fluoropolymers are a separate family of substances inside the PFAS group, even compared with the other fluorinated polymeric materials. Therefore, they should be also treated separately from other PFAS in relation to regulatory initiatives.

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Annex I: Degradation of fluoropolymers

Thermal degradation

In addition to the chemical structure, the key difference between FPs and SCFPs is their degradation potential. Fluoropolymers are inert and stable substances, and no degradation is expected under normal use.

Thermal degradation of FPs can be evaluated by means of Thermogravimetric Analysis (TGA). This analytical technique allows to determine the thermal stability of the material along with the fraction of volatile components and the thermal degradation by monitoring the weight variation occurred when a sample is heated at a constant rate.

An assessment of the thermal degradation of some FPs has been performed by running a TGA analysis under ambient atmospheric. The results are shown in Table 1 and Figures 6 to 11.

By assessing several FPs, the main conclusions that can be established are the following:

- Degradation of FPs does not occur at temperatures lower than maximum temperatures attained by these fluoropolymers during processing or end-use.
- Degradation of FPs starts at temperatures (Onset point) significantly higher than standard maximum temperatures of processing.
- FPs get destroyed completely below 650°C without leaving any residue. It is pertinent to note that most municipal incinerators operate above 800°C resulting in complete destruction of FP applications at their end of life.
- A negligible amount of weight loss is observed during the processing temperatures of FPs. These are mainly due to the moisture variations and elimination of the residual additives as surfactants or initiators, which are not PFAS substances.

Table 1. Summary of Thermogravimetric Analysis

Fluoropolymer	Melting point (°C)	Standard max T during processing (°C)	Onset point (°C)	Offset point (°C)
PTFE (suspension powder)	327	360-375	529	600
PTFE (emulsion type)	327	360-375	529	594
PFA	310	350-360	510	575
FEP	260	325-350	500	629
FKM	-	230	388	601
PVDF	166	180-220	449	571

Figure 6. TGA analysis of Polytetrafluoroethylene (PTFE) suspension powder

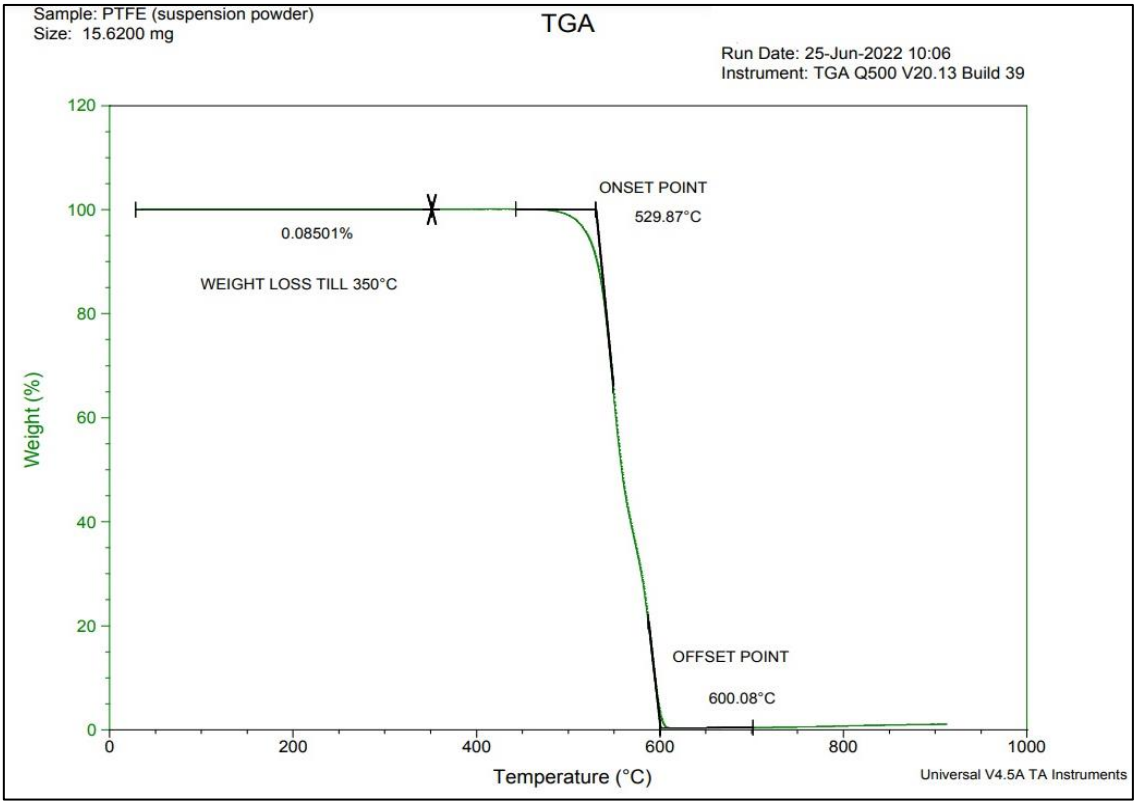


Figure 7. TGA analysis of Polytetrafluoroethylene (PTFE) emulsion powder

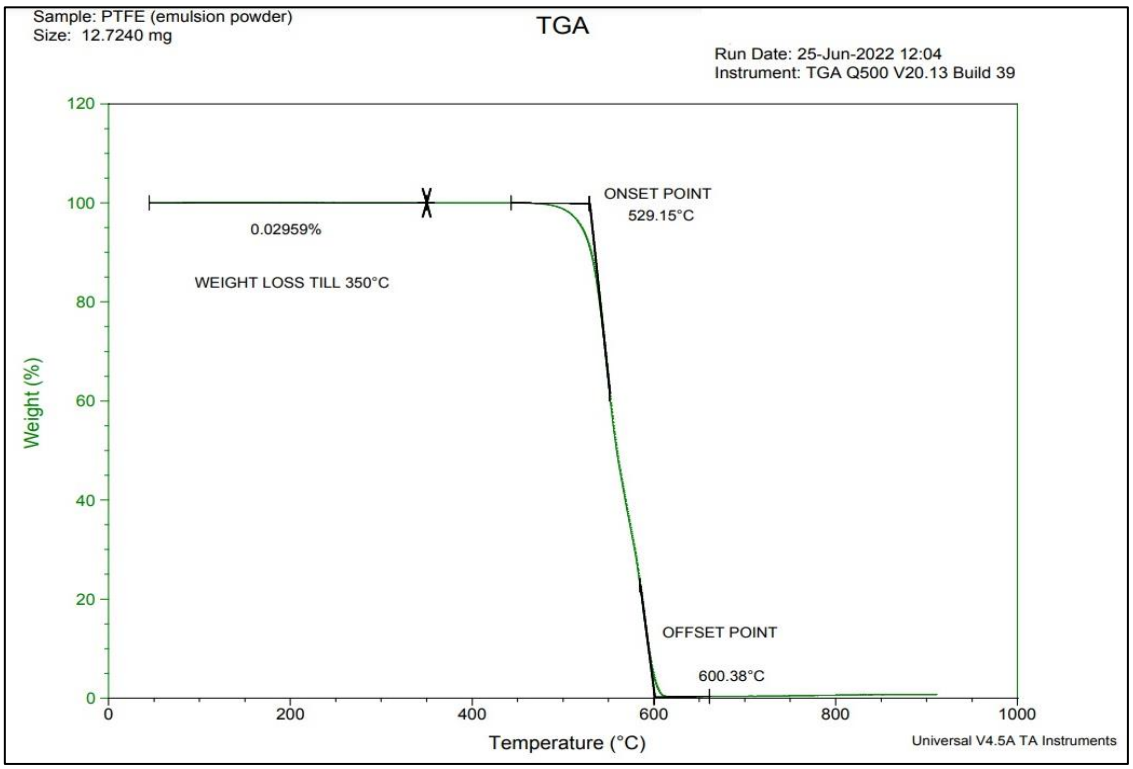


Figure 8. TGA analysis of Perfluoroalkoxy alkane (PFA)

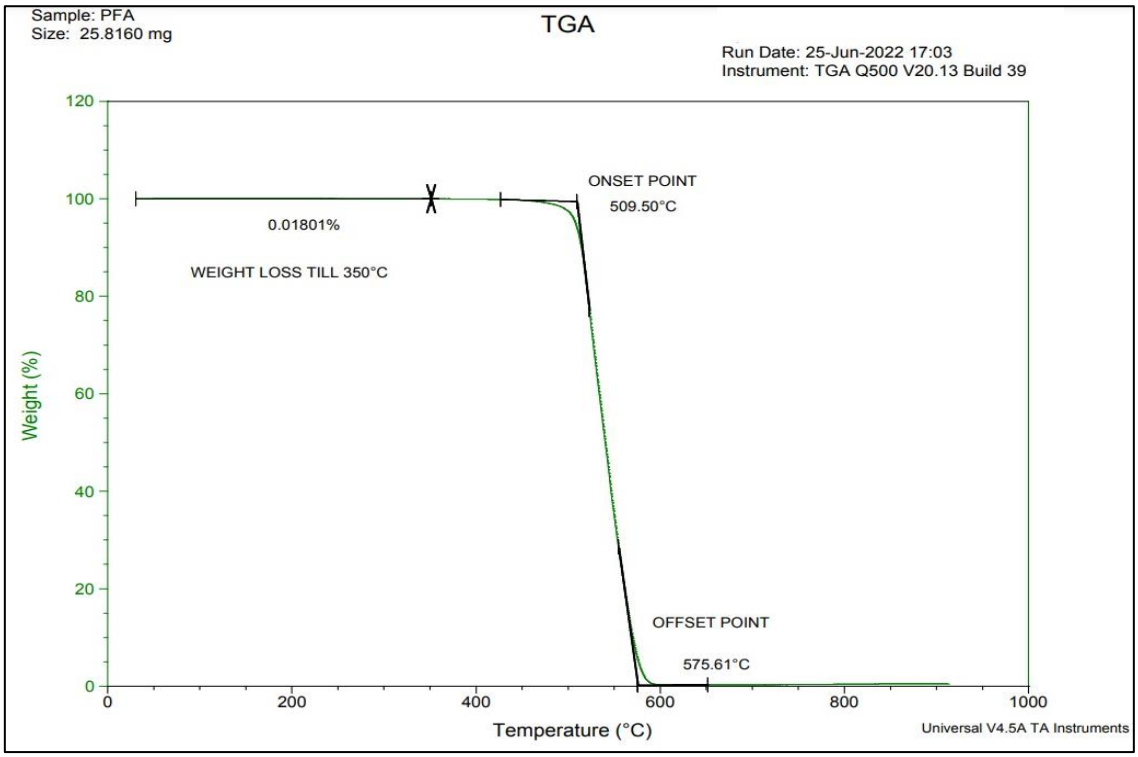


Figure 9. TGA analysis of Fluorinated ethylene propylene (FEP)

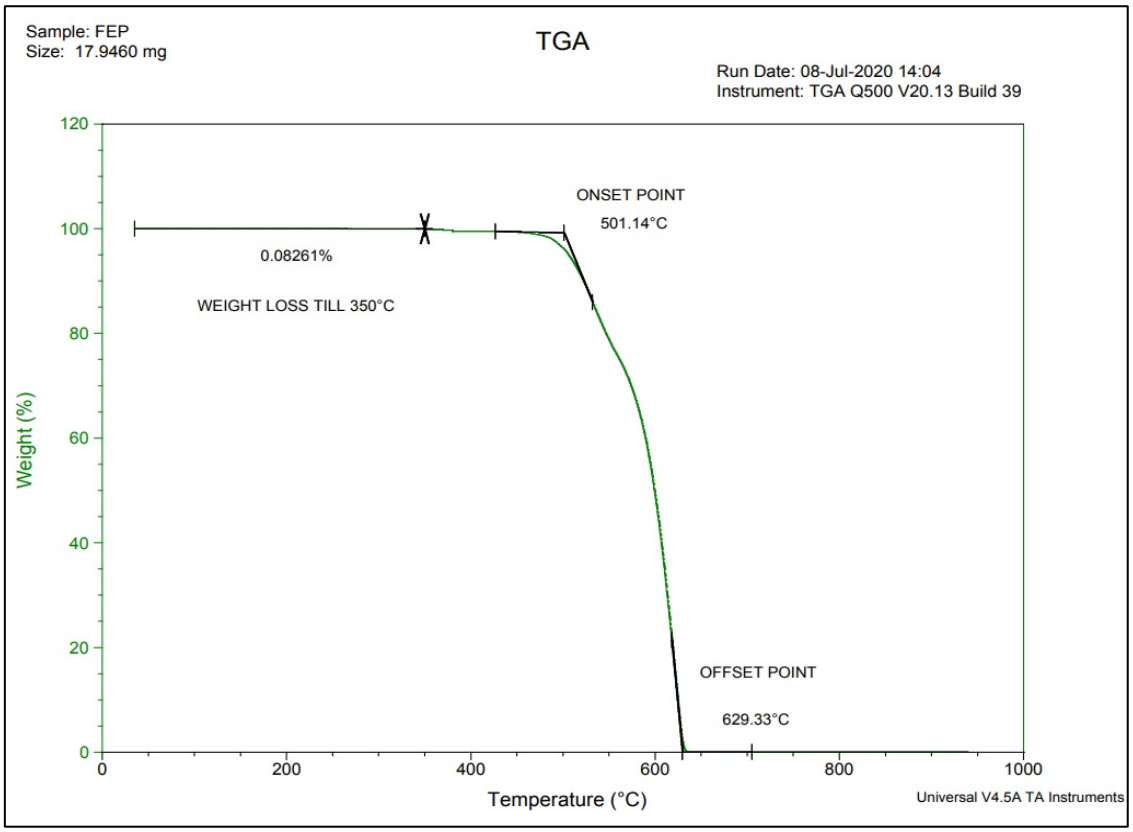


Figure 10. TGA analysis of Polyvinylidene difluoride (PVDF)

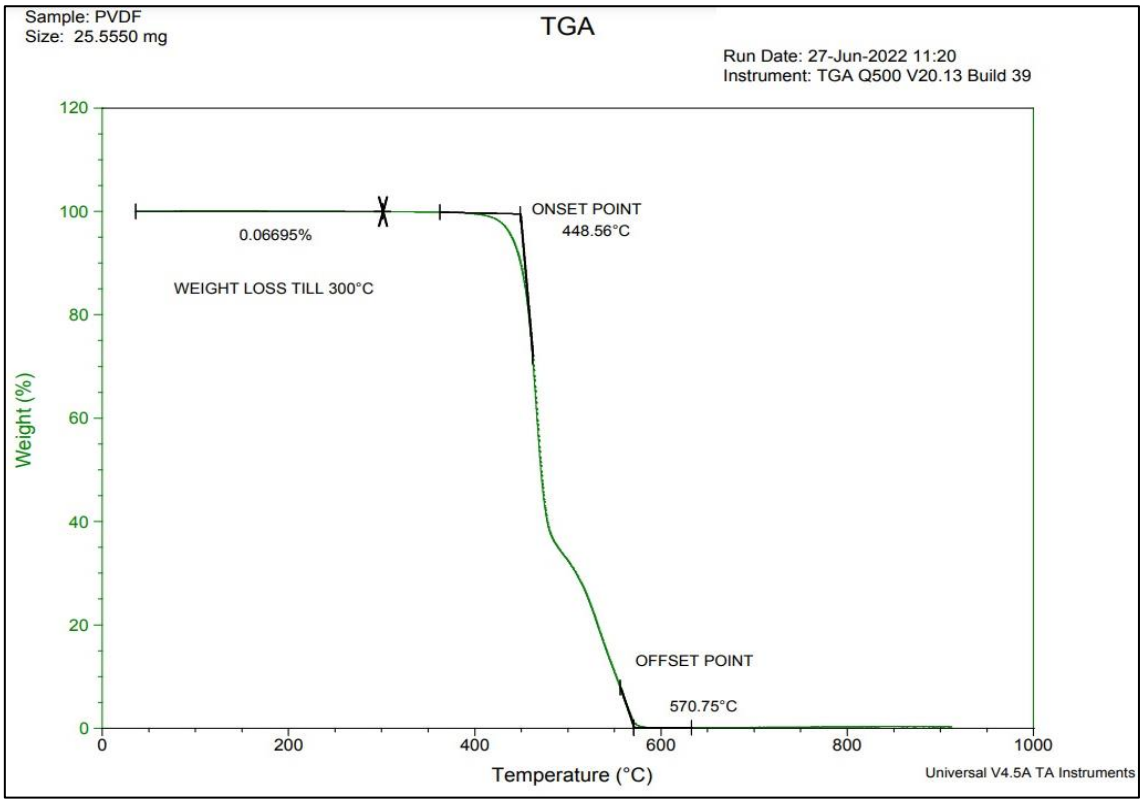
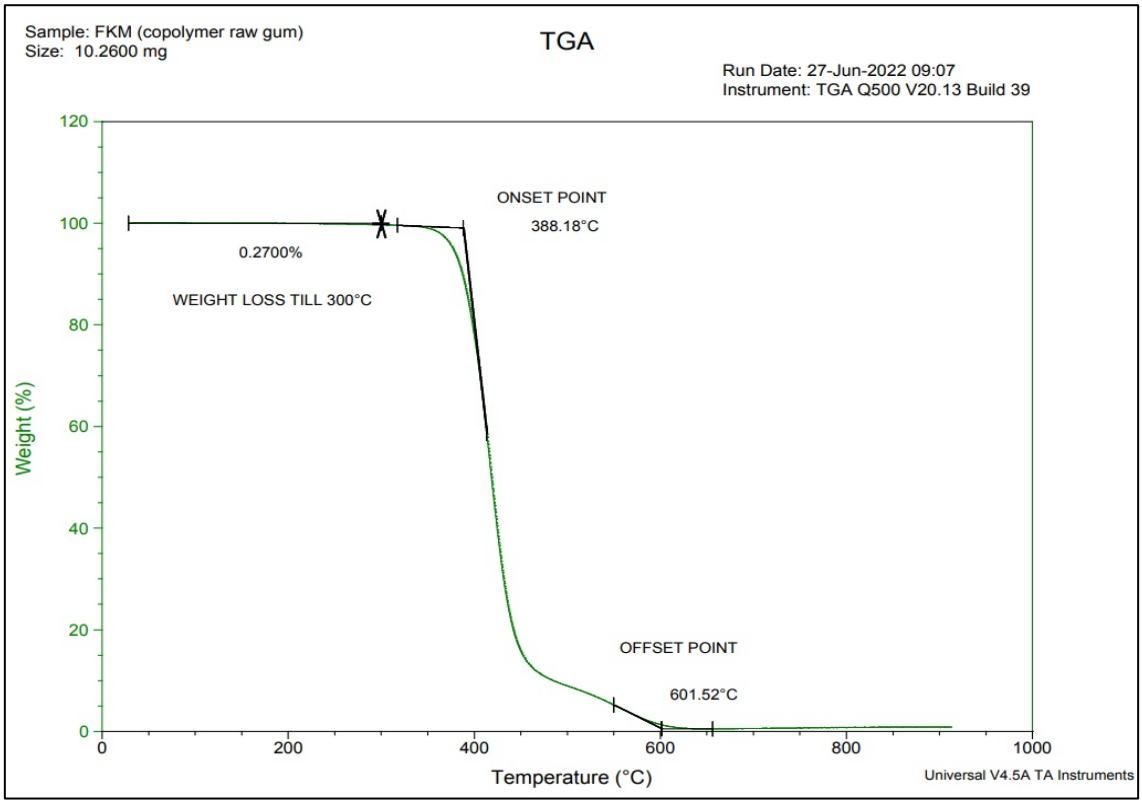


Figure 11. TGA analysis of Vinylidene fluoride-hexafluoropropylene copolymer (FKM)



Environmental degradation

Polymer degradation is a change in the properties of the polymer, such as tensile strength, colour, shape, and molecular weight, or of a polymer-based product under the influence of one or more environmental factors, such as heat, light, chemicals, or any other applied force. Degradation is often due to a change in the chemical and/or physical structure of the polymer chain, which in turn leads to a decrease in the molecular weight of the polymer.

During application many FP-based products are used in open environment. Polymers can be degraded by action of UV radiation and humidity. To understand effect of environmental condition (Sunlight, rain and humidity) over PTFE, an FP manufacturer has conducted a study to observe effect on mechanical properties of PTFE when kept in open environment.

For this study, Granular PTFE as well as PTFE Fine Powder have been analysed. Granular PTFE is manufactured using suspension polymerization while PTFE Fine Powder is manufactured using emulsion polymerization method, which ends up in different processing methods and applications. For Granular PTFE, resin is compression moulded into hollow billets and skived into 0.5 mm sheet, while, for PTFE Fine Powder, powder is compression moulded into 1.75mm thick disks and kept in open environmental condition at terrace to see effect of different environmental parameter such as sunlight, rain and humidity on PTFE.

After every 3 months samples were drawn out and their mechanical properties, such as tensile and elongation, were tested to check for any depletion of properties or polymer degradation as a result of harsh weather conditions under which they had been kept.

For the measurements, Tinius Olsen equipment was used with the following parameters: initial Jaw separation-22mm; sample shape- Dumbbell; strain rate – 50mm/min.

For this project, environmental conditions in the relevant region such as average temperature, monthly temperature variation, average rainfall and monthly rainfall variation were taken into consideration. For Granular PTFE, the study was developed between 1 August-2011 and 1 May 2021, and for PTFE Fine Powder, the study was started on 29 October 2021 and is still on-going. All the analysis is conducted according to ASTM standards for PTFE. The main results are shown in Figures 12 to 15.

The most relevant conclusions are as follows:

- No significant change in mechanical properties is observed.
- No significant amount of weight loss was observed; maximum approximately 0.5% weight loss is related to moisture variations and elimination of residual additives or surfactants, which are not PFAS substances.
- It is evident that PTFE is highly inert in nature and does not degrade by the action of environmental condition like sunlight, rain and humidity.

Figure 12. Effect of environmental conditions on Granular PTFE - tensile strength

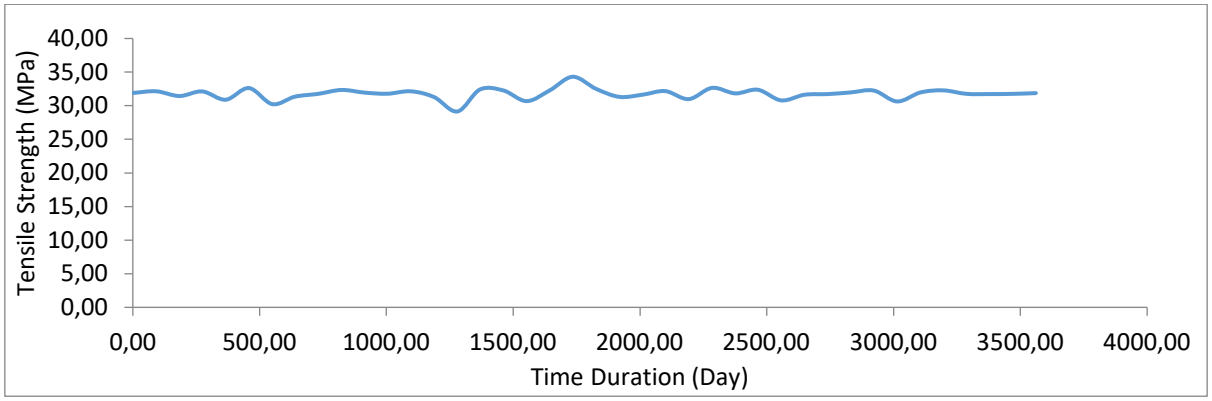


Figure 13. Effect of environmental conditions on Fine Powder PTFE - tensile strength

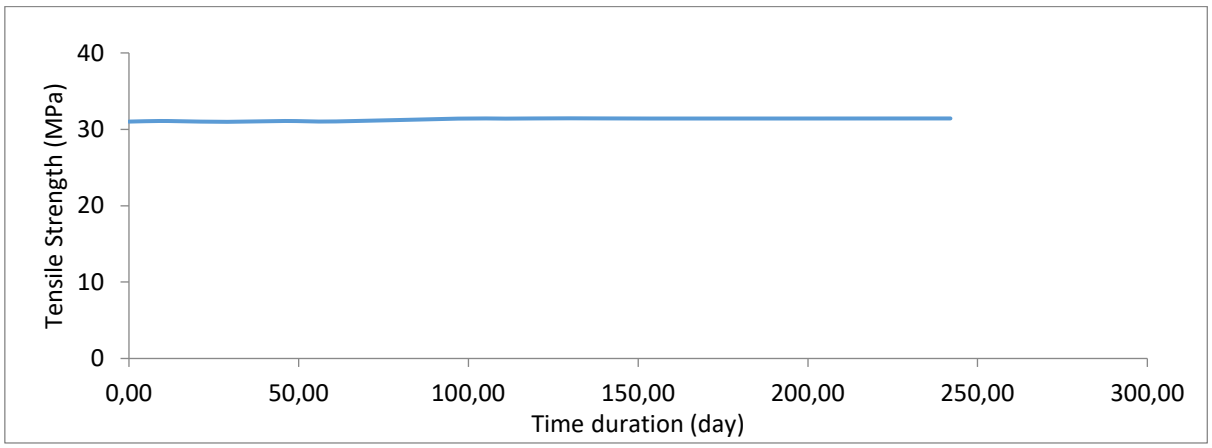


Figure 14. Effect of environmental conditions on Granular PTFE - elongation

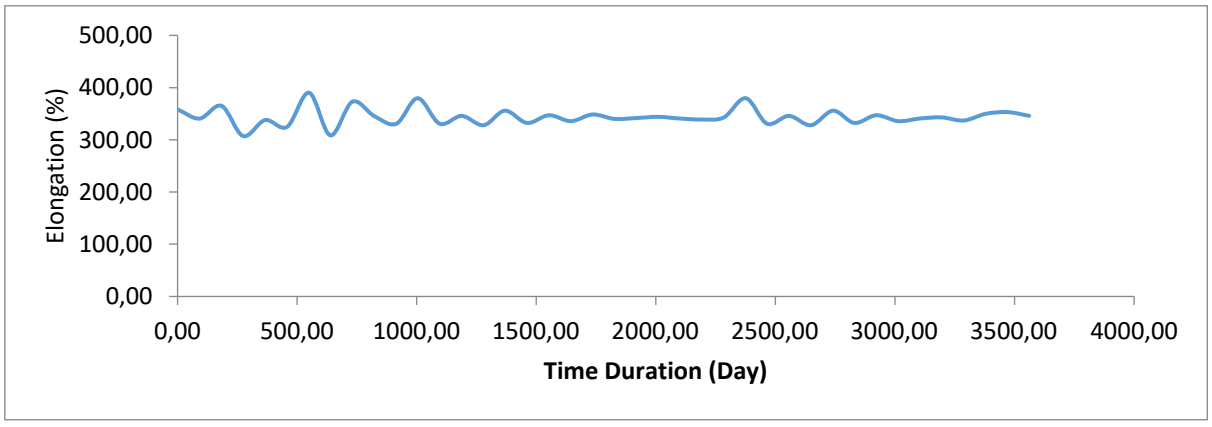
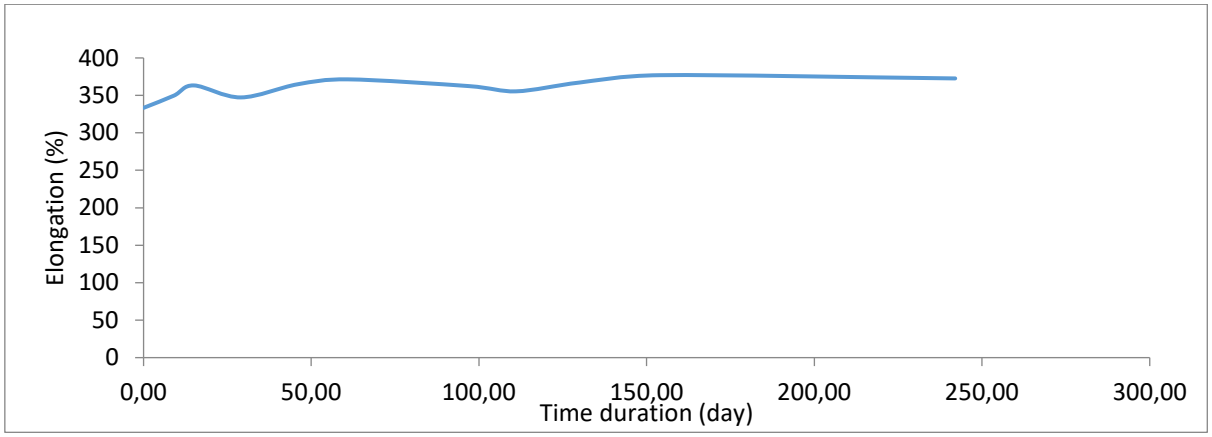


Figure 15. Effect of environmental conditions on Fine Powder PTFE - elongation



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Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle



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A cooperative agreement among **FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD**

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Executive Summary

Per- and polyfluoroalkyl substances (PFASs) comprise a class of synthetic compounds that have attracted much public attention since the early 2000s, when the persistence, hazards and ubiquitous occurrence of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wide range of PFASs. To date, research has primarily focused on understanding the identity, life cycle, hazard, occurrence and exposure, and risk of non-polymeric PFASs. This has informed development of many risk management measures at the national and international level. To ensure the sound management of the entire class of PFASs, it is equally important to understand polymeric PFASs, which include side-chain fluorinated polymers (SCFPs), fluoropolymers and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2019).

This report summarizes efforts by the OECD/UNEP Global PFC Group, between July 2021 and April 2022, in synthesizing publicly available scientific and technical information on the life cycle of SCFPs, which are polymers with a non-fluorinated polymer backbone and with substructures that meet the OECD PFAS definition (hereafter referred to as “PFAS moieties”) on the side chains.

The report provides a comprehensive overview on the chemical identities of SCFPs that have been on the global market, including a non-exhaustive list of 103 SCFPs and 42 monomers (Chapter 2). Based on the generic chemical structures identified, these SCFPs can be categorized according to the types of PFAS moieties present on the side chains, including n:2 fluorotelomers ($C_nF_{2n+1}CH_2CH_2-$), perfluoroalkanesulfonyl fluoride (PASF)-derivatives [$C_nF_{2n+1}S(O)_2-$], perfluoroalkanoyl fluoride (PACF)-derivatives [$C_nF_{2n+1}C(O)-$; $C_nF_{2n+1}CH_2-$] and perfluoropolyethers (PFPEs; containing a moiety such as $-CF_2-O-CF_2-$ in the fluorinated side chains), with varied fluorinated carbon chain lengths. Another way of categorizing the SCFPs can be according to the structural repeating units in the polymer backbone, with some simplifications, including acrylates {e.g., $[-CH_2-CH(C(O)OR_F)-]_n$}, ethoxylates {e.g., $[-O-CH_2-CH_2-]_n$}, oxetanes {e.g., $[-CH_2-C(CH_3)(CH_2OCH_2R_F)-CH_2-O-]_n$}, silicones {e.g., $[-Si(CH_2CH_2R_F)-O-Si(CH_2CH_2R_F)-]_n$} and urethanes {e.g., $[-NH-C(O)-O-]_n$}, where R_F is used to represent a fluorinated carbon chain moiety. In this report, the four chapters on the life cycle of different SCFPs are separated according to structural repeating units in the polymer backbone, specifically: acrylates and urethanes (Chapter 3), oxetanes (Chapter 4), silicones (Chapter 5), and ethoxylates (Chapter 6). In each chapter, the analysis focuses on the production and use of respective SCFPs, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, environmental releases of SCFPs, and other PFASs present in the commercial formulations, followed by a summary of critical knowledge and data gaps and options for a way forward. Chapter 7 focuses on overarching conclusions and recommendations. The key messages of chapters 3-6 are summarized at the start of each chapter. The report comes with an Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

Compared to many non-polymeric PFAS, SCFPs and their known and unknown degradation products have received comparatively little attention from scientists and regulators, despite their manifold industrial uses and high volumes, their propensity to release non-polymeric PFAS, and their potential environmental and health impacts.

Overall, a wide range of information on the chemical identities of SCFPs, other PFASs present therein, historical and ongoing production and use, degradation of SCFPs, and release of SCFPs and associated non-polymeric PFASs is identified in the public domain and has been synthesized in this report.

Despite the many knowledge and data gaps identified, the following can be concluded from the information synthesized here: A wide range of SCFPs have been produced and used in many different applications, with at least some SCFPs at high volumes (up to tens of thousands of tonnes/year). Many non-polymeric PFASs may be present in the commercial SCFP formulations, sometimes at percentage levels. During the production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs and associated non-polymeric PFASs may have been released. It is well expected that SCFPs can degrade and form non-polymeric PFASs, including PFCAs and/or PFSAs, in the environment and biota. Thus, many SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFASs including PFCAs and PFSAs.

Concerted action by all stakeholders is needed to address SCFPs in an efficient and effective manner. This includes identifying, making funding available and conducting research on those critical knowledge and data gaps that are most relevant for soundly regulating/managing SCFPs in different jurisdictions, building on the gaps identified in the respective chapters above. When addressing critical knowledge and data gaps, to increase efficiency, the following concerted action may be taken: (i) investigating additional information that is available in safety data sheets and patents (but was not actively searched and considered in this analysis due to time and resource constraints); (ii) working with manufacturers to enable open access to information that has been generated by them (and made available to specific regulators), but has not been made publicly available; and (iii) regularly gathering newly available public information and synthesizing them to further increase the knowledge base on SCFPs.

In parallel to action on critical knowledge and data gaps, concerted action may be taken to develop, facilitate and promote national and international stewardship programmes and regulatory approaches to reduce emissions of SCFPs and related PFASs and to work toward global elimination, where appropriate and technically feasible.

List of Acronyms

CAS	Chemical Abstracts Service
CASRNs	CAS Registry Numbers
CDR	Chenical Data Reporting
EU	European Union
FASAs	Perfluoroalkanesulfonyl amides
FASEs	Perfluoroalkanesulfonyl amidoethanols
FCN	Inventory of Effective Food Contact Substance Notifications
FTAcs	Fluorotelomer acrylates
FTCAs	Fluorotelomer carboxylic acids
FT-ethers	Fluorotelomer ethers
FTOs	Fluorotelomer olefins
FTOHs	Fluorotelomer alcohols
FTOH-aces	Fluorotelomer alcohols acetates
FTUCAs	Fluorotelomer unsaturated carboxylic acids
ICCM	International Conference on Chemicals Management
IUR	Inventory Update Reporting
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
N.A.	Not available
OECD	Organisation of Economic Co-operation and Development
PACF	Perfluoroalkanoyl fluoride
PASFs	Perfluoroalkanesulfonyl fluorides
PDMS	Polydimethylsiloxane

PFAIs	Perfluoroalkyl iodides
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkylcarboxylic acids
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFPEs	Perfluoropolyethers
PFSAs	Perfluoroalkanesulfonic acids
PMTFPS	Polymethyltrifluoropropylsiloxane
POSF	Perfluorooctanesulfonyl fluoride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SCFPs	Side-chain fluorinated polymers
SDS	Safety data sheets
SPIN	Substances in Preparations in Nordic Countries
t	Tonnes
UN	United Nations
UNEP	United Nations Environment Programme
US	United States
US EPA	US Environmental Protection Agency
US FDA	US Food & Drug Administration
yr	Year

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Table 6.1. Production/import volumes of ethoxylate SCFPs in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; and in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting). t = tonnes; yr = year. 47

1 Background, motivation and scope

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

This report summarizes recent efforts by the Group between July 2021 and April 2022 in synthesizing publicly available scientific and technical information on side-chain fluorinated polymers (SCFPs), a subset of per- and polyfluoroalkyl substances (PFASs)[2]. It focuses on the life cycle of SCFPs, including production and use, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, and environmental releases of SCFPs and other PFASs present in the commercial formulations. In brief, this report provides a comprehensive overview on the identities of SCFPs that have been on the global market (Chapter 2), on the life cycle of acrylate and urethane SCFPs (Chapter 3), of oxetane SCFPs (Chapter 4), of silicone SCFPs (Chapter 5), and of ethoxylate SCFPs (Chapter 6), and a brief summary (Chapter 7). The report comes with a separate Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

PFASs comprise a class of synthetic compounds that have attracted much public attention since the early 2000s, when the persistence hazards and ubiquitous occurrence of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wide range of PFASs.

In general, PFASs can be divided into two categories: non-polymeric and polymeric ones. To date, research has primarily focused on understanding the identity, life cycle, hazard, occurrence and exposure,

[1] "PFCs" here refer to "per- and polyfluorinated chemicals", and not to "perfluorocarbons". As stated below, "per- and polyfluorinated chemicals" was a term commonly used before the term "per- and polyfluoroalkyl substances" was recommended by Buck et al. (2011). As it is part of the Group official name, it remains unchanged.

[2] Following OECD (2021), this report uses the acronym "PFASs" for "per- and polyfluoroalkyl substances" as stated in Buck et al. (2011), and its corresponding singular form "PFAS" refers to either a perfluoroalkyl or polyfluoroalkyl substance. It is noted that there is a notion of using "PFAS" as the acronym for both the singular and plural forms. This report does not make any recommendation to address this notion. Readers may decide which acronym they would use.

and risk of non-polymeric PFASs, particularly perfluoroalkylcarboxylic acids (PFCAs), perfluoroalkanesulfonic acids (PFSAs), and some of their well-known non-polymeric precursors derived from fluorotelomers and perfluoroalkanesulfonyl fluorides (PASFs) such as fluorotelomer alcohols (FTOHs) and perfluoroalkanesulfonyl amides/amidoethanols (FASAs/FASEs)[3]. This has informed development of many risk management measures at the national and international levels.[4]

To ensure the sound management of the entire class of PFASs, it is equally important to understand polymeric ones, which include SCFPs, fluoropolymers, and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2019). In this spirit, the Global PFC Group have identified understanding of the life cycle of polymeric PFASs as a work priority. This is a first synthesis report on polymeric PFASs, focusing on SCFPs—defined as polymers with a non-fluorinated polymer backbone and with substructures that meet the OECD PFAS definition[5] (hereafter referred to as "PFAS moieties") on the side chains.[6]

SCFPs are of particular interest because many of them can act as a long-term significant source of non-polymeric PFASs such as PFCAs and/or PFSAs in the environment as a result of the following three factors: historical and likely ongoing high production volumes and widespread use, presence of (high levels of) other non-polymeric PFASs in the commercial formulations, and ability of releasing PFAS moieties on the side chains over time (these three factors are elaborated below). This has resulted in the inclusion of related SCFPs in regulatory actions in many jurisdictions when addressing some PFCAs and PFSAs.[7] For example, the recent listing of PFOA, its salts and PFOA-related compounds under the Stockholm Convention includes SCFPs that meet the definition, "PFOA-related compounds which, for the purposes of the Convention, are any substances that degrade to PFOA, including any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety (C_7F_{15})C as one of the structural elements" (Stockholm Convention, 2019; POPRC, 2021).

In addition, certain SCFP formulations have been applied in a way that can result in direct human exposure to monomers and their reaction products, causing adverse effects on human health. For example, upon inhalation of sprays containing 6:2 fluorotelomer silanes for surface treatment during application, the hydrolysis products of 6:2 fluorotelomer silanes may cause serious acute lung injury (e.g., Nørgaard et al. 2010, 2014). This has led to the restriction of (3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl)silanetriol and its

[3] These well-known non-polymeric PFCA/PFSA precursors are also common degradation intermediates of many other PFASs including certain SCFPs, which are elaborated in the sections below.

[4] https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/riskreduction/

[5] PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS (OECD, 2021).

[6] This is derived from the commonly accepted SCFP definition in Buck et al. (2011)—polymers that "do not have perfluorinated or polyfluorinated polymer backbones, but are composed of variable composition backbones with polyfluoroalkyl (possibly perfluoroalkyl) side chains". Other definitions of SCFP exist, e.g., "side-chain fluorinated polymers contain a nonfluorinated polymer backbone, off of which fluorinated side chains branch." by ITRC (https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/#2_2_3_1). The definitions agree with each other, but only have some different wordings for describing the PFAS moieties on the side chains.

[7] Note that degradation intermediates themselves may be toxic and have long lifetime in biota and humans, see, e.g., Kabadi et al. (2020) and Rice et al., (2020).

mono-, di- or tri-O-(alkyl) derivatives from their use in spray products under the European Union (EU) REACH regulation[8] and in Switzerland.[9]

This report aims to provide an overview of existing scientific and technical information on SCFPs, focusing on their identities and life cycle, and with a particular goal to map the existing landscape and highlight critical knowledge and data gaps. It builds primarily on a review of peer-reviewed scientific literature, regulator reports and databases, and technical documents published by companies. It is intended to be comprehensive, but not exhaustive. For instance, due to time and resource constraints, an active search and analysis of patents and safety data sheets (SDS) was not conducted for this report. Also, not all critical knowledge and data gaps are captured in this report, particularly unknown ones.

[8] Annex XVII to REACH, Entry 73 (https://echa.europa.eu/documents/10162/2906fed0-12ab-9593-23a1-72efd611fe70), including the following condition of restriction: *1. Shall not be placed on the market for supply to the general public after 2 January 2021 individually or in any combination, in a concentration equal to or greater than 2 ppb by weight of the mixtures containing organic solvents, in spray products.*

[9] https://www.fedlex.admin.ch/eli/cc/2005/478/en#lvl_d4e267/lvl_d4e268/lvl_3

2 Identities of Side-Chain Fluorinated Polymers on the Global Market

Chapter summary:

- A wide range of SCFPs and their monomers have been commercialized since the 1950s. Many of them have information on their generic chemical structures in the public domain, whereas for some others, only ambiguous descriptions are identified.
- The generic chemical structures of SCFPs allow for grouping them according to the types of PFAS moieties present on the side chains and/or the structural repeating units in the polymer backbone. Such grouping can, to a certain extent, inform about, e.g., their possible impurities, use patterns, and degradation mechanisms, which are elaborated in the following chapters.
- CASRNs and CAS names alone cannot be used to identify unique SCFPs (in other words, the same CASRN and CAS name can be used for different SCFPs with the same generic chemical structures, but different structural details such molecular-weight ranges and distribution).
- However, limited to no information is available on additional structural details of most commercial SCFPs, e.g., molecular-weight ranges and distribution, molecule parts other than the monomers or structural repeating units, and percentage compositions of individual monomers. This impedes the ability to more precisely assess environmental behavior and thus risks of individual SCFPs.
- Nevertheless, existing information shows that chemical identities, including molecular weight and PFAS moiety content in the molecular structure, can vary considerably across different types of SCFPs and across different SCFPs within the same type.
- Future efforts may further investigate technical datasheets from companies and patents, and work with manufacturers to have in-depth understanding of the chemical identities of commercial SCFPs, including by making existing measurements publicly available and by measuring commercial formulations. Such efforts can start with the SCFPs that are still in commerce and with high production volumes. Efforts are also needed to collect and make such information publicly available in an easily accessible manner (including development of unique identifiers other than CASRNs and CAS names).

A wide range of SCFPs have been commercialized since the 1950s. Aiming to capture a comprehensive overview of the SCFP diversity on the market, Table S1 in the Annex (an Excel sheet file provided separately) provides a non-exhaustive list of 103 SCFPs and 42 monomers, including information sources, Chemical Abstracts Service Registry Numbers (CASRNs), CAS names, synonyms (if available), molecular formula (if available), previously used CASRNs (if relevant), types of PFAS moieties and structural repeating units, fluorinated carbon chain length, CASRNs of the related PFAS monomers, and registration status in various national/regional chemical inventories. They were identified by a brief search of the OECD 2018 PFAS List, regulatory databases,[10] scientific literature,[11] technical documents published by companies and SciFinder.[12] These identities served as a basis for the search of production and use information discussed in the later sections.

2.1. General categorization of SCFPs

In most cases, the generic chemical structure(s) can be identified, ranging from homopolymers to co-polymers with one or more types of non-fluorinated co-monomers. In several other cases, the generic chemical structure(s) cannot be identified or cross-referenced from multiple sources because only ambiguous trade/trivial names or descriptions are available. For example, the substance with EC No. 458-200-2 is registered with the name "[No public or meaningful name is available]" under the EU REACH, while its Substance Infocard[13] provides a figure of some vague structures without explanation.

Based on the generic chemical structures identified, these SCFPs can be categorized in different ways. One way is according to the types of PFAS moieties present on the side chains, including primarily n:2 fluorotelomers ($C_nF_{2n+1}CH_2CH_2-$),[14] PASF-derivatives [$C_nF_{2n+1}S(O)_2-$], perfluoroalkanoyl fluoride (PACF)-derivatives [$C_nF_{2n+1}C(O)-$; $C_nF_{2n+1}CH_2-$[15]] and perfluoropolyethers (PFPEs; containing a perfluorinated ether moiety such as $-CF_2-O-CF_2-$ in the fluorinated side chains),[16] with varied fluorinated carbon chain lengths.

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[10] Sources: the Inventory of Effective Food Contact Substance (FCS) Notifications by the United States Food & Drug Administration (https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN); EU REACH registered substances (https://echa.europa.eu/information-on-chemicals/registered-substances); US EPA CDR database (https://chemview.epa.gov/chemview/)

[11] Sources: Dinglasan-Panlilio and Mabury (2006; https://pubs.acs.org/doi/10.1021/es051619%2B), Frömel and Knepper (2010; https://www.sciencedirect.com/science/article/pii/S0045653510006491), Wang et al. (2013; https://doi.org/10.1016/j.envint.2013.08.021), Wang et al. (2014A; https://doi.org/10.1016/j.envint.2014.04.013).

[12] Sources: two Solvay's presentations on Fluorolink®, a search of the brand names "PolyFox" (provided in Buck et al., 2011), "Zonyl" and "Capstone" in SciFinder.

[13] https://echa.europa.eu/substance-information/-/substanceinfo/100.104.618

[14] Historically, fluorotelomer manufacturers have also produced other types of fluorotelomers, such as [$(CF_3)_2CF-(CF_2CF_2)_n-CH_2CH_2-$] (Wang et al., 2014A), which might have also been made into SCFPs.

[15] For example, one monomer CASRN 3934-23-4 (2-Propenoic acid, 2-methyl-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl ester, $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$) was synthesized by 3M from PFOA that was derived from perfluorooctyl fluoride (Bank et al. 1994); therefore, such compounds are categorized as PACF-based derivatives here. Despite not being derived from the telomerization process, such PFASs have sometimes been termed as "n:1 fluorotelomers" in literature for readability. Future work may consider to identify more proper terminology for this PFAS group.

[16] Other types of PFAS moieties present on the side chains include perfluoroalcohols ($C_nF_{2n+1}O-$) (see Table S1) or a vinylene-intercepted polyfluorinated side chain [e.g., $-(CF_2)_6-CH=CH-(CF_2)_5CF_3$] (Shirai et al. 2021).

The SCFPs can also be categorized according to the structural repeating units in the polymer backbone, with some simplifcations, including acrylates[17] {e.g., $[-CH_2-CH(C(O)OR_F)-]_n$}, ethoxylates {e.g., $[-O-CH_2-CH_2-]_n$},[18] oxetanes {e.g., $[-CH_2-C(CH_3)(CH_2OCH_2R_F)-CH_2-O-]_n$}, silicones {e.g., $[-Si(CH_2CH_2R_F)-O-Si(CH_2CH_2R_F)-]_n$} and urethanes[19] {e.g., $[-NH-C(O)-O-]_n$}, where R_F is used to represent a fluorinated carbon chain moiety.

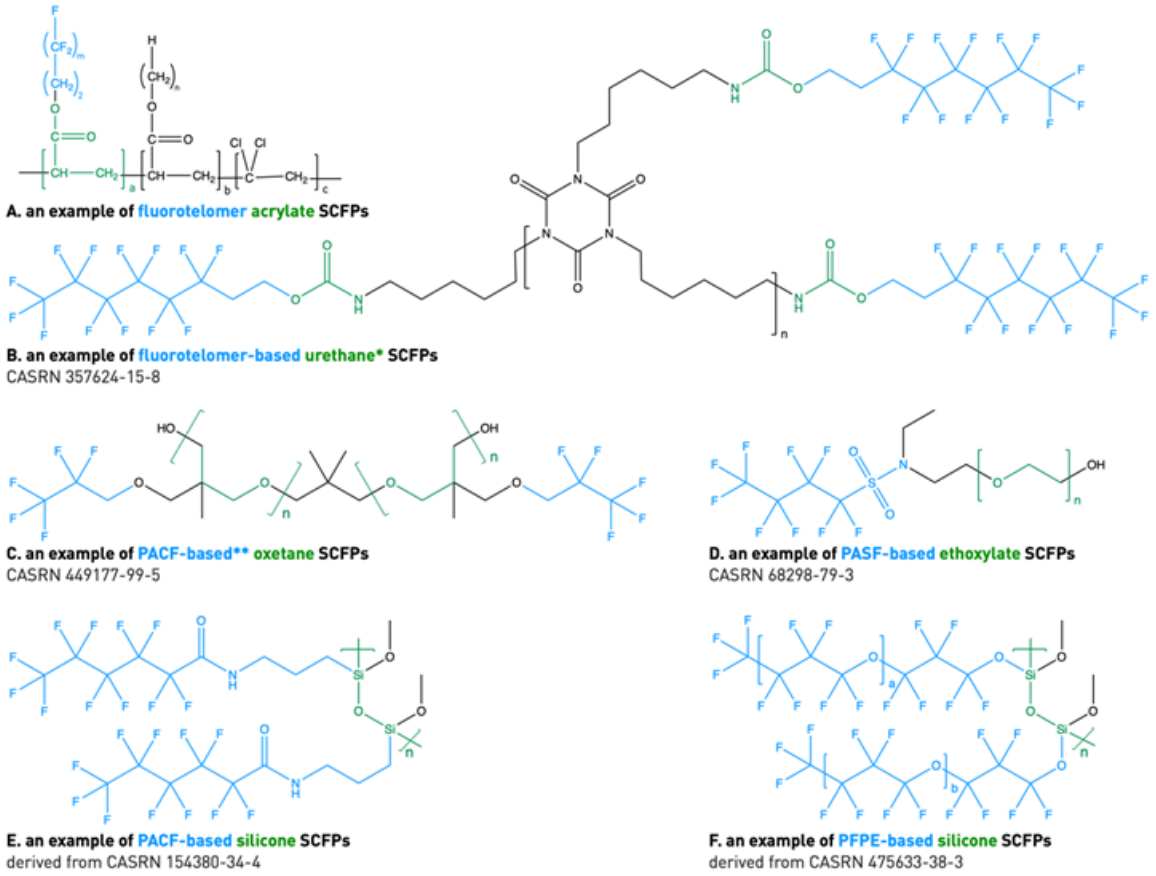
Examples of different types of SCFPs are illustrated in Figure 2.1. The two categorization methods bring different benefits. For example, categorization according to the types of PFAS moieties present on the side chains can inform about synthesis routes, possible impurities, and PFAS degradation products, whereas categorization according to structural repeating units in the polymer backbone can inform about possible use areas, possible impurities, degradation mechanisms, and so on. Depending on the exact purposes, readers may select either way of categorization, or a combination of both. In this report, the following four chapters on the life cycle of different SCFPs are separated according to structural repeating units in the polymer backbone, specifically: acrylates and urethanes (Chapter 3), oxetanes (Chapter 4), silicones (Chapter 5), and ethoxylates (Chapter 6).

[17] The term “acrylates” here also include methacrylates.

[18] Note that ethoxylates are different from other SCFPs, with often only one PFAS side chain connecting to the end of the polymer backbone. Given their polymer backbones $[(-OCH_2CH_2-)_n]$ are non-fluorinated, they are listed as SCFPs here.

[19] The term “urethanes” here include polyurethanes and related chemistry (such as polyallophanates and polyisocyanurates).

Figure 2.1. Examples of different types of side-chain fluorinated polymers. Blue colour highlights PFAS moieties, and green colour highlights structural repeating units in the polymer backbone.



2.2. Detailed structural information for individual SCFPs

As highlighted in Wang et al. (2021), for SCFPs and other polymers, individual CASRNs and chemical names often cover a wide range of substances with different compositions (such as different molecular-weight ranges, and numbers and types of functional groups) that may have distinct hazardous properties, environmental fate, bioaccessibility, degradation potential and implications for risk management. Therefore, it is important to have additional structural details of individual SCFPs such as molecular weight-ranges and distribution, molecule parts other than monomers or structural repeating units, and percentage compositions of individual monomers.

Currently, such additional structural details are sometimes available in the public literature (including technical datasheets provided by companies), but are scattered and often with limitations. For example, two biodegradation studies reported additional information on the chemical compositions of two commercial acrylate and urethane SCFPs, respectively (see Table 2.1; Russell et al., 2008 and 2010); however, due to a lack of CASRNs or other identifiers, such information cannot be linked to the SCFPs in Table S1. Further, the structural details of two commercial fluorotelomer-based ethoxylate SCFPs have

been reported by an analytical study and a biodegradation study: Zonyl FSO-100−with the perfluorocarbon chain length being between 2 and 14 carbon atoms and the degree of ethoxylation being between 0 and about 15 (Dinglasan-Panlilio and Mabury, 2006); and Zonyl FSH−with the perfluorocarbon chain length being at least between 4 and about 12 carbon atoms and the degree of ethoxylation being between 0 and at least 18 (Frömel and Knepper, 2010). In addition, Solvay reported the structural details of three PFPE-based ethoxylate SCFPs in one presentation (Solvay, no date (n.d.)), which were coincidentally identified during the preparation of this synthesis report.

Additional structural details can be identified in patents, but possibly in wide ranges. For example, Washington et al. (2015A) looked into two patents of fluorotelomer-based acrylate polymers and noted that the mass % of fluorotelomer in the polymers ranged from 79% to 85% in one patent and from 40% to 75% in the other. It is generally unknown how individual patents are translated into commercial practices (Freilich and Ouellette, 2019).

Further efforts have also been made by scientists to analytically determine compositions in commercial SCFPs. For example, Chu and Letcher (2014) measured a Scotchgard pre-2002 formulation and a Scotchgard post-2002 formulation, and detected one composition[20] in each formulation. Later, this analytical information was used to detect the presence of these compositions in different environmental media as an indicator of environmental fate and releases of the corresponding formulations (more details are elaborated in Section 3.4 below). Such analytical studies are so far limited, partially due to limited access by scientists to commercial formulations and analytical standards (Ng et al. 2021).

Therefore, it is generally challenging to capture an overview of the data availability of structural details for commercial SCFPs on the global market. Nevertheless, based on existing information, the chemical identities, including molecular weight and PFAS moiety content in the molecular structure, can vary considerably across different types of SCFPs and across different SCFPs within the same type.

Table 2.1. Additional structural details on the chemical compositions in commercial SCFP formulations reported in peer-reviewed scientific studies. N.A. = not available

References	Russell et al. (2008)	Russell et al. (2010)
SCFP type	Fluorotelomer-based acrylate polymer (Figure 2.1 A)	Fluorotelomer-based urethane polymer
Molecular weight	M_n = 40 000 Daltons*	M_n or M_w = 3 500 Daltons**
Fluorine content	10.095 weight%	10 weight%
SCFP weight% in the formulation	23–24%	23%
SCFP particle size in the formulation	100–300 nm	100–300 nm

* Here the authors used a number-average molecular weight (Mn), which is defined as the total weight of the molecules divided by the total number of molecules.

** Here it is not clear whether the authors referred to a number-average molecular weight (Mn) or a weight-average molecular weight (Mw), as both terms were mentioned for the same value in the Supporting Information of the study. A weight-average molecular weight depends not only on the number of molecules present, but also on the weight of each molecule. It can be calculated as $\sum w_i M_i$, where w_i is the weight fraction of polymer with molecular weight M_i. A

[20] They were able to detect mass spectral peaks at *m/z* 1315.0591 and 1634.3120 in each formulation, respectively. However, the authors did not report more details, except that the former mass peak contains a $[C_8F_{17}SO_2N(C_2H_5)]^-$ ion and the latter contains a $[C_4F_9SO_2N(CH_3)]^-$ ion.

weight-average molecular weight is larger than or equal to the corresponding number-average molecular weight for any given polymer.

2.3. Summary of critical knowledge and data gaps related to the chemical structure of SCFPs

A) In multiple cases in Table S1, the generic chemical structures of a given SCFP or its monomer(s) cannot be identified, even though their corresponding CASRNs were identified; such information gap impedes our understanding of these SCFPs (e.g., which non-polymeric PFASs may be released). Ways in which the information is lacking include: (i) Only the trade names were assigned to the CASRNs without further details, e.g., CASRNs 949581-65-1 (Scotchgard PM-3622), 940891-99-6 (Scotchgard PM-490), 923298-12-8 (Scotchgard PM-930) and 1224842-54-2 (Unidyne TG-5521); and (ii) the assigned CAS name is ambiguous, e.g., CASRN 328389-91-9 [Propanoic acid, 3-hydroxy-2-(hydroxymethyl)-2-methyl-, polymers with 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane and reduced Me esters of reduced polymd. oxidized tetrafluoroethylene, compds. with triethylamine].

B) CASRNs and CAS names alone cannot be used to identify unique SCFPs (in other words, the same CASRN and CAS name can be used for different SCFPs with the same generic chemical structures, but different structural details such molecular-weight ranges and distribution). Therefore, apart from the generic chemical structures of any given SCFPs, additional structural information is needed for studies and assessments of their hazardous properties, environmental fate, bioaccessibility, degradation potential, and implications for risk management, such as the molecular-weight range and distribution of the SCFP, the fluorine content, the molecular percentage of individual co-monomers, and how the co-monomers are connected (e.g., by providing a reaction scheme if available). In the public literature, additional structural information was identified for some commercial SCFPs; however, such information is scattered and often with limitations (e.g., due to a lack of CASRNs or other identifiers, reported information cannot be linked to specific SCFPs listed in Table S1). Analytical studies can help to measure the structural details of individual SCFPs, but such studies are generally challenging due to a lack of access by scientists to commercial formulations and analytical standards.

2.4. Options for a way forward

To address these two gaps, future efforts may further investigate technical datasheets from companies and patents, and work with manufacturers to better understand the chemical identities of commercial SCFPs, including by making existing measurement results publicly available and by measuring commercial formulations. To increase efficiency, priorities may be first given to those SCFPs that are still in commerce and with high production volumes. Efforts are also needed to collect and make such information publicly available in an easily accessible manner, e.g., via the OECD PFAS Web Portal, the OECD eChemPortal and/or work under the Stockholm Convention[21]; such efforts may engage the cheminformatics community, as unique identifiers other than CASRNs and CAS names would be needed for identifying unique SCFPs. This can greatly enable a better understanding of the environmental fate and degradation behaviour of

[21] The Secretariat of the Stockholm Convention, in consultation with the POPs Review Committee, has developed an indicative list for PFOA, its salts and PFOA-related compounds, including PFOA-related SCFPs, covered under the listing under the Stockholm Convention. It is expected that an indicative list of PFHxS, its salts and PFHxS-related compounds will be prepared if those chemicals are listed under the Stockholm Convention. For more details, see the Stockholm Convention webpage (www.pops.int).

individual SCFPs (which can vary greatly, given the large range of molecular weights and the mass percentage of PFAS moieties in the polymer reported for a few commercial SCFPs as outlined above), and estimation of generation and releases of non-polymeric PFASs from individual SCFPs. In parallel, a logical maximum percentage of PFAS moieties could be developed based on literature review (including patents) and stakeholder consultation, as a precautionary approach for estimating non-polymeric PFAS releases from SCFPs.

3 The Life Cycle of Acrylate and Urethane SCFPs

Chapter summary:

- Historically, many acrylate and urethane SCFPs containing *long-chain* PFAS moieties on the side chains (hereafter referred to as "*long-chain*" SCFPs) were produced in significant amounts, jointly on the scale of thousands of tonnes or more per annum (which were at least one order of magnitude higher than the production volumes of many non-polymeric PFASs including those used in fire-fighting foams). Currently, many long-chain acrylate and urethane SCFPs have been replaced by short-chain ones, while some long-chain ones may still be used (details unknown due to confidentiality). Despite limited information (due to no reporting requirements, confidentiality, etc.), it can be concluded that short-chain acrylate and urethane SCFPs are still being produced jointly on the scale of thousands of tonnes or more per annum.
- Acrylate and urethane SCFPs have been mainly used as surface protectors to impart water- and oil-repellency and soil-resistance to fabrics, textiles, and apparel articles (both for industrial pre-market treatment, or professional/consumer aftermarket treatment), and food contact paper and paperboard. Some acrylate and urethane polymers may also be used as fluorosurfactants in products such as fire-fighting foams, inks, and paints, lacquers and varnishes.
- Considerable amounts (up to 5 weight%) of other non-polymeric PFASs may be present in commercial formulations. They may originate from unreacted starting materials and reaction intermediates, contaminants from the raw materials, degradation products, and reaction byproducts. They may also be monomeric PFASs intentionally left in the formulations to keep the acrylate and urethane particles suspended in the formulations.
- Acrylate and urethane SCFP degradation may follow two main degradation mechanisms: direct cleavage of PFAS moieties from the side chains (e.g., hydrolysis of the ester bond), and breakdown of the polymer carbon–carbon backbone to form small oligomeric species which subsequently undergo ester bond cleavage.
- While existing degradation studies agree well on the degradation mechanisms, historical studies have reported a wide range of degradation half-lives, ranging from less than 1 year to over a thousand years. Some of these large variations observed are caused by experimental artefacts, which can be and were minimized/eliminated in more recent studies (where the degradation half-lives of two commercial fluorotelomer-based acrylate SCFPs were measured to be several decades).

Meanwhile, the variations observed also partially reflect the true variability of several parameters that may impact degradation, including molecular size of SCFPs, specific surface area of SCFP particles, substrate, temperature, pH values, and humidity. Such variability cannot be minimized/eliminated. Therefore, degradation half-lives of acrylate and urethane SCFPs in the environment and biota will remain to some extent uncertain. Nevertheless, it can be concluded that these SCFPs will degrade and thus serve as a long-term source of non-polymeric PFASs once released in the environment.

- In contrast to abiotic and biotic degradation, little is known about the fate of SCFPs during municipal waste incineration of SCFP-treated articles, and whether this would be a significant source of non-polymeric PFASs into the environment.
- Upon application for surface treatment, both SCFPs and other PFASs present in the formulations may partially be released via air, wastewater and/or solid waste, and partially transferred onto treated articles, which may be released during the subsequent processing, use and disposal. Due to various uncertainties and unknowns, the contribution of acrylate and urethane SCFPs to PFASs in the environment and biota is unclear. But it is likely significant, particularly in the long term, given the large volumes produced and used. Future efforts may collect further information and reduced the uncertainties to reach more precise estimates.

Given the similarities between acrylate and urethane SCFPs in many aspects in terms of use patterns, presence of other PFASs in the commercial formulations, and degradation mechanisms, they are jointly analysed and described in this chapter.

3.1. Historical and ongoing production and uses

Most acrylate and urethane SCFPs and acrylate SCFP monomers identified in Table S1 have been registered for production and use in many jurisdictions, but mostly with unknown commercial status[22]. Table 3.1 summarizes the production/import volumes of various acrylate and urethane SCFPs, containing various types of PFAS moieties with varied chain length on the side chains, as reported in the EU, in the United States (US), and in the Nordic Countries (Denmark, Finland, Norway and/or Sweden). Many are available in large tonnage ranges (e.g., >454 to <4540 tonnes/year), and many others have been claimed as confidential business information and sealed from the public. Therefore, these data are discussed together with other information identified in peer-reviewed scientific literature as follows.

Historically, acrylate and urethane SCFPs were the major SCFPs produced. Until the early 2000s, PASF-based SCFPs were mainly derived from perfluorooctanesulfonyl fluoride (POSF), i.e., long-chain C_8-based SCFPs.[23] Based on the then major producer–3M's reporting, it was estimated that prior to 2002, about

[22] The listing in most national/regional chemical inventories indicate whether the substances have been produced or used in the respective jurisdiction, but do not indicate whether they are currently being produced or used.

[23] Long-chains refer to perfluorocarboxylic acids (PFCAs) with carbon chain lengths C8 and higher, including perfluorooctanoic acid (PFOA); perfluoroalkane sulfonic acids (PFSAs) with carbon chain lengths C6 and higher,

55% of POSF (up to ca. 2400 tonnes in 2000) were used to produce different types of SCFPs (see Figure S8 in the Supplementary Data of Wang et al. 2014A); and a majority were made into acrylate (likely up to about 20% of POSF) and urethane (likely 23–32% of POSF) SCFPs. As a comparison, 3M reported that its estimated global production of POSF-derivatives for fire-fighting foams was about 150 tonnes in 2000, about 3% of 3M's total global production POSF-derivatives at that time (3M, 2000). Based on public records, the same study also estimated that after 2002 following 3M's global phase out, POSF-based SCFPs were (mostly) discontinued in Japan, Western Europe and the US, while Chinese manufacturers started large-scale production of POSF-based SCFPs in 2002, with a production volume of up to ca. 120 tonnes POSF-equivalent per year, and presumably discontinued most of this production after 2008. However, it is possible that some POSF-based acrylate SCFPs are still being produced and used. For example, the use of CASRNs 68298-62-4 and 68867-62-9 in some Nordic countries in 2019 has been reported, though it is unclear at what levels and for which purposes due to confidentiality (see Table 3.1).

Since 2002, POSF-based SCFPs in many applications such as textiles have largely been replaced by C_4 perfluorobutanesulfonyl fluoride (PBSF)-based SCFPs, i.e., short-chain ones (Wang et al. 2013, 2014A). The current production volumes of PBSF-based acrylate and urethane SCFPs are largely unknown, but are still on a significant level. For example, two PBSF-based acrylate SCFP monomers are registered in the EU with the production/import tonnage band of ≥110 to <1100 tonnes/year (see Table 3.1).

Similarly to PASF-based derivatives, most (80%) of the n:2 fluorotelomers manufactured by Asahi, Clariant, Daikin and Dupont were made into SCFPs (up to 7200 tonnes PFAI-equivalent in 2006), as reported by the "Telomer Research Program" in 2002 to the US Environment Protection Agency (EPA). At that time, n:2 fluorotelomers were produced as mixtures of different chain lengths with long-chain 8:2 and 10:2 as main components (Wang et al. 2014A). Since 2006, the major global fluorotelomer manufacturers have stepwise replaced mixture fluorotelomers with predominantly short-chain 6:2 fluorotelomer (>99%) and the transition was completed by 2015 (Wang et al., 2013; US EPA, n.d.). However, the use of two long-chain fluorotelomer-based acrylate SCFPs (CASRNs 142636-88-2 and 70969-47-0) and one long-chain fluorotelomer-based acrylate monomer (CASRN 27905-45-9) in some Nordic countries in 2019 has been reported (see Table 3.1). It is possible that CASRN 70969-47-0 was produced before the transition, given the long shelf-life of fire extinguish agents, in which it is used (see below). For CASRNs 142636-88-2 and 27905-45-9, it is unclear whether they were produced before or after the industrial transition, as no details are provided in the SPIN database.

Unlike for PASF-based derivatives, a break-down of the production of n:2 fluorotelomer SCFPs on the basis of SCFP types is not publicly available, but at least n:2 fluorotelomer acrylate SCFPs have been and are still being produced in large quantities, on the scale of hundreds to thousands of tonnes per annum (for examples, see acrylate SCFP monomers–n:2 fluorotelomers in Table 3.1).

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including perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS); and, precursors of these substances (https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/).

Table 3.1. Production/import volumes of acrylate and urethane SCFPs and their monomers in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting); and in the EU reported in the REACH dossiers. n.d. = no date; t = tonnes; yr = year.

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import mass reported
Acrylate SCFPs			
101896-32-6	n:2 fluorotelomers	unclear	**EU:** confidential (n.d.)
817203-49-9	n:2 fluorotelomers	6	**EU:** confidential (n.d.)
1071022-26-8	n:2 fluorotelomers	6	**SPIN:** 0.6 t + confidential (2012–2019)
1793072-86-2	n:2 fluorotelomers	6	**SPIN:** confidential (2016)
142636-88-2	n:2 fluorotelomers	8;10;12	**US:** <454 t/yr in 2012–2015 **SPIN:** confidential (2011–2019)
70969-47-0	n:2 fluorotelomers	6;8;10;12;14;16;18	**US:** <227 t in 2005, 57.9 t in 2011, <454 t/yr in 2012–2015 **SPIN:** 64.7 t + confidential (2001–2019)
304012-61-1	n:2 fluorotelomers	6;8;10;12	**SPIN:**confidential (2008–2016)
479029-28-2	n:2 fluorotelomers	6;8;10;12	**SPIN:** confidential (2004–2011)
1078712-88-5	n:2 fluorotelomers	2;4;6;8;10;12;14;16;18	**US:** 15.6 t in 2011
53515-73-4	PACF-derivatives	7	**SPIN:** confidential (2000–2003)
1017237-78-3	PASF-derivatives	4	**US:** <454 t/yr in 2012–2015 **SPIN:** confidential (2011, 2014–2019)
425664-29-5	PASF-derivatives	4	**SPIN:** confidential (2008–2019)
819069-72-2	PASF-derivatives	4	**SPIN:** confidential (2006–2007)
162568-17-4	PASF-derivatives	8	**SPIN:** confidential (2000–2015)
68298-61-3	PASF-derivatives	7;8	**SPIN:** confidential (2000)
68298-62-4	PASF-derivatives	7;8	**SPIN:** confidential (2000–2019)
68555-90-8	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68329-56-6	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68555-92-0	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2017)
68586-13-0	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68586-14-1	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68649-26-3	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68867-62-9	PASF-derivatives	4;5;6;7;8	**US:** >4.54 to <227 t in 2001 **SPIN:** confidential (2000–2019)
127133-66-8	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
Acrylate SCFP monomers			
1228350-17-1	n:2 fluorotelomers	6	**EU:** =1 to =10 t/yr (n.d.)
17527-29-6	n:2 fluorotelomers	6	**EU:** =100 to <1000 t/yr (n.d.) **US:** >4.54 to <227 t/yr in 1989, 1997 & 2001, confidential in 2011, <454 t in 2012, >454 to <908 t/yr in 2013–2015 **SPIN:** confidential (2000, 2004–2010)
2144-53-8	n:2 fluorotelomers	6	**EU:** =1000 to <10000 t/year (n.d.) **US:** >4.54 to <227 t in 1985, confidential in 2011, >454 to <4540 t in 2012, >272 to <454 t in 2013, >454 to <4540 t/yr in 2014 and 2015 **SPIN:** confidential (2003–2019)
27905-45-9	n:2 fluorotelomers	8	**US:** >4.54 to <227 t/yr in 1989 and 1997, >227 to <454 t in 2001, >454 to <4540 t in 2005, confidential in 2011, >45.4 to <227 t in 2012, <454 t/yr in 2013–2015 **SPIN:** confidential (2000, 2004–2019)

17741-60-5	n:2 fluorotelomers	10	**US:** >4.54 to <227 t/yr in 1989, 1997 and 2001, >454 to <4540 t in 2005, confidential in 2011, >45.4 to <227 t in 2012, <454 t/yr in 2013–2015 **SPIN:** confidential (2000, 2004–2005)
34395-24-9	n:2 fluorotelomers	12	**US:** >4.54 to <227 t/yr in 1989, 1997 and 2001, <227 t in 2005, <454 t/yr in 2012–2015 **SPIN:** confidential (2000, 2004–2005)
34362-49-7	n:2 fluorotelomers	14	**US:** >4.54 to <227 t/yr in 1989, 1997 and 2001, <227 t in 2005, <454 t/yr in 2012–2015 **SPIN:** confidential (2004–2005)
85631-54-5	n:2 fluorotelomers	6;8;10;12	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2000–2012)
352-87-4	PACF-derivatives	1	**EU:** =1 to <10 t/yr (n.d.) **SPIN:** confidential (2008–2009, 2015–2017)
355-93-1	PACF-derivatives	4(1H)	**EU:** =10 to <100 t/yr (n.d.)
67584-55-8	PASF-derivatives	4	**EU:** =100 to <1000 t/yr (n.d.) **US:** >4.54 to <227 t/yr in 1985, 1989, 1993 and 1997, confidential in 2011, <454 t/yr in 2012–2015 **SPIN:** confidential (2000–2019)
67584-59-2	PASF-derivatives	4	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2000–2017)
212335-64-3	PASF-derivatives	4	**US:** confidential in 2011, <454 t/yr in 2012–2015
3063-94-3	Unclear*	1	**EU:** =0 to <10 t/yr (n.d.)
Urethane SCFPs			
357624-15-8	n:2 fluorotelomers	6	**SPIN:** confidential (2011–2014)
118102-37-7	n:2 fluorotelomers	6;8;10;12	**SPIN:** confidential (2000–2014)
118102-38-8	n:2 fluorotelomers	6;8;10;12	**SPIN:** confidential (2000–2014)
68990-40-9	n:2 fluorotelomers	2;4;6;8;10;12;14;16	**SPIN:** confidential (2000–2003)
135228-60-3	n:2 fluorotelomers	4;6;8;10;12;14;16;18	**SPIN:** confidential (2003–2016)
144468-32-6	n:2 fluorotelomers	4;6;8;10;12;14;16;18	**SPIN:** confidential (2000–2010)
162491-88-5	n:2 fluorotelomers	Unclear	**SPIN:** confidential (unclear)

Both acrylate and urethane SCFPs have been used in a wide range of applications, which are divided into several major use areas and separately described below. Similar to the production volumes, use information reported to the SPIN database has mostly been claimed as confidential business information (see Table S2). Furthermore, although some data were reported by 3M in the past (see Figure S8 in the Supplementary Data of Wang et al. 2014A), it is generally unknown how much acrylate and urethane SCFPs have been used in which applications.

Fabrics, textiles, and apparel articles

To date, a wide range of commercial SCFP products have been used to treat fabrics, textiles, and apparel articles to impart water- and grease-repellency and soil-resistance, usually applied in combination with hydrocarbon water-repellent adjuvants, resins, and/or monomeric PFASs that demonstrate some synergistic effects (Bank et al., 1994). These SCFPs include many acrylate (e.g., CASRN 68298-62-4) and urethane[24] (e.g., 3M Scotchgard Fabric Protector; 3M, 2018) SCFPs. They can also be a mixture containing both acrylate and urethane SCFPs (e.g., Teflon Advance Carpet Protector), as reported by Dinglasan-Panlilio and Mabury (2006). In these SCFPs, nonfluorinated co-monomers serve the functions of extending fluorine efficiency, providing functionality to enhance durability, and/or modifying the hand feel of the treated fabric (Bank et al. 1994). The treatments of textiles can be done both pre-market by manufacturers,

[24] Urethane SCFPs, typically based on the reaction of fluorinated diol intermediates with diisocyanates, were particularly used for the treatment of 100% cotton and cotton-blend textiles (Bank et al., 1994).

and aftermarket by professional services and consumers (3M, 1999). For more examples and technical details, see Table S1, 3M (1999) and Bank et al. (1994).

Food-contact paper and paperboard

Many acrylate and urethane SCFPs have been used as an oil- and water-resistant agent in paper and paper board. As such, these SCFPs can prevent the paper material from soaking up fats and water, with the applications particularly targeting fatty foods especially those intended to be heated in packaging or stored for an extended period, and as moisture barriers (OECD, 2020). These SCFPs can be used either by the addition to the pulp during paper production (internal sizing), or as a surface treatment to the paper (external sizing) (Uehara et al., 2021; OECD, 2020). More technical details on the internal and external sizing, including respective advantages and disadvantages can be found in OECD (2020).

Currently, 15 fluorotelomer-based acrylate[25] and 1 PFPE-based urethane SCFPs are listed on the US Food & Drug Administration (FDA)'s Inventory of Effective Food Contact Substance Notifications (FCN) database[26] for such uses. Additional information on the concentration limits for using SCFPs in making the food-contact paper and paperboard in the US can be found in the US FDA FCN database.[27] Furthermore, several major manufacturers have reached agreement with the US FDA to voluntarily phase out their sales of 6:2 fluorotelomer-based SCFPs for use in food contact applications in the US by 2023 (see Table S2; US FDA, n.d.).

Others

One acrylate SCFP (CASRN 70969-47-0) has been reported as fluorosurfactants in fire-fighting foam formulations (e.g., Solberg 1x3 ATC, Sigma AFFF; Solberg, n.d.; Sigma, n.d.) that are used in extraction of crude petroleum and natural gas, manufacture of coke and refined petroleum products, and wholesale trade (except of motor vehicles and motorcycles) (see Table S2; US EPA, 2016; SPIN, n.d.). CASRN 68298-62-4 has been reported for use in the following application areas with no further details available (likely as fluorosurfactants): paints, lacquers and varnishes; reprographic agents; adhesives and binding agents; printing inks; and glossing agents (see Table S2; SPIN, n.d.).

[25] The number here counts different salts of a SCFPs as different SCFPs. If different salts of a SCFP would be counted as one SCFP, there would be 11 distinct fluorotelomer-based acrylate SCFPs.

[26] https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN

[27] Further US-FDA generated documents on the chemistry and exposure, toxicology, and environmental impacts of the PFASs that were approved by US FDA for food contact substances between 2002 and 2016 can be found at https://www.edf.org/sites/default/files/EDF-PFAS-FOIA-FCN-Chemistry-Memos.pdf.

3.2. Presence of other PFASs in the commercial formulations

Commercial acrylate and urethane SCFP formulations are generally available in the form of aqueous dispersion of SCFP particles (Russell et al. 2008, 2010; Uehara et al. 2021; Washington et al. 2014). A range of non-polymeric PFASs have been detected in several fluorotelomer-based commercial acrylate and urethane SCFP formulations (see Table S3), including perfluoroalkyl iodides (PFAIs), PFCAs, and fluorotelomer acrylates (FTAcs), alcohols (FTOHs), alcohol acetates (FTOH-aces), carboxylic acids (FTCAs), ethers (FT-ethers), olefins (FTOs) and unsaturated carboxylic acids (FTUCAs).

The levels of non-polymeric PFASs may vary considerably across commercial formulations (see Table S3). One study reported residuals at the level of over 5 weight % of the solids in one fluorotelomer-based commercial formulation tested (see Table S1 of Washington et al. 2014). 3M reported that most of its PASF-based formulations for industrial applications typically contain monomer residuals at 1 percent or lower levels, though it is not clear whether the 1 percent or lower levels referred to the ratio of non-polymeric PFAS residuals to the SCFP content in dispersions or to the total dispersion mass (3M, 1999). In another two PASF-based commercial urethane SCFP formulations, no non-polymeric PFASs were detected (Chu et al. 2014; Letcher et al. 2020); however, this result may be an artefact.[28]

The detected non-polymeric PFASs can be grouped into four categories based on origins (by comparing to the general synthesis routes of SCFPs; see Figure 3.1), with some belonging to more than one category: (i) unreacted raw materials and reaction intermediates used in the synthesis (e.g., PFAIs, FTOHs, FTAcs); (ii) impurities from the starting materials (e.g., PFOA)[29]; (iii) degradation products of the unreacted raw materials and reaction intermediates (e.g., FTAcs → FTOHs → FTCAs, FTUCAs, and PFCAs; Young and Mabury, 2010, Liu and Avendaño, 2013, and Evich et al., 2022) and SCFPs (see Section 3.3 below); and (iv) reaction byproducts of PFASs in the previous three categories (e.g., 8:2 FTOH → 8-8 ether; 8:2 FTOH + PFOA → 8-2-8 ester)[30].

In addition to being impurities from the starting materials and synthesis in the formulations, some non-polymeric PFASs (e.g., FTOHs) can also be intentionally left at significant levels in commercial formulations as dispersants to keep the SCFP particles suspended in the aqueous phase.

Commercial formulations are applied to materials such as textiles and pulp whereby the SCFP particles are strongly adsorbed and, in some cases, chemically bound to the material surface, and the rest application suspension is discharged to wastewater (Russell et al. 2008, 2010; Uehara et al. 2021; Washington et al. 2014). Thus, during application of commercial formulations, PFAS impurities therein are partially released (via air, wastewater and/or solid waste; Heydebreck et al., 2016), and partially transferred onto products (for examples of the detection of some non-polymeric PFASs in SCFP-treated products, see Table S3). The levels of PFAS impurities released and remaining in treated products may be highly

[28] The non-detection could be due to several reasons: (i) the dilution that the concentration of SCFPs was estimated to be <3% in the formulations (i.e., at least about an order of magnitude lower than the other studies), resulting in the PFAS impurity levels below the detection limit; (ii) possible key compounds such as FASEs (Wang et al., 2014A) were not monitored; and/or (iii) the analytical methods used in that particular study are not effective for capturing non-polymeric PFASs, particularly those that are still co-associated with the polymer (Larsen et al. 2006; Washington et al. 2009, 2014). Washington et al. (2014) provides a solid analytical workflow for measuring levels of PFAS other than the SCFPs in the commercial formulations.

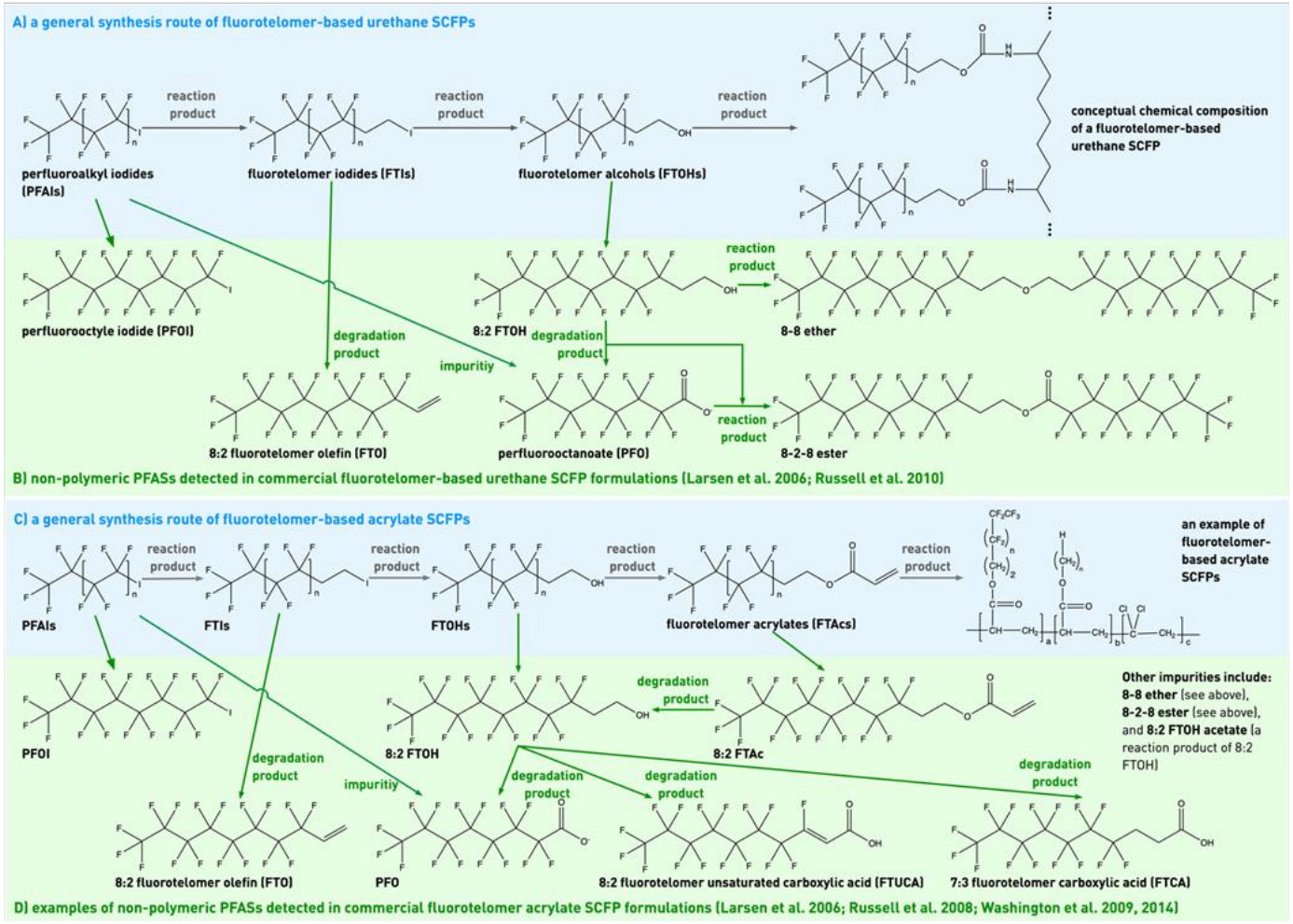
[29] PFOA was detected in the perfluoroalkyl iodides (PFAIs) starting material for synthesizing fluorotelomers; for more details, see the Supplementary Data of Wang et al. (2014A).

[30] The acronyms “8-8 ether” and “8-2-8 ester” are taken from the original publications. Future terminology may harmonized them in the same manner as “8:2 FTOH” for “8:2 fluorotelomer alcohol”.

variable, depending on the processes and control measures.[31] No mass balance studies of the fate and distribution of non-polymeric PFAS during application of commercial SCFPs are identified.

[31] Some patents describe flash drying, e.g., at 127 ℃, is included in the application of SCFPs. When Washington et al. (2014) dried a commercial SCFP at 127 ℃, the PFAS impurities dropped 2- to 3-orders of magnitude to constant concentrations within about 10 minutes.

Figure 3.1. A comparison of detected non-polymeric PFASs to the general synthesis routes of commercial fluorotelomer acrylate and urethane SCFPs.



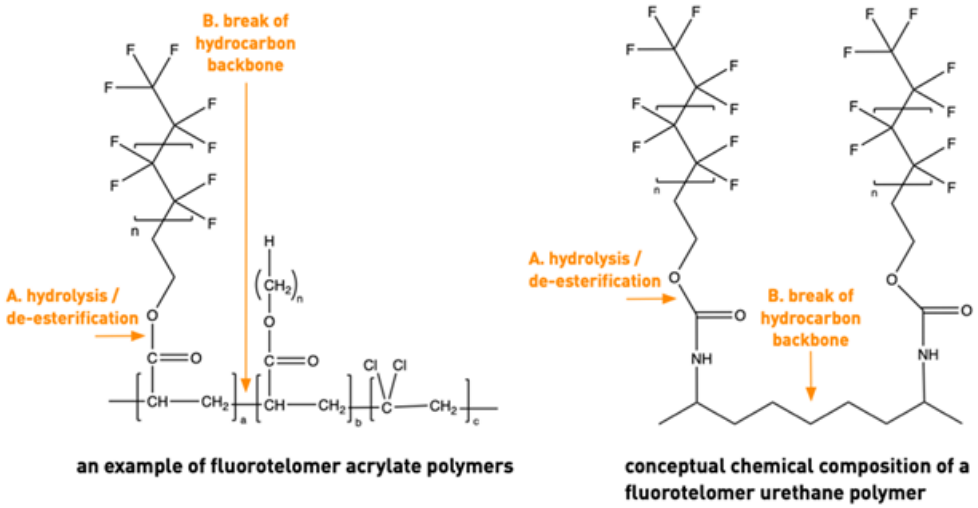
3.3. Degradation of SCFPs during use and after end-of-life

Acrylate and urethane SCFP degradation may follow two main degradation mechanisms (see Figure 3.2): A) direct cleavage of PFAS moieties from the side chains (e.g., hydrolysis of the ester bond); and B) breakdown of the polymer carbon−carbon backbone to form small oligomeric species which subsequently undergo ester bond cleavage (Russell et al. 2008, 2010).

Existing degradation studies have shown that the PFAS moieties may be released during abiotic or biotic degradation (i.e., the occurrence of the mechanism A), which can then subsequently further degrade and form PFCAs and/or PFSAs in the environmental and biota following rather well-characterized degradation pathways of non-polymeric PFASs [which have been well synthesized in Young and Mabury (2010), Liu and Avendaño (2013) and Evich et al. (2022)].

These studies did not show whether the mechanism B also occurred, whereas a recent study by Schellenberger et al. (2022) detected release of SCFP-containing microplastic fibres from functional textiles during washing, suggesting the mechanism B may occur during certain conditions (which may be learned from the research field of microplastic formation in the future).

Figure 3.2. Schematic illustration on two main degradation mechanisms of acrylate and urethane SCFPs.



While existing degradation studies agree well on the degradation mechanisms, historical studies have reported a wide range of degradation half-lives[32] (see Table 3.2), ranging from less than 1 year, to a couple of years, to decades to roughly a century, to over a thousand years. These large variations are partially caused by limitations in the experimental design of some previous studies (e.g., whether non-polymeric PFAS residues were all removed; Larsen et al., 2006, Washington et al., 2009, Washington et al. 2015B). In other words, some of the large variations observed are caused by experimental artefacts, which can be and were minimized/eliminated in more recent studies (where the degradation half-lives of two fluorotelomer-based acrylate SCFPs were measured to be several decades; Washington et al., 2015A and

[32] Note that the degradation half-lives here refer to the initial degradation step(s) of cleaving PFAS moieties from the polymer backbone.

2015B). More technical details and discussion on this possible source of error, as well as a recommended analytical workflow to minimize/eliminate it, can be found in Washington et al. (2014).

At the same time, the variations observed also partially reflect the true variability of several parameters that may impact degradation, including 1) molecular size of SCFPs (only three studies reported, with the number/weight-average molecular weight ranging from nearly 3000 Dalton to 40,000 Dalton, which can influence, e.g., bioavailability); 2) specific surface area of SCFP particles (which can influence areas available for degradation; Washington et al. 2009); 3) substrate (as hydrophobicity may well be diminished when water can come through the substrate and result in hydrolysis / de-esterification without or with less interference from the side chains, see Figure 3.2); 4) temperature, 5) pH values (shorter degradation half-lives with increasing alkalinity above pH = 8; Washington et al. 2015B), and 6) humidity (the same SCFP degraded more slowly when it was dry in comparison to when it was water-submerged; Washington et al. 2015A,B). Such variability cannot be minimized/eliminated.

Therefore, the degradation half-lives of acrylate and urethane SCFPs in the environment and biota will remain to some extent uncertain, in part reflecting real-world variability associated with the factors described above. Still, more of this uncertainty is because the characterization of many of these parameters are not available in the public domain (e.g., molecular size and specific surface areas of SCFP particles in commercial formulations) and may change over time (e.g., molecular size decreases when the degradation mechanism B occurs). Nevertheless, it can be concluded that these SCFPs generally will degrade under environmental conditions, with half-lives often falling roughly at a century or less, and thus serve as a long-term source of non-polymeric PFASs in the environment and biota.

In contrast to abiotic and biotic degradation, little is known about the fate of acrylate and urethane SCFPs during municipal waste incineration of SCFP-treated articles.[33] Yamada et al. (2005) investigated the thermal degradation of a polyester/cellulose fabric substrate treated with a fluorotelomer acrylate SCFP (that was described in the US Patents 4742140 and 5344903) under laboratory conditions with an average temperature of 1000 ºC or greater[34] over approximately 2 seconds of residence time. The results observed thermal degradation of the SCFP started at ca. 600 ºC and increased with increasing temperature (90% sample destruction at ca. 850 ºC, and 99.9% sample destruction at 1000 ºC), with no formation of PFOA. Fluorinated radicals such as $\bullet CF_3$ and $\bullet CF_2CH{=}CH_2$ were major extracted species at 600 ºC, and their levels decreased with increasing temperature (they still existed at 1000 ºC, but the relative amount remaining was ≤0.1%). It is currently unknown whether other non-polymeric PFASs would be generated during incineration, as they were not monitored in the study.

[33] More is known about incineration of other PFASs including fluoropolymers. For more details, see, e.g., Olsavsky et al., 2020 (https://doi.org/10.3390/app10196921) and Winchell et al., 2020 (https://doi.org/10.1002/wer.1483).

[34] Note that in Europe, the flue gases from municipal waste incinerators are meant to run at a temperature of 850 °C for at least two seconds, see https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=LEGISSUM:l28072&from=EN.

*Table 3.2. Reported experimental degradation half-lives of commercial acrylate and urethane polymers.**

Reference	SCFP type (characterization)	Degradation half-life [years]	Notes
Russell et al. 2008	A commercial n:2 fluorotelomer acrylate SCFP (number-average molecular weight of 40000 Dalton and 10.095 weight% fluorine)	Alfisol soil: 217 (SAS calculations) / 1140 (Excel calculations) Inceptisol soil: 95 (SAS calculations) / 637 (Excel calculations) Mollisol soil: 202 (SAS calculations) / 1270 (Excel calculations) Ultisol soil: >2000 (SAS calculations & Excel calculations)	These degradation half-lives may be an overestimate, as the study did not follow the recommendation by Larsen et al. (2006) to capture all non-polymeric residues remained in the polymer – an issue that was detailed in Washington et al. (2009).
Washington et al. 2009	A commercial n:2 fluorotelomer acrylate SCFP that is pre-treated by the manufacturer to minimize non-polymeric residue level (unknown)	870–1400 for coarse-grained test polymer in soil 10–17 for more-finely grained polymers in soil (based on modelling, assuming degradation is surface-mediated)	The specific area of the test SCFP was about 0.05 m^2/g, lower than the specific area of a typical commercial acrylate SCFP at about 14 m^2/g.
Russell et al. 2010	A commercial n:2 fluorotelomer urethane SCFP (number/weight-average molecular weight of 3500 Dalton and 10 weight% fluorine)	Alfisol soil: 241 Inceptisol soil: 72 Molisol soil: 219 Ultisol soil: 28 (use data through day 273) to 79 (use all data)	These degradation half-lives may be an overestimate, as the study did not follow the recommendation by Larsen et al. (2006) to capture all non-polymeric residues remained in the polymer – an issue that was detailed in Washington et al. (2009).
Washington et al. 2015A	Two commercial n:2 fluorotelomer acrylate SCFPs – FTP3 and FTP4 (unknown)	Quantitative rate-constant treatment: Appling (ultisol) soil (FTP4, drying at 127 °C, soil moisture saturated, endogenous microbial community, 7 sampling rounds, 5 microcosms per sample rounds) = 65 (use C_8 data and 80% recovery)–112 (first-order sum of all analytes and 100% recovery); Semi-quantitative range-finding treatments: 5 sample media (2 ultisol soils, 1 alfisol soil, 1 commercial soil, and 1 water); 2 moisture states (moist and saturated); FTP3 and FTP4; 2 FTP dispersion drying temperatures (22 ? and 127 ?); 2 assumed recoveries (80% and 100%) = 30–77; Best composite estimate: 33–112	Abiotic hydrolysis control unexpectedly degraded to form FTOHs roughly at the same rate as soil treatments.
Washington et al. 2015B	A commercial n:2 fluorotelomer acrylate SCFP – FTP3 (unknown)	Abiotic hydrolysis at 25 °C ca. 55 (based on C_8 data) / 89 (based on C_{10} data) at pH = 5–8 34 (based on C_8 data) / 34 (based on C_{10} data) at pH = 9 15 (based on C_8 data) / 18 (based on C_{10} data) at pH = 10 4.9 (based on C_8 data) / 5.1 (based on C_{10} data) at pH = 11 0.7 (based on C_8 data) / 0.66 (based on C_{10} data) at pH = 12	Half-lives for pH>8 not expected to represent common environmental conditions, but these data aid elucidation of hydrolysis mechanism.

* Note that the degradation half-lives here refer to the initial degradation step(s) of cleaving PFAS moieties from the polymer backbone. Additionally, Rankin et al. (2014) studied two non-commercial, custom-synthesized homopolymeric n:2 fluorotelomer acrylate SCFPs and observed degradation half-lives of 8–111 years. It should be noted that the number-average molecular weight in this study were 3000–3800, roughly an order of magnitude less than common commercial acrylate SCFPs.

3.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

As stated above, significant amounts of acrylate and urethane SCFPs, and other PFAS impurities present in the commercial formulations, have been and are released via air, waste water and solid waste along the life cycle of SCFPs: during the application of commercial formulations (e.g., Heydebreck et al., 2016), during the processing of treated materials into articles (e.g., 3M, 1999; Liu et al., 2009, 2014), and during the use and disposal of treated articles (e.g., Freriksson et al., 2020; Schellenberger et al., 2022; van der Veen et al., 2022).

3M estimated that total PFAS losses during surface treatment of uncut fibre, textile or leather raw materials using POSF-based SCFPs and downstream industrial operations (e.g., drying, cutting, shearing, packaging and shipping) could range between 10 and 25 percent (3M, 1999);[35] it is unclear how the reported levels are relevant for the SCFPs and processes being used today.

Further, three studies have investigated the presence of target urethane SCFP compositions in two pre- and post-2002 Scotchgard fabric protection formulations in lake sediment, soil samples, sludge from wastewater treatment plants and landfill leachates (see Table S5) (for more analytical details, see, e.g., Chu and Letcher, 2017). Interestingly, the SCFP compositions could be detected in most of the samples tested, showing that the SCFPs may be directly released and act as a long-term source of perfluoroalkyl acids in the environment. Also, the three studies indicate that sludge can be a main source of at least some SCFPs in the environment, particularly when they are subsequently used as biosolids to treat agricultural land. This is in line with another study investigating releases of SCFP-treated textile fibres during washing, where considerable releases of SCFP-containing fibres were detected in washing and rinsing water (Schellenberger et al., 2022), many of which may then be retained in sewage sludge at wastewater treatment plants (Wu et al. 2021). It was also shown that landfill leachate might not be a significant source of some SCFPs themselves (Fredriksson et al. 2020). Nevertheless, landfill leachates can be a significant source of other non-polymeric PFASs (e.g., Lang et al., 2017; Masoner et al. 2020), which may partially originate from SCFP-related sources.

3.5. Summary of critical knowledge and data gaps

It can be qualitatively concluded that production, use and disposal of acrylate and urethane SCFPs are significant sources of non-polymeric PFASs in the environment, particularly in the long term, as also demonstrated in several simplified modelling simulation studies (Wang et al., 2014B; Wang et al., 2017; Li et al. 2017). This is because of historical and ongoing high production volumes, possible presence of high levels of non-polymeric PFASs in the formulations, ability to degrade and form non-polymeric PFASs in the environment and biota, and multiple release pathways along the life cycle.

However, due to presence of the following critical knowledge and data gaps, it is currently not possible to more precisely estimate the contribution of acrylate and urethane SCFPs to non-polymeric PFASs in the environment: (i) a lack of detailed information on the production and use volumes of individual acrylate and

[35] The levels were calculated using material flow analyses, based on 3M's internal sales data, knowledge of product handling and use practices from field sales and technical personnel, best estimates of end-use applications from known customer activities, and knowledge of worldwide activities (where applicable) by St. Paul-based personnel. Calculation details are provided in the original document submitted to the US EPA, but are to a large extent redacted in the publicly accessible version of the document.

urethane SCFP (with many not reported in the public domain due to confidentiality or no reporting requirements), (ii) a lack of a comprehensive overview of acrylate and urethane SCFPs on the market, particularly in terms of their structural details and thus degradation potential, (iii) a lack of understanding of their fate in municipal waste incinerators.

3.6. Options for a way forward

A better understanding of the production, use and releases of acrylate and urethane SCFPs can inform a better understanding of the sources, human and environmental exposure routes, true environmental and human body burden of PFASs. Thus, it can assist in the identification of possible overlooked hotspots/blindspots, particularly as the current analytical and monitoring capability and capacity of PFASs are limited due to various reasons. Future action may include addressing both existing information and current information gaps. Addressing existing information may include: (i) more in-depth research and analysis of additional information sources such as companies' individual technical handbooks and brochures, SDS and patents, and harmonizing reported structural and use information (in terms of, e.g., the level of details, terminologies, and data format), and (ii) exploring ways to make publicly available the structural and use information that has been reported to regulators, but has not been claimed as confidential business information. Addressing current information gaps may include further research on their fate in municipal waste incinerators.

4 The Life Cycle of Oxetane SCFPs

Chapter summary:

- Limited information is available on the historical and current production of oxetane SCFPs.
- They have been primarily used as wetting, flow and levelling agents in different use areas such as coatings, electronic applications, floor finish, and inks, and some may also be used as reactive intermediates for solvent-based coatings, adhesives, electronics and lubricants.
- Little is known about other PFASs present in commercial oxetane SCFPs, but likely include at least two types of other PFASs: unreacted raw materials and intermediates, and reaction by-products (e.g., cyclic oligomers of the oxetane monomers).
- Also, little is known about the degradability of oxetane SCFPs. On one side, in comparison to the ester bonds in acrylate and urethane SCFPs, the ether bonds (–O–) in oxetane SCFPs are more stable. On the other side, many commercial oxetane SCFPs appear to have lower average molecular weight (e.g., about 1500 Dalton for PolyFox PF-136A, PF-656 and PF-2003), which may indicate higher bioavailability than many commercial acrylate and urethane SCFPs.
- No studies on the releases of oxetane SCFPs and other PFASs present in the formulations were identified. However, it is likely that oxetane SCFPs and other PFASs present in the formulations are released during use (given their use patterns as wetting, flow and levelling agents in open applications such as coatings, floor finish, and inks) and end-of-life treatment.
- Overall, little is known about oxetane SCFPs. Future action may first make the current production and use volumes of oxetane SCFPs publicly available and accessible, and then the priority level of investigating oxetane SCFPs in comparison to other SCFPs can be determined by relevant stakeholders.

4.1. Historical and ongoing production and uses

In comparison to acrylate and urethane SCFPs, limited public information is identified on the production of oxetane SCFPs. A range of PACF-based oxetane SCFPs with varied fluorinated carbon chain lengths have been marketed under the brand name "PolyFox" (see Table S1). At least four of them are registered in the EU under REACH; however, the production/import volumes of three have been claimed as confidential, whereas the production/import volume of one monomer is reported to be ≥1 to <10 tonnes/year (see Table 4.1). The oxetane SCFP monomer[36] has also been registered for production in or import into Japan, Vietnam and the US with unknown amounts (see Table S1).

According to the manufacturer, oxetane SCFPs have been primarily used as wetting, flow and levelling agents in different use areas such as coatings, electronic applications, floor finish, and inks, and some may also be used as reactive intermediates for solvent-based coatings, adhesives, electronics and lubricants (see Table S2).

Table 4.1. Production/import volumes of oxetane SCFPs and monomers in the EU reported in the REACH dossiers. n.d. = no date

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported
oxetane SCFPs			
449204-80-2	PACF-derivatives	1	**EU:** confidential (n.d.)
1182261-26-2	PACF-derivatives	1	**EU:** confidential (n.d.)
449204-81-3	PACF-derivatives	2	**EU:** confidential (n.d.)
Oxetane SCFP monomer			
449177-94-0	PACF-derivatives	2	**EU:** =1 to <10 tonnes/year (n.d.)

4.2. Presence of other PFASs in the commercial formulations

From the limited public information identified, at least two types of other PFASs can be present in the commercial formulations: unreacted raw materials and intermediates, and reaction by-products. The former is deduced from Dinglasan-Panlilio and Mabury (2006): the authors detected several FTOHs ($C_nF_{2n+1}CH_2CH_2OH$) – the likely starting materials – in a non-commercialized fluorotelomer-based oxetane SCFP that was specially prepared by the oxetane SCFP manufacturer (who produces commercial oxetane SCFPs from $C_nF_{2n+1}CH_2OH$; Buck et al., 2011).

Reaction by-products have been reported by Wesdemiotis et al. (2006); the authors observed that during the polymerization of an oxetane monomer and other co-monomers/reactants (like other commercial oxetane SCFPs; Kausch et al., 2002), cyclic oligomers of the oxetane monomers were formed in small yields (about 5%), with the tetramer being predominant (at least one order of magnitude more abundant than other oligomers).

Commercial oxetane SCFPs are available both in the form of aqueous dispersion (e.g., PolyFox PF-2003; Synthomer, 2020A) and in pure form (e.g., PolyFox PF-656; Synthomer, 2020B). It is unknown whether

[36] Oxetane (or 1,3-propylene oxide) is a heterocyclic organic compound with the molecular formula C_3H_6O, and has a four-membered ring. Oxetanes are highly reactive as they are strained cyclic ethers, and frequently used as reactive intermediates for further organic molecular synthesis.

the impurities mentioned above would be removed from the commercial products before being put on the market.

4.3. Degradation of oxetane SCFPs during use and after end-of-life

No studies on the degradation of oxetane SCFPs during use and after end-of-life are identified.[37] It is also challenging to theoretically project the degradation behaviour of oxetane SCFPs from the chemical structures. On one side, in comparison to the ester bonds in acrylate and urethane SCFPs (see point A in Figure 3.2), the ether bonds (–O–) in oxetane SCFPs are more stable. On the other side, many commercial oxetane SCFPs appear to have lower average molecular weight (e.g., about 1500 Dalton for PolyFox PF-136A, PF-656 and PF-2003; Synthomer, 2020A,B,C), which may indicate higher bioavailability than many commercial acrylate and urethane SCFPs. Future studies investigating the degradation of oxetane SCFPs during use and after end-of-life are needed.

4.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

No studies on the environmental releases of oxetane SCFPs and other PFASs present in the commercial formulations are identified.[38] However, it is likely oxetane SCFPs and other PFASs present in the commercial formulations are released during use (given their use patterns as wetting, flow and levelling agents in open applications such as coatings, floor finish, and inks) and end-of-life treatment. Future studies investigating their releases during use and after end-of-life and environmental presence are needed.

4.5. Summary and options for a way forward

Overall, little is known about oxetane SCFPs. Future action may first make the current production and use volumes of oxetane SCFPs publicly available and accessible, and then the priority level of investigating oxetane SCFPs in comparison to other SCFPs can be determined by relevant stakeholders.

[37] Google Scholar searches using the combination of keywords “fluoro”, “oxetane”, “polyfox”, “stability”, “degradation”, “thermolysis” and/or “pyrolysis” did not return relevant results.

[38] Google Scholar searches using the combination of keywords “fluoro”, “oxetane”, “polyfox”, “environmental”, “presence”, “occurrence” and/or “release” did not return relevant results.

5 The Life Cycle of Silicone SCFPs

Chapter summary:

- Various silicone SCFPs and monomers, belonging to different categories of PFAS moiety types with varied fluorinated chain lengths, have been and are being produced and used. Ultrashort-chain silicone SCFPs (where fluorinated carbon chain length = 1) have been produced at the scale of tens of thousands tonnes per annum, whereas less is known about longer-chain silicone SCFPs (due to confidentiality, no reporting requirements, etc.).
- Commercial silicone SCFPs are available in a wide range of different forms, including different polymers that are manufactured at the industrial scale, and commercial formulations (e.g., spray) containing monomers of silicone SCFP which can then form silicone SCFPs on the material surface upon application.
- Silicone SCFPs have been used in a wide range of applications, including as surface protectors to treat different materials, in medical applications, in personal care products, as antiformers, as lubricants, and in rubber applications.
- Similar to acrylate, oxetane and urethane SCFPs, at least two types of other PFAS impurities can be found in the silicone SCFPs, at likely significant levels: unreacted raw materials and intermediates, and reaction byproducts. For PFAS silane-based commercial formulations, presence of non-polymeric PFASs on the final treated products depends not only on the compositions in commercial formulations, but also the reactions that take place on the material surface upon application.
- Similar to acrylate and urethane SCFPs, degradation of silicone SCFPs may occur at the side chains and/or at the silicone polymer backbone, thus releasing various PFAS degradation products including cyclic PFAS siloxanes and PFCAs during use and after end-of-life. The dominant degradation half-lives, mechanisms and products depend on the PFAS moieties and conditions. Once released, cyclic PFAS siloxanes can further degrade under different mechanisms, and possibly form highly stable PFCAs as the end products.
- Significant amounts of SCFPs and other PFASs present in the commercial formulations may be and are released from the production, use and disposal, via air, wastewater and solid waste, with elevated levels of ultrashort-chain monomers detected close to the manufacturing sites in China, and in sewage sludge and sediments in several parts of the world.
- Similar to acrylate and urethane SCFPs, given the high production volumes and wide use of silicone SCFPs, possible presence of high levels of other PFASs in the commercial formulations, and their ability to degrade to non-polymeric PFASs including PFCAs, silicone SCFPs are very likely significant sources of non-polymeric PFASs in the environment. Future efforts may collect further information and reduce the uncertainties to reach more precise estimates.

5.1. Historical and ongoing production and uses

Various silicone SCFPs[39] and monomers, belonging to different categories of PFAS moiety types with varied fluorinated chain lengths, have been registered for production/import in many jurisdictions (see Table S1). Table 5.1 summarizes the production/import volumes of various silicone SCFPs and monomers reported in the EU, in the US, and in the Nordic Countries (Denmark, Finland, Norway and/or Sweden). Many are available in large tonnage ranges (e.g., >454 to <4540 tonnes/year), and many others have been claimed as confidential business information and not made public.

Nevertheless, it can be concluded that significant amounts of silicone SCFPs have been and are being produced, from the numbers reported in Table 5.1. Furthermore, in 2016, the total global production of trifluoropropyl-based silicone SCFPs (i.e., fluorinated carbon chain length = 1) was reported to be about 43600 tonnes, with the demand from China being about 3000 tonnes (Xiang et al., 2021).

[39] They are often called “polysiloxanes” in the technical literature.

Table 5.1. Production/import volumes of silicone SCFPs and monomers in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; and in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting); and in the EU reported in the REACH dossiers. t = tonnes; yr = year; n.d. = no date.

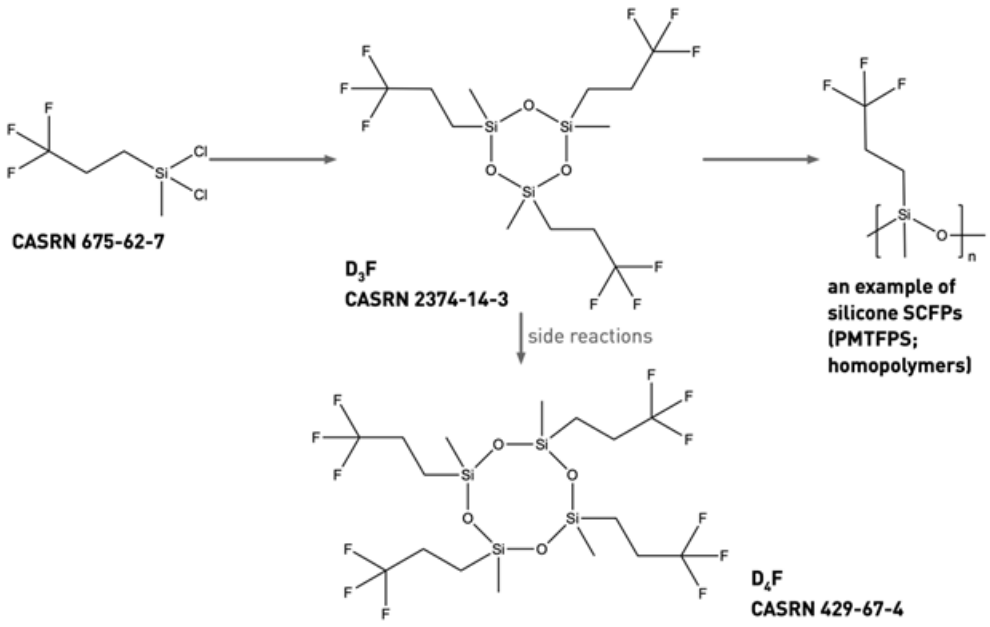
CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported [tonne; t]
silicone SCFPs			
104780-70-3	n:2 fluorotelomers	6	**SPIN:** confidential (2000–2019)
115340-95-9	n:2 fluorotelomers	6	**SPIN:** confidential (2000–2019)
262292-17-1	n:2 fluorotelomers	6	**SPIN:** confidential (2001–2019)
273737-91-0	n:2 fluorotelomers	6	**SPIN:** 0.3 t + confidential (2007–2019)
125476-71-3	n:2 fluorotelomers	8	**US:** confidential in 2011, <454 t/yr in 2012–2015 **SPIN:** confidential (2013–2019)
143372-54-7	n:2 fluorotelomers	8	**SPIN:** confidential (2000–2019)
146632-08-8	PASF-derivatives	8	**SPIN:** confidential (2001–2017)
162567-79-5	Perfluoroalcohol	8;9;10;11;12;13;14	**SPIN:** confidential (2000–2019)
silicone SCFP monomers			
429-60-7	n:2 fluorotelomers*	1	**SPIN:** confidential (2018–2019)
675-62-7	n:2 fluorotelomers*	1	**EU:** =100 to <1000 t/yr (n.d.) **US:** >454to <4540 t/yr in 1985 and 1989, >227 to <454 t/yr in 1993, >454to <4540 t/yr in 1997, 2001, 2005 and 2011, >454 to <908 t/yr in 2012–2015
2374-14-3	n:2 fluorotelomers*	1	**EU:** =100 to <1000 t/yr (n.d.) **US:** >454 to <4540 t in 1985, >227 to <454 t/yr in 1989 and 1993, >454 to <4540 t/yr in 1997 and 2001, <227 t in 2005, confidential in 2011, >454 to <4540 t/yr in 2012–2015 **SPIN:** confidential (2001–2019)
85877-79-8	n:2 fluorotelomers	4	**EU:** confidential (n.d.)
85857-16-5	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2017–2019)
51851-37-7	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2003–2019)
73609-36-6	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.)
78560-45-9	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.)
96383-55-0	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.)
101947-16-4	n:2 fluorotelomers	8	**EU:** confidential (n.d.)
137606-16-7	n:2 fluorotelomers	8	**EU:** confidential (n.d.)
83048-65-1	n:2 fluorotelomers	8	**SPIN:** confidential (2015–2019)
475644-38-3 358750-76-2	PFPEs	Unclear	**EU:** confidential (n.d.)
EC 458-200-2	Unclear	Unclear	**EU:** confidential (n.d.)
EC 429-350-6	Unclear	Unclear	**EU:** confidential (n.d.)
EC 442-180-7	Unclear	Unclear (likely 1)	**EU:** confidential (n.d.)
EC 442-330-1	Unclear	Unclear	**EU:** confidential (n.d.)

* Strictly speaking, these are not n:2 fluorotelomers, as the synthesis of the starting material, trifluoropropene, does not involve fluorotelomerization. Rather, trifluoropropene has been used in telomerization with other telogens/reagents (Boschet et al., 2012). For the purpose of simplification, they are included here in the category of n:2 fluorotelomers.

Commercial silicone SCFPs are available in a wide range of different forms. Industrially, PFAS silanes are first converted into cyclotrisiloxanes, which are then polymerized alone (into high molecular weight polymers, or so-called fluorosilicone gums with about 5000 monomer units), with end-blocking agents (into lower molecular weight polymers, or so-called fluorosilicone fluids/oils; Gelest, n.d.), or with co-monomers (into co-polymers); for an example, see Figure 5.1. The different forms are for different applications. For example, fluid polymers are used as is, or formulated for specific applications. If a reactive end blocking group is incorporated during polymerization, the fluid polymer is then useful for making a coating, a sealant, or a liquid rubber product. Gums can be further processed to produce various rubber products. More details on industrial polymerization of PFAS silanes and subsequent processing can be found in Kirk-Othmer (2006) and Yang et al. (2022).

In addition, commercial products (e.g., sprays) are also available in the form of formulations containing PFAS silane monomers [e.g., $C_nF_{2n+1}CH_2CH_2Si–(R)_3$, R = Cl, OCH_3 or OC_2H_5]. The active terminal groups R attached to silicon in the molecular structures can be easily hydrolysed to form reactive silanol (Si–OH) groups. Upon application, mono, double or triple functional silanol groups can either react with the hydroxyl groups on the material surface (e.g., SiO_2/Si surface) to form siloxane (Si–O–Si) linkages, or form intermolecular polysiloxane network, i.e., silicone SCFPs directly on the material surface (ECHA 2016; Zhu et al. 2019; Adamopoulos et al. 2021).

Figure 5.1. An example of synthesis routes of silicone SCFPs from PFAS silanes and side reactions



Different forms of silicone SCFPs have been used in a wide range of applications, including the following several major use areas (more uses and additional technical details can be found in Kirk-Othmer, 2006). It should be noted that much of the use information reported to the SPIN database has been claimed as confidential business information (see Table S2).

Surface protection

Solutions of silicone SCFPs can be used to impart oil and water repellent finishes to nylon-cotton fabrics (Kirk-Othmer, 2006). Furthermore, as stated above, PFAS-based silanes have been incorporated into commercial/consumer impregnation spray products for surface treatment of a wide range of materials with

non-absorbing surfaces such as stone, glass and enamels and with absorbing surfaces such as leather and textiles, providing water- and oil-repellency (ECHA, 2016). For instance, Dynasylan F 8261 has been used for treatment of automotive glass, coating of float glass, easy-to-clean coatings on ceramics and other silicate substrates including silica, quartz powder, sand, sandstone, cristobalite, wollastonite, mica, kaolin, and talc (ECHA, 2016). Fluowet ETC 100 and ETC 140 (likely fluorotelomer-based) have been specifically marketed for ceramic tiles in kitchens, glass doors of shower cabins, ceramic sanitary ware, wash basins, bath tubs and enamel (ECHA, 2016). Protectosil® Antigraffiti has been applied to surfaces of concrete, brick, concrete masonry units and natural stone to allow easy removal of a wide variety of graffiti (ECHA, 2016). X-Shield FluroSil 100 (likely based on PFAS-based silanes) has been marketed for protection of reinforced concrete structures, e.g., highways, bridge structures, parking decks, commercial buildings, marine structures and industrial facilities (X-Calibur, n.d.). Previously, a perfluorohexanoic acid (PFHxA)-derivative [CASRN 154380-34-4; $CF_3(CF_2)_4CONH(CH_2)_3Si(OCH_3)_3$] was marketed by the then Miteni as a surface treatment for glasses, natural stones, metals, wood, cellulose, cotton, leather and ceramics (Wang et al. 2013).

Medical applications

Different silicone SCFPs are used in many medical applications (Kirk-Othmer, 2006). For example, medical devices such as gastric feeding tubes use silicone SCFP-based rubber balloons for feeding tube retention while resisting gastric fluids. The low permeability of silicone SCFPs versus dimethylsilicone is utilized to control the rate of release in drug devices and in medical tubing to stop the migration of active ingredients into the tubing. Silicone SCFP fluids are used in the treatment of detached retina and other eye diseases. It is reported that from 1982 to 1993, Dow Corning produced polydimethylsiloxane (PDMS) implants with a total content of 2% PMTFPS (Kählig et al., 2009).

Personal care products

Silicone SCFP fluids and copolymers are used in a variety of personal care products, e.g., cosmetic foundations (where silicone SCFPs can provide durable water- and oil-repellency) (Kirk-Othmer, 2006). In addition, the low permeation of silicone SCFPs provides a degree of protection as a hand lotion.

Antifoams

Silicone SCFP fluids and copolymers are effective antifoams in nonaqueous systems (Kirk-Othmer, 2006). Successful application in the petroleum industry allows the full capacity of gas–oil separators to be used on offshore production platforms. Diesel fuels also require fluorosilicone antiforms due to the profoaming nature of dimethylsilicones in nonaqueous systems.

Lubricants

Silicone SCFP fluids are used as lubricants for pumps and compressors in harsh chemical service, such as those using acids, bases, and halogenated compounds and solvents (Kirk-Othmer, 2006). Silicone SCFP fluids are also found in many automotive and aerospace lubrication applications, since they are not easily leached by fuels from mechanical joints (Gelest, n.d.). In addition, silicone SCFPs, particularly the co-polymers, have been employed as lubricants for electrical contacts and precision timing devices (Gelest, n.d.). Greases formulated from silicone SCFPs and solid fluoropolymer thickeners have been used in sealed transmission and other extreme pressure applications (Gelest, n.d.).

Rubber applications

The majority of silicone SCFPs is used in elastomers/rubber applications (Kirk-Othmer, 2006). Silicone SCFP elastomers can be formulated to provide specific durometer (hardness), tear strength, modulus, and solvent resistance properties. It is used as O-rings for fuel lines containing gasoline and aviation fuels, particularly for low temperature sealing.

5.2. Presence of other PFASs in the commercial formulations

Similar to acrylate, oxetane and urethane SCFPs, at least two types of other PFAS impurities can be found in the silicone SCFPs, at likely significant levels (Fei et al., 2014): unreacted raw materials and intermediates (e.g., D_3F is often present as an impurity in PMTFPS; see Figure 5.1), and reaction by-products (e.g., the synthesis of PMTFPS from D_3F could form its other cyclic homologues such as the tetramer homologue–D_4F; see Figure 5.1). The levels of impurities may vary considerably among commercial silicone SCFP products depending on the actual synthesis conditions (Fei et al., 2014) and whether purification process may take place. A market overview could not be found using Google Scholar searches of keywords "PMTFPS", "fluorosilicones", "poly[methyl(3,3,3-trifluoropropyl)siloxane]", "impurities", and/or "residuals".

For PFAS silane-based commercial formulations, presence of non-polymeric PFASs on the final treated products depends not only on the compositions in commercial formulations, but also the reactions that take place on the material surface upon application. For the former, Zhu et al. (2019) investigated several commercial antifingerprint formulations with a focus on fluorotelomer silanes, and detected, in addition to 6:2, 8:2 and 10:2 fluorotelomer silanes as expected, also 7:2 fluorotelomer silanes and perfluorooctyl vinyl ether ($C_8F_{17}OCH{=}CH_2$)[40] in some formulations. The origin of 7:2 fluorotelomer silanes is unclear, whereas perfluorooctyl vinyl ether was likely intentionally added as a co-monomer for generating a highly ordered copolymer thin film (Zhu et al., 2019). Future work may investigate the mass balance of different compositions on the material surface after application.

5.3. Degradation of silicone SCFPs during use and after end-of-life

Similar to acrylate and urethane SCFPs, degradation of silicone SCFPs may occur at the side chains (similarly to point A in Figure 3.2) and/or at the silicone polymer backbone (similarly to point B in Figure 3.2), thus releasing various PFAS degradation products during use and after end-of-life. The dominant degradation half-lives, mechanisms and products depend on the PFAS moieties and conditions.

- Degradation of anti-sticking layers based on Optool DSX [$R–(CF_2CF_2CF_2O)_n–Si(OCH_3)_3$] and F_{13}-TMS [$C_6F_{13}CH_2CH_2–Si(OCH_3)_3$] in UV nanoimprint lithography was observed during use and at the side chains (Truffier-Boutry et al., 2010).
- PMTFPS products suffer from poor thermal stability and tend to degrade when exposed to temperatures over 200 ℃ for extend periods of time, with cyclic siloxanes such as D_3F and D_4F being the primary products (You et al., 2020). When thermolysis was carried out at a relatively high temperature (600 ℃), an additional decomposition product, trifluoropropene, was observed (You et al., 2020). Such thermolysis mechanisms, i.e., re-arrangement of the silicone backbone (causing

[40] In this case, the unique formula $[C_{10}H_4F_{17}O]^+$ was assigned within the mass error of 5 ppm, which was tentatively identified as perfluorooctyl vinyl ether through database search (e.g., PubChem CID 54096250).

formation of D_3F and D_4F in the example) and removal of the side chains (causing formation of trifluoropropene in the example), might occur for other silicone SCFPs as well, though possibly at different temperatures and with different yields.

- Photodegradation of the self-assembled monolayer derived from a 8:2 fluorotelomer silane [$C_8F_{17}CH_2CH_2Si(OCH_3)_3$], which contained likely 8:2 fluorotelomer silicone SCFP, was observed after UV–visible light exposure. After a 10-day exposure, the authors observed the formation of PFCAs (a mean molar yield of 0.2%), 8:2 fluorotelomer carboxylic acid (8:2 FTCA; a mean molar yield of 0.06%) and 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA; a mean molar yield of 0.009%) (Zhu et al., 2019). However, the study did not investigate the degradation mechanisms.

Once released, PFAS cyclic siloxanes can further degrade under different mechanisms, and possibly form highly stable PFCAs as the end products.

- They may undergo hydrolysis, and yield various transformation products including homologues (e.g., $D_3F \rightarrow D_4F$) and breakdown products [e.g., D_3F and $D_4F \rightarrow CF_3(CH_2)_2MeSi(OH)_2$] (Zhi et al., 2018). Zhi et al. (2018) further reported that under the laboratory conditions, the hydrolysis half-lives of D_3F and D_4F at different pH values (5.2, 6.4, 7.2, 8.3, and 9.2) varied from 80.6−154 h and from 267−533 h, respectively.
- They may also undergo biodegradation, e.g., in sludges. Their biodegradation half-lives are likely longer than their hydrolysis half-lives, with one study reported 41.1 d for D_3F and about 55 days for D_4F (Huang et al., 2020). The same authors also reported, from the degradation of D_3F and D_4F, the formation of $CF_3(CH_2)_2MeSi(OH)_2$ (similarly to hydrolysis) and $MeSi(OH)_3$ (which was not observed in the hydrolysis study by Zhi et al., 2018). The latter means that PFAS moieties were released, which may be further transformed into highly stable of PFCAs; a recent study shows that n:2 fluorotelomer silanes [e.g., $C_8F_{17}CH_2CH_2Si(OCH_3)_3$] can be easily oxidized to corresponding PFCAs using the total oxidizable precursor assay (Zhu et al., 2019).

5.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

Given the high levels of historical and ongoing production as well as the myriad of uses, significant amounts of silicone SCFPs and other PFASs present in the commercial formulations are expected to have been released from production, use and disposal, via air, wastewater and solid waste. For example, Zhi et al. (2018) reported elevated levels of D_3F and D_4F in surface water (up to 291 ng/L for D_3F and up to 168 ng/L for D_4F) and sediment (up to 5478 ng/g for D_3F and up to 6277 ng/g for D_4F) near a fluorinated methylsiloxane manufacturing plant in Weihai, China. In addition, both Truffier-Boutry et al. (2010) and Zhu et al. (2019) provide evidence of significant levels of non-polymeric PFASs present in the silicone SCFP layer after applying PFAS silanes, which can be released during use and disposal. Furthermore, van Bavel et al. (2016) detected D_3F and D_4F in the leachates from the ISI and Lindum landfills in Norway, showing releases from solid waste treatment.

Several other studies have also detected elevated levels of D_3F and/or D_4F in the sewage sludge from Sweden and sediment from some lakes in Sweden and Norway (McLachlan et al., 2014), in the effluents of two WWTPs in Norway (van Bavel et al., 2016), and in about 20% of the sludge samples from 29 WWTPs at 25 cities distributed over seven geographic regions of China (Huang et al., 2020). These studies did not report the likely sources of these observations.

5.5. Summary and options for a way forward

Silicone SCFPs share many similarities to acrylate and urethane SCFPs. They are likely significant sources of non-polymeric PFASs in the environment, particularly in the long term because their high production volumes and wide use, possible presence of high levels of non-polymeric PFASs in the formulations, ability to degrade and form non-polymeric PFASs in the environment and biota, and multiple release pathways along the life cycle. Also, due to the presence of many critical knowledge and data gaps such as on the production volumes, use patterns, levels of other non-polymeric PFAS impurities in the formulations, and degradation potential, it is currently not possible to more precisely estimate the contribution of silicone SCFPs to non-polymeric PFASs in the environment.

A better understanding of the production, use and releases of silicone SCFPs can better inform the sources, human and environmental exposure routes, true environmental and human body burden of PFASs. Thus, it can assist in the identification of possible overlooked hotspots/blindspots. Future action may include addressing both existing information and current information gaps. Addressing existing information may include the following activities: (i) more in-depth research and analysis of additional information sources such as companies' individual technical handbooks and brochures, SDS and patents, (ii) harmonizing reported structural and use information to the same level, and (iii) exploring ways to make public available the structural and use information that has been reported to regulators but has not been claimed as confidential business information. Addressing current information gaps may include further research on their material flows and degradation behaviour.

6 The Life Cycle of Ethoxylate SCFPs

Chapter summary:

- Limited information is available on the production of ethoxylate SCFPs, with several that may have been produced up to hundreds of tonnes per annum.
- Ethoxylate SCFPs have mainly been used as surfactants/surface active agents in industrial processing, commercial applications and consumer uses. Some ethoxylate SCFPs may also be used to treat certain material surfaces (e.g., glasses) to impart water- and oil-repellency.
- Significant presence of unreacted residuals (up to 4%) has been reported in fluorotelomer- and PASF-based ethoxylate SCFPs.
- The ethoxy part in ethoxylate SCFPs can likely undergo biotic degradation and release the PFAS moieties over time.
- The use pattern of ethoxylate SCFPs will likely result in (uncontrolled) releases of the ethoxylate SCFPs themselves, other PFASs present in the commercial formulations, and their degradation products into the environment during use and after disposal, via air, wastewater, landfill leachates, etc.
- Future action may look into the current production and use volumes of ethoxylate SCFPs, as well as longer-term degradation behaviour, and thus provide a better understanding of PFASs releases from the production, use and disposal of ethoxylate SCFPs.

6.1. Historical and ongoing production and uses

Limited information on the historical and ongoing production of ethoxylate SCFPs was identified in the national/regional chemical inventories. Reporting to the US EPA by manufacturers/importers via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act is summarized in Table 6.1. In addition, at least 12 ethoxylate SCFPs were identified on the SPIN database, but their production or import volumes (and uses) have been mostly claimed as confidential business information and thus sealed from the public. For more details, see Table S1, Table S2, and the corresponding entries in the national/regional chemical inventories.

Table 6.1. Production/import volumes of ethoxylate SCFPs in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; and in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting). t = tonnes; yr = year.

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported
68298-79-3	PASF-derivatives	4	**SPIN:** confidential (2000–2011)
68298-80-6	PASF-derivatives	5	**SPIN:** confidential (2000–2011)
56372-23-7	PASF-derivatives	6	**SPIN:** confidential (2000–2011)
68298-81-7	PASF-derivatives	7	**SPIN:** confidential (2000–2011)
68958-60-1	PASF-derivatives	7	**SPIN:** confidential (2000–2006)
68958-61-2	PASF-derivatives	8	**US:** >4.54 to <227 t in 2001* **SPIN:** confidential (2000–2006)
29117-08-6	PASF-derivatives	8	**US:** >4.54 to <227 t in 2001* **SPIN:** confidential (2000–2011)
52550-44-4	n:2 fluorotelomers	6	**SPIN:** confidential (2013–2019)
65545-80-4	n:2 fluorotelomers	6;8;10;12;14;16**	**US:** >4.54 to <227 t in 2001, >11.3 to <45.4 t/yr in 2012–2015 **SPIN:** confidential (2000–2019)
200013-65-6	PFPEs	unclear	**US:** <454 t/yr in 2012–2015 **SPIN:** confidential (2015–2017)
162492-15-1 1000390-73-7	PFPEs	Unclear	**SPIN:** confidential (2008–2019)
56467-05-1	Perfluoroalcohol	6	**SPIN:** confidential (2000–2006, 2017)

* According to another reporting by 3M to the US EPA, it produced >10.6 tonnes of CASRN 68958-60-1 and about 10–30 tonnes of CASRN 29117-08-6 in the US in 1997 (US EPA Administrative Record 226, #580, #582, and #600).
** The fluorinated carbon chain length of CASRN 65545-80-4 is retrieved from the SDS of DuPont's Zonyl FSN fluorosurfactant (e.g., https://www.yumpu.com/en/document/view/10055541/zonyl-fsn-fluorosurfactant-msds-dupont) and the patent US 8367756 B2 (https://patentimages.storage.googleapis.com/88/07/2a/6fc07e409a037c/US8367756.pdf).

On the use side, more information is available, showing a wide range of use areas for ethoxylate SCFPs, particularly as surfactants/surface active agents in industrial processing, commercial applications and consumer uses. For example, Zonyl FSO-100 (CASRN 122525-99-9) is described as a non-ionic surfactant able to impart low aqueous surface tensions at low concentrations, and thus has been incorporated into applications such as caulks, paints, coatings and adhesives (Dinglasan-Panlilio and Mabury, 2006). Similar surfactant use has also been reported for other PASF-, fluorotelomer- and PFPE-base ethoxylate SCFPs, though in some cases incorporated into formulations for broader application areas including ink, oil and gas drilling, soap and cleaning products, automotive care products, lubricants, food packaging (e.g., CASRN 200013-65-6) and fire-fighting foam agents (e.g., CASRN 65545-80-4). For more details, see Table S2.

In a recent study, fluorotelomer-based ethoxylate SCFPs have also been detected as the major fluorinated components in several anti-fog sprays and cloths purchased from Amazon.com (Herkert et al. 2022). This is in line with 3M's reporting that PASF-based ethoxylate SCFPs were "used as received or diluted with water or butyl acetate to impart soil or water repellency to surfaces (including printed circuit boards or photographic film)" (3M, 1999). 3M also reported that some formulators used PASF-based ethoxylate SCFPs as a thickener to aqueous coatings used to protect tile, marble and concrete.

6.2. Presence of other PFASs in the commercial formulations

Significant presence of unreacted residuals (i.e., n:2 FTOHs) in two commercial fluorotelomer-based ethoxylate SCFPs has been reported (see Table S3): Zonyl FSO 100 contained 6:2, 8:2 and 10:2 FTOHs (1.03% of dry weight; Dinglasan and Mabury, 2006), and Zonyl FSH contained 6:2 FTOH (0.54%) and 8:2 FTOH (0.29%) (Frömel and Knepper, 2010).[41] These levels are also in line with recent measurements of 6:2 FTOH in two anti-fog sprays primarily based on 6:2 fluorotelomer-based ethoxylate SCFP formulations (Herkert et al. 2022).[42] Further, 3M reported that PASF-based ethoxylate SCFPs typically contained 4% or less PFAS residuals (3M, 1999). Due to the high volatility of FTOHs, they may be released during the production, use and disposal of commercial ethoxylate SCFPs. Similar levels of unreacted residuals might be expected to be present in other commercial ethoxylate SCFPs unless they were purified.

6.3. Degradation of SCFPs during use and after end-of-life

The ethoxy part in ethoxylate SCFPs can likely undergo biotic degradation and release the PFAS moieties over time, as concluded by an assessment of Capstone FS-30–a n:2 fluorotelomer-based ethoxylate SCFP–by NICNAS that "over time, the notified polymer is expected to ultimately degrade into perfluorohexanoic acid (PFHxA)" (NICNAS, 2018). However, such degradation may take a long time and thus ethoxylate SCFPs themselves may be persistent in the environment. For example, Frömel and Knepper (2010) studied biodegradation of a n:2 fluorotelomer-based ethoxylate SCFP. The authors observed that the alcohol group at one end of the polymer chain can be oxidized and form a carboxylic group, i.e., $C_nF_{2n+1}CH_2CH_2(OCH_2CH_2)_mOH \rightarrow C_nF_{2n+1}CH_2CH_2(OCH_2CH_2)_{m-1}OCH_2COOH$. The authors further hypothesized that the ether bond can be cleaved, as observed for non-fluorinated ethoxylate polymers, and such chain-shortening continues until the ethoxylate SCFP is transformed to the corresponding n:2 FTOHs, which are precursors to PFCAs. The authors noticed that the ethoxylates did not further degrade once the chain length was shortened to a certain degree (where $m < 9$), but the authors noted the limited testing time period (48 days) might be too short to observe full transformation. In another biodegradation study of $C_9F_{19}CH_2CH_2O(CH_2CH_2O)_nH$ following the OECD guideline 301C, the ethoxy unit profile hardly changed during the 28-day test (Yamamoto et al., 2014).

6.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

The use pattern of ethoxylate SCFPs (see Section 5.1 above) will likely result in (uncontrolled) releases of the ethoxylate SCFPs themselves, other PFASs present in the commercial formulations, and their degradation products into the environment during use and after disposal, via air, wastewater, landfill

[41] The results from the two studies cannot be directly compared due to the use of different methods.

[42] The authors also screened for 4:2, 8:2, 10:2, 12:2, 14:2 and 16:2 FTOHs in all sampled anti-fog spray and cloth products, but did not detect them in any of the products except one (this specific product is likely based on an old formulation, with 8:2 and 10:2 fluorotelomers being the dominant species).

Furthermore, the authors also tested another two anti-fog sprays and reported higher levels of 6:2 FTOH, up to ca. 40%; however, in these two products, 6:2 FTOH and 6:2 fluorotelomer ethoxylates could explain only ca. 60% of the total organic fluorine. It is likely that other 6:2 fluorotelomer-based substances were added in the two anti-fog sprays, interfering the data interpretation. Therefore, the levels of 6:2 FTOH in these two anti-fog sprays are not considered in the comparison here.

leachates, etc. For example, the presence of a fluorotelomer-based ethoxylate SCFP [$C_9F_{19}CH_2CH_2O(CH_2CH_2O)_nH$] in the leachates from a disposal facility located in the Kansai area in 2010 was reported by Yamamoto et al. (2014).

6.5. Summary and options for a way forward

Their historical and current production and use volumes, as well as degradation half-lives, are key parameters that need to be improved in order to better understand the contribution of ethoxylate SCFPs to PFASs in the environment.

7 Conclusions

Compared to many non-polymeric PFAS, SCFPs and their known and unknown degradation products have received comparatively little attention from scientists and regulators, despite their manifold industrial uses and high volumes, their propensity to release non-polymeric PFAS, and their potential environmental and health impacts.

Overall, a wide range of information on the chemical identities of SCFPs, other PFASs present therein, historical and ongoing production and use, degradation of SCFPs, and release of SCFPs and associated non-polymeric PFASs is identified in the public domain and has been synthesized in this report.

Despite the many knowledge and data gaps identified in the respective chapters above, the following can be concluded from the information synthesized here: A wide range of SCFPs have been produced and used in many different applications, with at least some SCFPs at high volumes (up to tens of thousands of tonnes/year); as a comparison, 3M reported that its estimated global production of POSF-derivatives for fire-fighting foams was about 150 tonnes in 2000 (3M, 2000). Many non-polymeric PFASs may be present in the commercial SCFP formulations, sometimes at percentage levels. During the production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs and associated non-polymeric PFASs may have been released. It is well expected that SCFPs can degrade and form non-polymeric PFASs, including PFCAs and/or PFSAs, in the environment and biota. Thus, many SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFASs including PFCAs and PFSAs.

Therefore, concerted action by all stakeholders is needed to address SCFPs in an efficient and effective manner. This includes identifying, making funding available and conducting research on those critical knowledge and data gaps that are most relevant for soundly regulating/managing SCFPs in different jurisdictions, building on the gaps identified in the respective chapters above. When addressing critical knowledge and data gaps, to increase efficiency, the following concerted action may be taken: (i) investigating additional information that is available in SDSs and patents (but was not actively searched and considered in this analysis due to time and resource constraints[43]); (ii) working with manufacturers to enable open access to information that has been generated by them (and made available to specific regulators), but has not been made publicly available; and (iii) regularly gathering newly available public information and synthesizing them to further increase the knowledge base on SCFPs.

In parallel to action on critical knowledge and data gaps, concerted action may be taken to develop, facilitate and promote national and international stewardship programmes and regulatory approaches to reduce emissions of SCFPs and related PFASs and to work toward global elimination, where appropriate and technically feasible.

[43] It should also be noted that SDS often contain inaccurate or missing information; and the listed chemical(s) could be found at higher concentrations than what the SDS listed. Thus, the information would need to be evaluated during review.

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This report provides an overview of existing scientific and technical information on side-chain fluorinated polymers (SCFPs), focusing on their identities and life cycle, and with a particular goal to map the existing landscape and highlight critical knowledge and data gaps.

It focuses on the life cycle of SCFPs, including production and use, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, and environmental releases of SCFPs and other PFASs present in the commercial formulations.

The report comes with a separate Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

oe.cd/pfass



Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions

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Significance and Motivation

A recent study by Conversio, a consultancy based in Germany, has shown that at its end-of-life approximately 85% of all fluoropolymers end up in waste-to-energy recovery incinerators. A subsequent question of regulators was: Do fluoropolymers get fully incinerated without any formation of short chain or long chain PFAS? A recent project executed by the Karlsruhe Institute of Technology (KIT) in cooperation with Société Générale de Surveillance (SGS) was conducted to assess the same.

Experimental Parameters

Main applications of the four highest volume fluoropolymers (PTFE, PVDF, PFA and FKM) representing more than 80% of commercial fluoropolymer production based on data from Pro-K (German association of polymers processors) were considered. Post-use samples from these applications were incinerated as a mixture under standard operating conditions for municipal and industrial waste incineration. Figure 1 presents the experimental conditions. Experiments were conducted under two sets of conditions over a period of 9 days. The first experiments were conducted at a process setting of 860°C and 2.0 s residence time. These experiments were conducted in three stages. Initially, background tests were performed using natural gas and 100 kg/h wood chips. This was followed by the same fuel conditions with the addition of 320 g/h of fluoropolymer. The final test involved switching back to background conditions. The duration of each of these tests ranged from 9 – 13 hrs. A second set of experiments was conducted at a process setting of 1100°C and 2.0 s residence time. These tests were conducted in the same sequence as the first set of tests. The feed rates for the wood chips and the fluoropolymer mixture were identical to the tests at 860°C and 2.0 s residence time. The test duration for this second set of tests also ranged from 9 – 13 hrs.

test	parameters	number of HF and PFAS sampling	locations	duration [hrs]	RUN	date / remarks		day
start-up with natural gas and oil				24		25.2.23; 10 a.m.	day 1 and 2	
starting solid feeding (wood chips)				24		26.2.23; 10 a.m.		
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips	T_{PCC}: 860 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	1	27.2.2023; 9 am	day 3	Monday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	2	28.2.2023; 9 am	day 4	Tuesday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	3	01.03.2023; 9 am	day 5	Wednesday
Change of temperature post combustion chamber				12		over night		
background of rotary kiln / combustion chamber with oil, natural gas and wood chips	T_{PCC}: 1100 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	4	02.03.2023; 9 am	day 6	Thursday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	5	03.03.2023; 9 am	day 7	Friday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	6	04.03.2023; 9 am	day 8	Saturday
shut down				24			day 9	

Material	Mass fraction [wt.-%]
PTFE tubes	63,00
PTFE tape	7,00
PVDF	18,00
PFA	6,00
FKM rubber	6,00

mass flow = 320 g/h

Figure 1: Experimental setup

The fluoropolymers were fed as a mixture at relative proportions that correspond to the mass fractions sold in the European marketplace. These data are also shown in Figure 1. Suspension and emulsion polymerized PTFE application samples represented about 70 mass percent of the fluoropolymer feed rate.

The main operational parameters for the two sets of tests are summarized in Figure 2. The temperature of the flue gas outlet exiting the rotary kiln was in the range of 800-900°C. The temperature of the flue gas post-combustion chamber outlet was very close to the targets for these tests (860°and 1100°C in the combustion chamber for setting 1 and 2, respectively). The O_2 and CO measurements for setting 1 and 2 varied somewhat. For setting 1, the values were 11.2 vol % dry and 0.2 mg/m^3, respectively, while for setting 2 the O_2 measurements were somewhat lower (7.0 % with an increase in the CO concentration (1.2 mg/m^3). The water vapor concentration as measured in the boiler exit ranged from 6.2% in setting 1 to 8.49% in setting 2.

			setting S1	setting S2
		unit	RUN 1, 2, 3	RUN 4, 5, 6
Rotary kiln	mass flow wood chips	kg/h	98	98
	main air	m_N^3/h	418	423
	mass flow heating oil	kg/h	61	46
	volume flow natural gas	m_N^3/h	4	4
	volume flow combustion air	m_N^3/h	872	753
	inclination	°	2	
	rotation speed	rev p.m.	0.2	0.4
	temperature flue gas outlet	°C	800 - 900	
	thermal power	MW	1.1	0.9
combustion chamber	volume flow natural gas to burner D4.1	m_N^3/h	22	35
	sum of volume flow combustion air to burner D4.1	m_N^3/h	671	429
	volume flow natural gas to burner D4.2	m_N^3/h	22	35
	sum of volume flow combustion air to burner D4.2	m_N^3/h	671	428
	residence time	s	2	
	temperature flue gas post-combustion chamber outlet (with control)	°C	860	1095
	CO (level E2)	mg/m^3	0.2	1.2
	O_2 (level E2)	Vol.-% dry	11.2	7.0
	thermal power	MW	0.46	0.72
	total thermal power rotary kiln and post combustion chamber	MW	1.59	1.67
boiler / fluegas	volume flow	m_N^3/h	3958	3238
	O_2	Vol.-% dry	11.9	9.0
	CO	mg/m^3	1.35	1.64
	water vapour	Vol.-% wet	6.20	8.49

Figure 2: Main operational parameters at two experiments

There were multiple sampling locations for this study. Flue gas was sampled near the exit of the combustion chamber (location 1), at the exit of the boiler (location 2), and at the entrance to the stack (location 3), while liquids and residues were also sampled and analyzed after each RUN (see Figure 3, Test facility sampling locations).

The test facility BRENDA comprises a rotary kiln with a post-combustion chamber, a boiler for heat recovery and a flue gas cleaning system, which complies with German emission regulations (17 BImschV). The thermal power of the rotary kiln is of maximum 1.5 MW, while that of the post-combustion chamber is about 1 MW, which results in a total thermal output of BRENDA of maximum 2.5 MW.

The fluoropolymers mixture after blending with wood chips and consequent weighing was delivered to the rotary kiln. To secure optimal combustion conditions, natural gas and heating oil were supplied additionally to the rotary kiln, while the post combustion chamber was supplied with natural gas only.

The mass flow of the fluoropolymers mixture was set at 320 g/h, which corresponds to a pure Fluorine mass flow of 230 g/h. This level increases the fluoropolymer ratio to fuel, while at the same time keeps the Fluor-concentration below the total halogen limit of 1%, as set by the legislature.

The combustion gases of the rotary kiln enter the post combustion chamber (PCC). It contains two natural gas burners staggered in an antiparallel manner, with a slight shift to each other. The temperature and the residence time in PCC were adjusted mainly with the help of the above mentioned burners, supported by a slight shift of about 200 kW into the post combustion chamber.

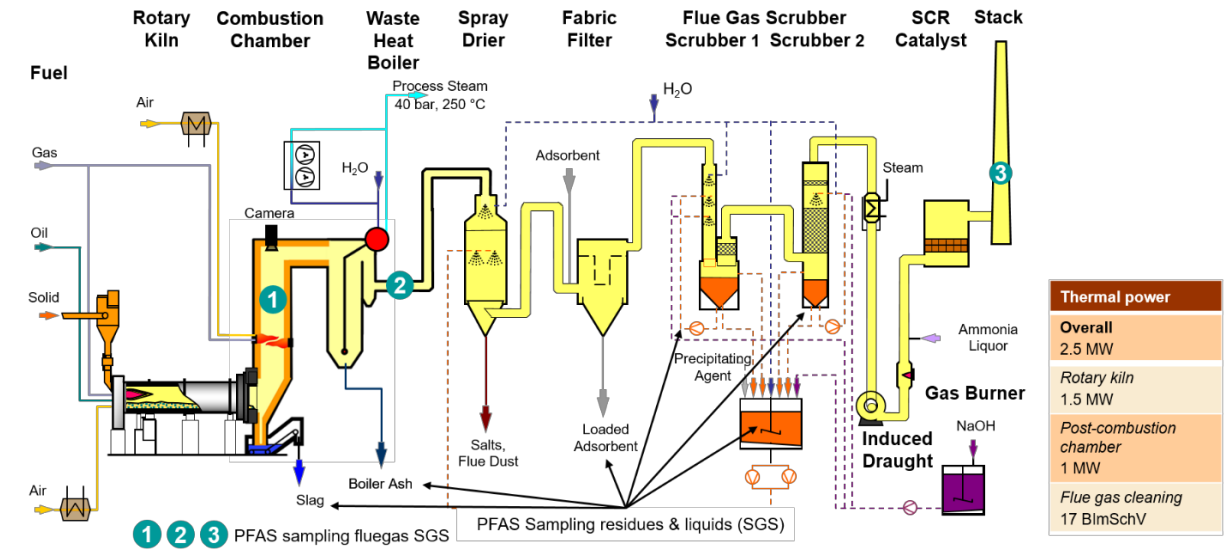


Figure 3: Test facility-BRENDA at KIT

The minimum residence time is calculated according the methodology of the German Technical Supervision Agency ("TÜV") from 2007. The data which were published in the report were re-calculated and then adapted to the operational conditions in this study (Setting 1 and Setting 2). Figure 4 presents the layout of the post combustion chamber with the geometry relevant for the determination of the residence time.

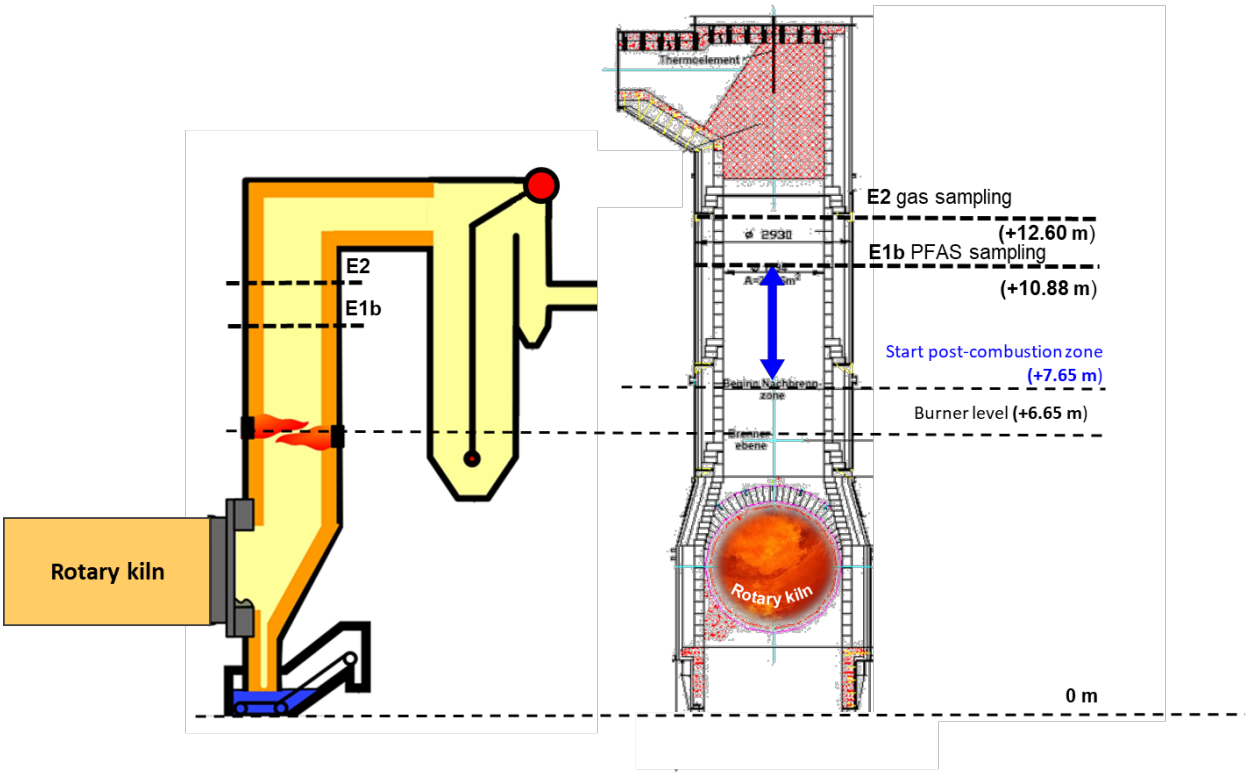


Fig. 4: BRENDA layout with details relevant for the residence time

Table 1 shows the detailed values for the design of the settings.

The volume flow of the required flue gas amount to reach the two seconds was calculated with a target value search.

Table 1. Parameters calculated for the residence time in the PCC

PFAS Project, Level E1b		
	setting 1	**setting 2**
Start post combustion zone [m] 1 meter above the burners	7.65	7.65
Temperature in the post combustion chamber (PCC) [°C]	860	1100
Volume flow V_{PCC} [m_N^3/h wet] after boiler	3947	3257
Cross section PCC [m^2]	2.82	2.82
Volume flow V_{PCC} [m^3/h]	16,382	16,382
Height h [m] level E1b	10.88	10.88
Residence time from start PCC zone to level E1b [s]	**2.00**	**2.00**

The two seconds are the residence time of flue gas from start of post-combustion zone until PFAS sampling point E1b, calculated with calibrated temperature measurements on the top of post combustion chamber (PCC).

The flue gas was sampled for both short-chain and long-chain PFAS in addition to organic and inorganic fluoride. Volatile organic C_1-C_4 fluorocarbons were also sampled using a tedlar bag at all three sampling locations. At location 2, gas-phase HF was measured in near real-time using a tunable diode laser (TDL). The purpose of the three gas-phase sampling locations was to assess the potential emissions of PFAS at different locations in the system and to use this data to assess potential sources of PFAS in this system. PFAS sampling of residues and liquids is also shown in Figure 3. In addition to these three sampling points, flue gas scrubber water upstream of the SCR catalyst was collected and analyzed for PFAS.

Table 2 provides a list of analytes measured in this study and the Limit of Quantification (LOQ). In addition to PFAS and fluoride ion, volatile C_1-C_4 fluorocarbons and trifluoroacetic acid (TFA) were also measured. The C_1-C_4 fluorocarbons were measured by gas chromatography coupled to mass spectrometry (GC-MS). Adsorbable organic fluoride (AOF) was measured using Combustion Ion Chromatography (CIC) and inorganic fluorine in impinger samples were measured by Ion Selective Electrode. TFA was measured using Ion chromatography (IC) and long chain PFAS from impinger samples were measured using Ultrahigh-Performance Liquid Chromatography coupled to tandem Mass Spectrometry (UPLC-MS/MS). HF was also measured at the post-combustion zone location using TDL spectroscopy.

Appendix 1 presents a list of long-chain PFAS measured in this study.

Table 2. Analytes and reporting limits

Analyte	LOQ
Volatile C1-C4 Compounds	5-30 ug/m^3
(CF4, CHF3, C2F6, C2HF5, CF2=CF-CF3, cy-C4F8)	
Adsorbable Organic Fluorine	2 ug/L
Inorganic Fluorine	0.1 ug/L
Trifluoroacetic Acid	0.02 ug/L
PFAS (see Appendix for list of compounds measured)	0.02 ug/L

Note: LOQ for AOF, Inorganic fluorine, TFA, and PFAS are for aqueous samples.

Experimental Results

Fluorine Recoveries

Fluorine recoveries ranged from 69 to 84% using the TDL (at sample location 2). The variability in these data from run to run was low. In contrast, the impinger data analyzed at the same sample location showed about 10 to 20% lower fluorine recoveries. The data are summarized in Table 3. The TDL data provide strong evidence for complete mineralization of fluoropolymer feed mixture.

Table 3: Fluorine Recovery (TDL Measurement)

Run	Settings	HF (TDL)	volume flow @standard wet conditions	volume flow @270 °C	Fluorine	Fluorine Recovery
		mg/m_B^3 wet Gas	[m_N^3/h]	[m_B^3/h]	g/h	%
2	860°C, > 2s, oil + nat. gas + wood chips + 230 g/h F	23.50	3,956	7,866	175.64	76%
		23.93	3,952	7,859	178.62	78%
		25.80	3,943	7,841	192.16	84%
5	1100°C, > 2s, oil + nat. gas + wood chips + 230 g/h F	25.44	3,299	6,560	158.53	69%
		26.58	3,231	6,424	162.23	71%
		26.93	3,217	6,397	163.64	71%

Long-chain PFAS

A large majority of the PFAS measured in impinger samples were near or below reporting limits (>98% of data collected at 860°C and >96% of data collected at 1100°C). Table 3 presents PFAS data for 4 compounds where measurements exceeded reporting limits in several cases. Of particular note is a HFPO-DA measurement which exceeded reporting limits by a factor of 47. Maximum PFBA, PFBS, and 6:2 FTS measurements exceeded reporting limits by much lower factors, ranging from 9 – 12.

These data was re-analyzed to assess the veracity of data. The results are also presented in Table 4. The results indicate that the high measurement values for HPFO-DA could not be reproduced. The results for PFBA and PFBS were also lower when re-analyzed. The lack of reproducibility of data and the lower

measurement values upon re-analysis suggests that cross-contamination is a possible reason for high measurement values for HPDO-DA, PFBA, and PFBS in the initial analysis.

PFAS analyses of wastewater and ash residue samples indicated a large majority of the samples were below reporting limits. One notable exception was a deslagger water bath sample where HFPO-DA was a factor of 16 above the report limit.

Table 4. PFAS Analysis of Impinger Samples

Initial Analysis

PFAS Compound	RL (ng/m^3)	# > RL	ng/m^3 (max)
PFBA	2.8	5	35.8
PFBS	1.4	22	19.5
6:2 FTS	1.4	17	12.5
HFPO-DA	1.4	31	66.3

Re-Analysis

PFAS Compound	RL (ng/m^3)	# > RL	ng/m^3 (max)
PFBA	2.8	0	2.8
PFBS	1.4	7	10.7
6:2 FTS	1.4	11	16.2
HFPO-DA	1.4	16	25.2

Note: For each data set, the total number of measurements equal 54: 27 for each combustion condition.

Short-chain PFAS

TFA was non-detect for all 76 impinger samples analyzed, at a reporting limit of 14 $\mu g/m^3$ (ppb).

Volatile Fluorocarbons (FC)

Tetrafluoromethane (CF_4) was the only volatile FC detected in the GC-MS analysis. Values of CF_4 at stack were near detection limits (20-27 $\mu g/m^3$) and detected in 2 of 14 samples. The results are considered questionable because CF_4 was only detected in one post-combustion sample. There is no plausible reason for larger CF_4 values downstream of the combustion unit unless a non-combustion source is considered.

Discussions

There is one prior published pilot-scale study of the combustion of PTFE (Aleksandrov et al. 2019). Combustion tests were performed at two conditions: 870°C and 4 s residence time and 1020°C and 2.7 s residence time and wood chips were used as the supplemental fuel. The prior study burned 0.3 wt % PTFE. Sampling was performed at a single location, downstream of the waste heat boiler. Thirty-one PFAS compounds were sampled and analyzed (see Table 1 of Aleksandrov et al. for a list of PFAS measured).

Fluorine recoveries were determined indirectly via IR water vapor measurements. The fluorine recoveries ranged from 56 to 78%, with three of the four tests yielding recoveries less than 70%. Eleven PFAS compounds were detected from the combustion and/or control samples and each at a level above 100 ng/m^3 in at least one sample. PFOA was detected in all but one sample and at values as high as 2.7 $\mu g/m^3$ (see Table 3 of Aleksandrov et al.).

The current study differs from the prior test in two important ways. The fluorine recoveries in this study were determined from direct spectroscopic measurements and were above 70% in five of the six tests. Secondly, PFAS reporting limits were on the order of 1 ng/m^3 or less and a large majority of samples (>98%) were at or below reporting limits. The current study provides strong evidence that incinerating a mixture of fluoropolymers under representative municipal waste combustion conditions leads to complete mineralization of the C-F bonds, no significant emissions of long-chain PFAS, and no significant emissions of TFA or light fluorocarbons such as CF_4 or C_2F_6. The prior study did not provide evidence that the PFAS detected were from sources other than the combustion of PTFE.

Conclusions

The study clearly demonstrated that fluoropolymers are converted to inorganic fluorides and carbon dioxide. The inorganic fluorides detected were hydrogen fluoride. A large majority of samples indicated that long-chain PFAS were below levels of 1 ng/m^3 (> 99% of samples associated with 860°C condition and > 98% of samples associated with 1100°C condition). There were no short chain PFAS detected post incineration. TFA was non-detectable in all samples with a reporting limit of 14 $\mu g/m^3$. **The results confirm that fluoropolymers at their end of life when incinerated under representative European municipal incinerators conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment.**

The main reason to include fluoropolymers in the EU PFAS restriction proposal was persistence (resistance to degradation in the environment) in the environment. The absence of organic fluorides and more specifically PFAS in tests representative of municipal waste incineration confirms complete mineralization of fluoropolymers and provides critical data in support for exempting Fluoropolymers from the EU REACH PFAS restriction proposal.

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Appendices

1. List of long-chain PFAS analytes analyzed in this study

Common Name[a]	Abbreviated Name	CAS[b] Registry Number	Isotopic Pre-Extraction Pair
Perfluoroalkylcarboxylic acids (PFCAs)			
Perfluorobutanoic acid[1,3,4]	PFBA	375-22-4	$^{13}C_4$-PFBA
Perfluoropentanoic acid[1,3,4]	PFPeA	2706-90-3	$^{13}C_5$-PFPeA
Perfluorohexanoic acid[1,2,3,4]	PFHxA	307-24-4	$^{13}C_2$-PFHxA
Perfluoroheptanoic acid[1,2,3,4]	PFHpA	375-85-9	$^{13}C_4$-PFHpA
Perfluorooctanoic acid[1,2,3,4]	PFOA	335-67-1	$^{13}C_4$-PFOA
Perfluorononanoic acid[1,2,3,4]	PFNA	375-95-1	$^{13}C_5$-PFNA
Perfluorodecanoic acid[1,2,3,4]	PFDA	335-76-2	$^{13}C_2$-PFDA
Perfluoroundecanoic acid[1,2,3,4]	PFUnDA	2058-94-8	$^{13}C_2$-PFUndA
Perfluorododecanoic acid[1,2,3,4]	PFDoA	307-55-1	$^{13}C_2$-PFDoA
Perfluorotridecanoic acid[2,3,4]	PFTrDA	72629-94-8	$^{13}C_2$-PFDoA
Perfluorotetradecanoic acid[2,3,4]	PFTeDA	376-06-7	$^{13}C_2$-PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	$^{13}C_2$-PFHxDA
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	$^{13}C_2$-PFDoA
Perfluorinated sulfonic acids (PFSAs)			
Perfluoro-1-butanesulfonic acid[1,2,3,4]	PFBS	375-73-5	$^{13}C_3$- PFBS
Perfluoro-1-pentanesulfonic acid[1,3]	PFPeS	2706-91-4	$^{13}C_3$-PFHxS Or $^{13}C_3$-PFBS
Perfluoro-1 -hexanesulfonic acid[1,2,3,4]	PFHxS	355-46-4	$^{18}O_2$-PFHxS or $^{13}C_3$-PFHxS
Perfluoro-1-heptanesulfonic acid[1,3]	PFHpS	375-92-8	$^{13}C_4$-PFHpA
Perfluoro-1-octanesulfonic acid[1,2,3,4]	PFOS	1763-23-1	$^{13}C_4$-PFOS
Perfluoro-1-nonanesulfonic acid[3]	PFNS	68259-12-1	$^{13}C_4$-PFOS
Perfluoro-1-decanesulfonic acid[3]	PFDS	335-77-3	$^{13}C_4$-PFOS
Perfluorododecane sulfonate	PFDoS	79780-39-5	$^{13}C_4$-PFOS
Perfluorinated sulfonamides (FOSAs)			
Perfluoro-1-octanesulfonamide[3,5]	FOSA	754-91-6	$^{13}C_8$-FOSA
N-Methylperfluorooctanesulfonamide [5]	MeFOSA	31506-32-8	d3-MeFOSA
N-ethylperfluorooctanesulfonamide [5]	EtFOSA	4151-50-2	d5-EtFOSA
Perfluorinated sulfonamidoacetic acids (FOSAAs)			
N-methyl perfluorooctanesulfonamidoacetic acid[2,3]	MeFOSAA	2355-31-9	d3-MeFOSAA
N-ethyl perfluorooctanesulfonamidoacetic acid[2,3]	EtFOSAA	2991-50-6	d5-EtFOSAA
Fluorotelomer sulfonates (FTS)			
1H,1H,2H,2H-Perfluorohexane sulfonic acid[1,3]	4:2 FTS	757124-72-4	M2-4:2 FTS
1H,1H,2H,2H -Perfluorooctane sulfonic acid[1,3]	6:2 FTS	27619-97-2	M2-6:2 FTS
1H,1H,2H,2H -Perfluorodecane sulfonic acid[1,3]	8:2 FTS	39108-34-4	M2-8:2 FTS
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2 FTS	120226-60-0	M2-10:2 FTS
Fluorinated Replacement Chemicals			
4,8-Dioxa-3H-perfluorononanoic acid	ADONA[1]	919005-14-4	$^{13}C_4$-PFOS
Hexafluoropropylene Oxide Dimer Acid	HFPO-DA (GenX)[1]	13252-13-6	$^{13}C_3$-HFPO-DA
Additional Targets			
Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate)[4]	PFecHS	67584-42-3	$^{18}O_2$-PFHxS

Fluorinated Replacement Chemicals			
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS (F-53B Major)[1]	756426-58-1	$^{13}C_4$-PFOS
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid OR 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate[a]	11Cl-PF3OUdS (F-53B Minor)[1]	763051-92-9 83329-89-9	$^{13}C_4$-PFOS

Perfluorinated sulfonamide ethanols (FOSEs)			
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol[5]	N-MeFOSE	24448-09-7	d7-N-MeFOSE
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol[5]	N-EtFOSE	1691-99-2	d9-N-EtFOSE
Additional Targets			
Nonafluoro-3,6-dioxaheptanoic acid[1,5]	NFDHA	151772-58-6	$^{13}C_5$-PFHxA
Perfluoro(2-ethoxyethane)sulfonic acid[1,5]	PFEESA	113507-82-7	$^{13}C_3$-PFBS
Sodium perfluoro-1-dodecanesulfonate[5]	PFDoS	1260224-54-1	$^{13}C_4$-PFOS
Perfluoro-4-methoxybutanoic acid[1,5]	PFMBA	863090-89-5	$^{13}C_5$-PFPeA
Perfluoro-3-methoxypropanoic acid[1,5]	PFMPA	377-73-1	$^{13}C_4$-PFBA
3:3 Fluorotelomer carboxylic acid[5]	3:3 FTCA	356-02-5	$^{13}C_2$-FHEA
5:3 Fluorotelomer carboxylic acid[5]	5:3 FTCA	914637-49-3	$^{13}C_2$-FHEA
7:3 Fluorotelomer carboxylic acid or 3-perfluoropheptyl propanoic acid[4, 5]	7:3 FTCA or FHpPA	812-70-4	$^{13}C_2$-FOEA
2H-perfluoro-2-decenoic acid[4]	8:2 FTUCA or FOUEA	70887-84-2	$^{13}C_2$-FOUEA
2-perfluorodecyl ethanoic acid[4]	10:2 FDEA	53826-13-4	$^{13}C_2$-FDEA
2-perfluorooctyl ethanoic acid[4]	8:2 FTA or FOEA	27854-31-5	$^{13}C_2$-FOEA
2H-perfluoro-2-octenoic acid[4]	6:2 FHUEA	70887-88-6	$^{13}C_2$-FHUEA
2-perfluorohexyl ethanoic acid[4]	6:2FTCA or 6:2 FHEA	53826-12-3	$^{13}C_2$-FHEA

SUMMARY OF THE PTFE STUDIES PERFORMED WITH INDEPENDENT LABORATORIES TO INVESTIGATE PERSISTENCE, DEGRADATION, TRANSFORMATION TO OR RELEASE OF SUBSTANCES OF CONCERN

Background

Polytetrafluoroethylene, PTFE (CAS no. 9002-84-0) is a polymer of tetrafluoroethylene. PTFE comes in three forms: granular (the highest volume used globally; made without polymerization aids), aqueous dispersion (made with polymerization aids), fine powder (per ASTM D4895; made with polymerization aids). There are many textbooks and peer-reviewed publications on the properties of PTFE and how to manufacture and process it.

The form of PTFE used in W. L. Gore & Associates products is fine powder PTFE meeting the ASTM D4895-18 standard and the OECD criteria for Polymer of Low Concern. The ASTM standard covers dry-powder resins of PTFE produced from aqueous dispersion. The specification states that the resin shall be uniform and shall contain no additives or foreign material and that the color shall be natural white. The specification does not include mixtures of PTFE with additives such as colors, fillers, or plasticizers, reprocessed or reground resin or any fabricated articles because the properties of such materials have been irreversibly changed when they were fibrillated or sintered. 100% of the PTFE used by Gore meets this ASTM 4895 standard. This is critical to point out because it limits the substances that may leach from the polymer into the environment or living organisms.

Given the extreme durability/persistence of PTFE and interest in what, if anything leaches from the fluoropolymer into biota or the environment, this body of work was undertaken with independent contract laboratories to investigate degradation, release or transformation and leachability of substances of concern into media that may be potential routes of exposure: air, water, and soil. The following studies were performed at the Charles River Labs in Den Bosch, the Netherlands. Standard OECD (and US EPA) efate protocols were used. Studies were performed under Good Laboratory Practices. They were performed to investigate if persistence implies future degradation, release, or transformation into a continuous source of substances of concern. The plan to conduct these studies as well as the results have been shared at scientific meetings including SETAC (NA and EU), FLUOROS Global 2021, and Emerging Contaminants.

Studies to Address Potential Partitioning to Water

OED 105 Water Solubility

Soluble substances may contaminate drinking, surface and ground water and move with the water. Results of this study were that PTFE was insoluble in water.

Ready Biodegradation OECD 301B

This is a biotic stability test which looks for biodegradability within 28 days. PTFE was determined not to be biodegradable.

Inherent Biodegradation OECD 302C

This is a biotic stability test for biodegradability. PTFE was determined not to be biodegradable in this test.

These data confirm the low probability of water exposure to PTFE, degradants or leachables.

Studies to Address Potential Partitioning to Soil

Molecular Weight OECD 118

This test was performed to determine if low molecular weight fractions are available for migration out of the polymer, and, if the polymer is bioavailable.[1] Molecular weights above 1,000 Da do not pass through the cell membrane and are considered not to be bioavailable or, therefore, bioaccumulative. PTFE was determined not to be sufficiently soluble for gel permeation chromatography even after sonication and stirring for 19 hours in tetrahydrofuran, dichloromethane, dimethylformamide, or dimethyacetamide. Using alternative methods of standard specific gravity and melt flow rheology, the molecular weight was determined to be above 500,000 Da.

1. PTFE cannot penetrate a cell membrane via passive or active transport and does not bind or interact with the cell surface because: of its size; the lack of lipid solubility; the lack of oxygen and nitrogen atoms estimating groups accepting hydrogen atoms. PTFE is highly hydrophobic and has little or no hydrogen bond donating potential. PTFE is not structurally similar to steroids, peptides, or other natural compounds which may be exceptions to Lipinski's "Rule of 5". Active transport and cell surface binding/signaling is dependent on shape, volume/size, rotational bonds, etc. and requires interaction with cell surface. (De Mello WC., Ed., Cell-to-Cell Communication, Plenum Press, NY, 1987, p34; Beyer EC, Gap Junctions. Inter. Rev. Cytol. 137, 1993 p2; Molecular Biology of the Cell, 3rd Ed., Alberts B, Bray D, Lewis J et al., Garland Science, NY, 1994, pp 958, 963; Paul Leeson, From Drug discovery: Chemical beauty contest, Nature 481, 455–456, 26 January 2012; Ming-Qiang Zhang and Barrie Wilkinson. Drug discovery beyond the 'rule-of-five'. Current Opinion in Biotechnology 2007, 18:478–488.)

Soil Adsorption OECD 106
This study was performed to determine the likelihood of the substance partitioning to soil and/or to the sediment. Results of this study are still pending.

Phototransformation on Soil Surfaces OECD draft document
This is an abiotic stability test for degradation in sunlight on soil surfaces. Results of this study are still pending.

Based on the high molecular weight, no partitioning to soil is anticipated.

Studies to Address Potential Partitioning to Air

Molecular Weight OECD 118
See above.

Vapor Pressure OECD 104
This study was performed because volatility helps predict the likelihood of partitioning to air and long-range transport potential. The vapor pressure was determined to be very low less than 1 x 10-10 mm Hg @ 20°C.

Melting Temperature OECD 102
Performance of the melting temperature supports thermal stability at environmentally relevant temperatures. The melt transition was around 350°C. No further melting or decomposition occurred at less than 400°C.

Thermal Stability OECD 113
This test is for degradation from heat at environmentally relevant temperatures. No decomposition or chemical reaction was observed at less than 150°C.

Thermal Gravimetric Analysis
This is a method of thermal analysis where mass is measured over time as the temperature changes and mass is lost to the air. No observable weight loss below 549°C, however at 549°C a 5% weight loss was observed.

This data supports the lack of inhalation exposure potential at environmentally relevant temperatures.

Leaching Potential

Because there were no OECD guidelines specifically addressing the potential of a polymer to leach substances under environmental conditions, a first tier leaching potential test, Toxicity Characteristic Leaching Potential (US EPA SW-846 Test Method 1311), was performed by ALS Laboratories in Kelso, Washington (USA). This test has historically been used by EPA to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. This TCLP test generates a leachate in a lab setting designed to simulate landfill conditions to evaluate potential environmental impact from uncontrolled land disposal.

Tier 1: Toxicity Characteristic Leaching Potential EPA SW-846 Test Method 1311
100 grams of each of two PTFE fine powder samples were tumbled, in 5.7 ml of glacial acetic acid per 1 liter of reagent water, at room temperature for 18-20 hours at 30 rpm, before being filtered using a borosilicate glass fiber filter with a 0.6 to 0.8 µm pore size. 100 ml of the extraction fluid was then extracted in 60 ml of dichloromethane for approximately 3 hours at room temperature. The extracts were analyzed by GC/MS for this list of EPA analytes. The TCLP test was passed.

Conclusions from the Charles River Laboratory and ALS study

These results support the stability of PTFE and lack of transformation to other PFAS, such as perfluoroalkyl acids. PTFE will not partition to air, water, or soil. Potential inhalation, oral or dermal exposure to PTFE for biota or the environment is unlikely based on this data.

Dr. Barbara Henry
January 2022

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FIGURE 1 100-foot diameter shop fabricated PTFE secondary containment liner ready for final QC and packaging.



Contamination from a leaking geomembrane—A necessary and imminent evil?

Using an inert geomembrane solution with 100% PTFE material is one possibility.

By John Tippett, P.E., and Michael Goard, P.Eng.

One major purpose of a geomembrane in many lining applications around the world is to prevent the contamination of groundwater (water below the ground that can affect rivers, lakes, oceans and drinking water sources) by the chemicals contained above the geomembrane. Geomembranes have other purposes, but maintaining clean and healthy drinking water is likely the most important one.

For many geomembrane materials, a 10- or 20-year warranty is typical. With the concept of long-term sustainability being ever-present in every facet of life and industry, can owners and operators realistically afford to think in terms of geomembrane barriers that will degrade and leak due to corrosion? Should a geomembrane be considered "successful" if contamination of groundwater occurs after the warranty period?

Recent evolution within the last decade of material science allows us to consider inert geomembrane materials. An inert geomembrane material is a barrier that is unaffected by any chemical, regardless of time. By using an inert geomembrane material, "lifetime" containment and indefinite protection of groundwater can be considered a realistic target. Certainly, if the bar is set higher and the overall target to prevent contamination is "lifetime" containment rather than "warranty-life" containment, the higher expectation will ultimately result in a cleaner world.

The corrosion variable

In any containment application using a polymeric geomembrane liner, numerous variables present design challenges. The recent paper "Protecting the Environment from Contamination with Barrier Systems: Advances and Challenges" (Rowe, Jefferis, et al. 2022) highlights the complexities involved in the design of containment systems and the selection of a liner material. Tensile/tear/puncture/burst strength, temperature

PROJECT HIGHLIGHTS

400 DEGREES "HOT TANK" ABOVE GROUND STORAGE TANK SECONDARY CONTAINMENT

OWNER
Refinery in Canada

LOCATION
Alberta, Canada

CONTRACTOR
Terrafix Geosynthetics Inc.

CONSTRUCTION COMPANY
Cyntech Construction

ENGINEERS
Cyntech Construction

GEO PRODUCT
Everliner 2130

GEO MANUFACTURER
Textiles Coated International (TCI)

John Tippett, P.E. holds a degree in chemical engineering from Dartmouth College and is CEO of Textiles Coated International (TCI), a world leading manufacturer of fluoropolymer films and related products based in Manchester, N.H.

Michael Goard, P.Eng. holds a degree in civil engineering from McGill University and is a product manager who has worked in the manufacturing of industrial products and materials for over 25 years. He is based near Montreal, Quebec, Canada.

resistance, thermal stability characteristics, chemical resistance, UV resistance, seam strength, permeability, coefficient of friction and many other properties may need to be taken into consideration. This article explores how this task can be simplified by removing one of the most important and potentially less predictable variables: corrosion.

John Scheirs' 2020 webinar and document on the "Periodic Table of Geomembranes" illustrates the wide range of available materials to select from. Each has its advantages and disadvantages, but each also has some susceptibility to corrosion—except one category.

Many geomembrane materials contain additives that help provide or enhance needed properties like UV protection and crack resistance. While the base material may be suitable for the foreseen conditions, these antioxidants/plasticizers/stabilizers can be subject to chemical attack or degradation.

Inert liners eliminate the corrosion variable

Different geomembrane materials can be selected to guard against corrosion, depending on the expected chemical exposure. During the early design phase, it is critical to know what chemicals the liner will be expected to be exposed to and therefore to resist. A material selection can then be made, and clear instructions/directives for its use can be established and provided to the user. During the entire life of the liner, it is then critical to ensure that only the chemicals the liner was designed to contain are what the liner ends up being exposed to. While every attempt can be made to predict what will be put into a landfill or containment area, there is always a risk that something unforeseen may be introduced.

There are situations when exposure to certain amounts of a particular chemical is expected. One such challenging industrial process, the Bayer Process for manufacturing alumina (and ultimately aluminum metal), results in bauxite residue with an average pH of 11 (pH range of 9–13). With such severe alkaline exposure, an inert liner is a necessity to avoid long-term contamination. Clearly, this is an industrial case where a typical high-density polyethylene (HDPE) liner will not be a long-term barrier to leakage due to corrosion.

There are also unexpected results that can lead to entirely unpredicted concentrations of chemicals. Most, if not all, geomembrane applications are susceptible to combinations of chemistry, temperature and/or moisture. Chemistry can change over time as the contained materials decompose and mix with each other. As the biodegradation takes place, heat may result, thus hastening the degradation of a geomembrane. As moisture gets introduced, new chemicals may result from the new molecules that have formed as the result of biodegradation. Geomembrane materials with an inability to handle the full pH range of 0–14 are ill-equipped to survive a witch's brew scenario in a challenging landfill with many variables.

There are many items considered household hazardous waste (HHW) that are not permitted in landfills. These include paints, solvents, bleach, batteries, household cleaners, glue and adhesives, electronics, oil mixtures, etc. Many of the HHW items are extreme pH products that are incompatible with geomembrane materials. Given the extensive list of HHW products used in the typical household, it is not hard to conceive that even households with the best intentions put extreme pH products into their garbage.

Should the world rely upon perfect behavior of household and business disposal practices or is it safer to assume bad behavior and noncompliance? From a long-term safety perspective, assuming good behavior over bad behavior results in failure. Systems must be designed around bad behavior to provide an indefinite safety sustainability. The same is true for geomembrane systems. The geomembrane material should be

compatible to the full pH range of 0–14 in case bad behavior persists, and extreme pH products enter landfills.

Inert liners are made from materials that will not corrode regardless of the chemical exposure. PTFE is an example of an inert material. PTFE will not corrode when exposed to virtually any known chemical, and it is compatible to the full pH range of 0–14. Selecting such an inert material simply removes one of the most critical variables, corrosion, from the equation. The consideration of compatibility to chemicals for PTFE is an easy one, as the table below reflects.

Reduce the number of different materials—additives and reinforcements

Many geomembrane materials contain additives that help provide or enhance needed properties like UV protection and crack resistance. While the base material may be suitable for the foreseen conditions, these antioxidants/plasticizers/stabilizers can be subject to chemical attack or degradation, thereby leading to losses in the desired properties over time. In some cases, these additives may migrate to the surface of the material and become a contaminant.

This is another aspect that introduces a variable into the effective life span of a liner. How long will the additive remain functional? If both the geomembrane base material and the additives sustaining the life of the geomembrane are not fully inert materials, two corrosion variables must be considered instead of one.

One plus one does not equal two when combining an inert material with a chemically susceptible material.



FIGURE 2 Shop fabricated PTFE liner accordion folded and ready for shipment and rapid deployment at site.

CHEMICAL	PVC-EIA	HDPE	PVDF	PTFE
Acetic acid (50%)	Chemically attacked	Chemically resistant	Chemically resistant	Chemically resistant
Acetone	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Ammonium hydroxide	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Benzene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Diesel	Chemically resistant	Chemically attacked	Chemically resistant	Chemically resistant
Ethyl acetate	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Furfural	Chemically attacked	Chemically resistant	Chemically resistant	Chemically resistant
Gasoline	Chemically resistant	Chemically attacked	Chemically resistant	Chemically resistant
Methyl ethyl ketone	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Methyl isoamyl ketone	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Nitric acid (50%)	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Perchloroethylene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Phenol	Chemically attacked	Chemically resistant	Chemically resistant	Chemically resistant
Sulphuric acid	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Toluene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Xylene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant

TABLE 1

Consistent with ordinary geomembrane installation, the geosynthetic instal… established … target seam… temperature, …peed and pressure appropriate for the geomembrane material and ambient weather conditions.

NEW PQ

Until recently, the only way to realistically employ a fluoropolymer like PTFE, with its extreme corrosion resistance and high temperature capability, was by using it in combination with other materials that compensate for certain properties, like strength.

Supported geomembrane materials may have improved tensile strength, owing to a reinforcement (scrim) that is incorporated into the material. In applications where high strength is paramount, this reinforcement can give the material the necessary property. A weakness of scrim-reinforced material can occur if the scrim becomes subject to degradation due to corrosion. While the scrim is intact, it gives the material the strength it is intended to provide. However, the scrim can be chemically attacked at discontinuities such as seams. At every seam, there is a likely interruption in the protection of the scrim by the base material. Exposure to corrosive chemicals at the exposed edges will lead to corrosion of the reinforcement and loss of the property it is there to provide—strength.

A general way of thinking about it is that if all the strength of a material comes from a component that can be chemically degraded in time, then the geomembrane will have a regression of strength over the years that eventually leads to failure/leakage. The strength of the liner must come from inert material that will not weaken over time due to chemical exposure. Using a material that never weakens from chemical exposure eliminates the corrosion variable and prevents the strength of the geomembrane from regressing toward zero, which may result in leakage.

By combining an inert material with a chemically susceptible material, chemical attack can still occur. The corrosion variable must still be considered. But by simply using an inert material, chemical attack cannot happen. The corrosion variable no longer needs to be considered. Further, by joining or seaming one inert material with another, the concern for edge exposure at a seam is eliminated. This is also true for repairs or patches that may be required on-site if damage occurs.

100% PTFE—Nothing else

One possibility for an inert geomembrane solution is a 100% PTFE material. PTFE is one of the family of fluoropolymers, well known in many industrial applications for their amazing chemical resistance and high temperature properties. Because the geomembrane is inert across the pH scale of 0–14, the corrosion variable is eliminated with PTFE. Even with long-term severe chemical exposure, the properties of PTFEs will not change.

In addition, the temperature range of PTFE of -400°F to 600°F (-240°C to 316°C) eliminates concern for geomembrane failure due to significant excursion temperature situations. Even the biodegradation temperature of 149°F (65°C), which can often be found in a landfill, does not get anywhere near the maximum temperature capability of an all-PTFE material.

Ultraviolet exposure is also a major cause of destruction of geomembranes. An inert liner will be one that is unaffected by severe and continuous exposure to sunlight.

Equal or better in terms of other properties

Testing done by ExcelPlas Polymer Testing demonstrates that multilayer, laminated PTFE has:

- Better/comparable tear strength to that of HDPE
- Significantly better puncture resistance than HDPE

- Significantly better flex fatigue resistance than HDPE and linear low-density polyethylene (LLDPE)

For any application where the tear, puncture and flex fatigue characteristics of HDPE meet the requirements, one can be confident that PTFE will meet them as well. See **Table 2**.

Fatigue Resistance per AS 4878.9–2001 Results Summary	
SAMPLE ID	**CYCLES UNTIL FAILURE**
Cross-laminated PTFE 1.5mm	5,390,648 (No Failure Observed)
HDPE 1.5mm	105,366

Excelplas Polymer Analysis

TABLE 2

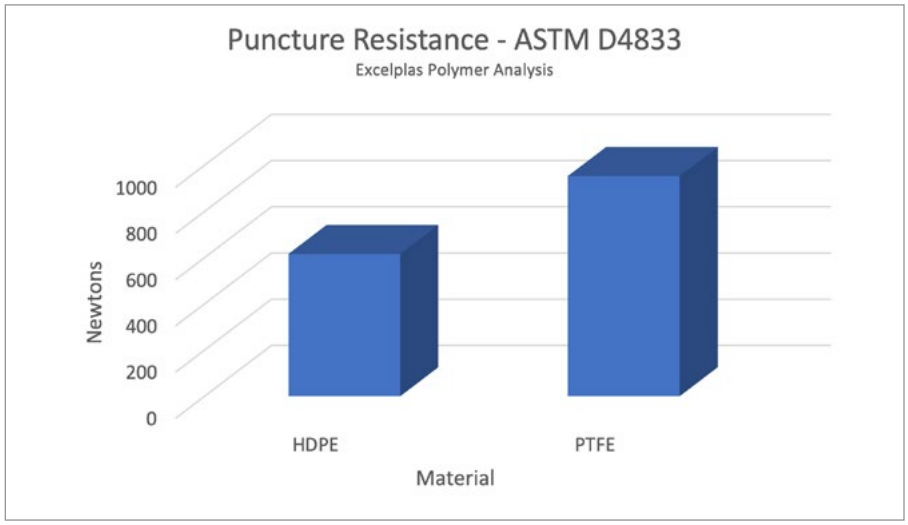


FIGURE 3

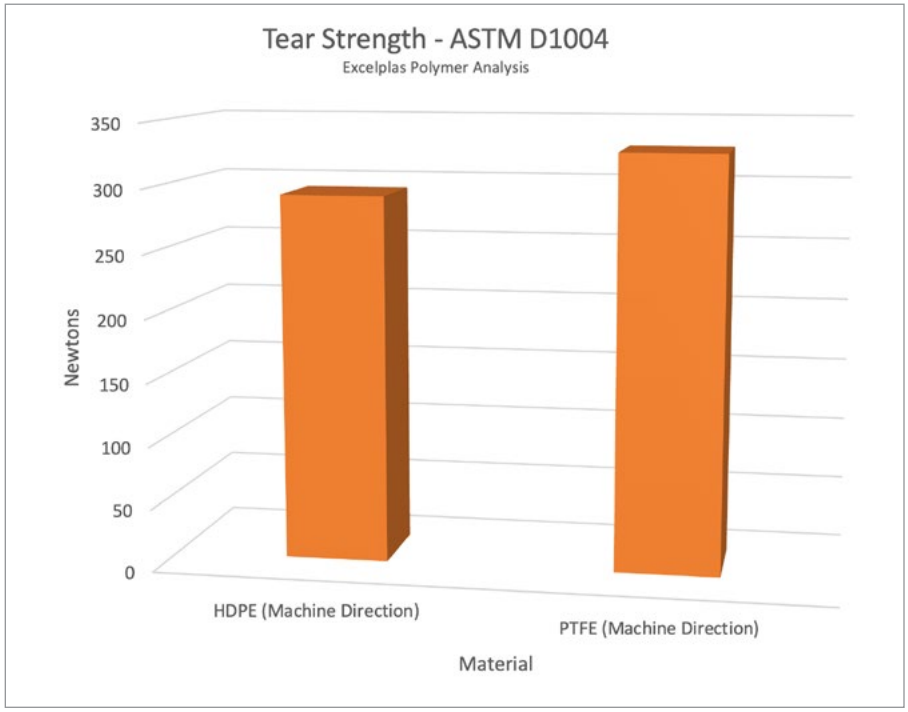


FIGURE 4

Conclusion

Contamination of rivers, lakes, oceans and drinking water sources should not occur in the future due to corrosion of geomembranes. The job of installing a geomembrane system without leaks is a challenging one with many design considerations.

Furthermore, the absence of the corrosion variable sets the bar much higher for the geomembrane industry. Instead of discussing a potential life for a geomembrane in terms of years or decades, the industry can start focusing on design consideration to achieve "forever" containment using inert materials. In the past, "forever" could not be a realistic target when using materials susceptible to corrosion. But the use of inert materials eliminates corrosion and makes "forever" a realistic target; certainly, rivers, lakes, oceans, drinking water sources and future generations deserve this inspirational target.

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UPDATE

Developments in Fluoropolymer Manufacturing Technology to Remove Intentional Use of PFAS as Polymerization Aids

Bruno Ameduri, Jaime Sales and Michael Schlipf*

Fluoropolymers are heavily impacted by the restriction proposal on per- and polyfluoroalkyl substances (PFAS) that has been recently published under the EU REACH Regulation.[1] While matching the definition of PFAS due to their chemical composition and structure, fluoropolymers are significantly different from other substances in the PFAS family. The only substantial reason for concern associated to fluoropolymers is the use of non-polymeric PFAS as polymerization aids during the manufacturing process. In the past, environmental pollution caused by PFOA and PFOS, which are prominent non-polymer substances in the PFAS family, has attracted regulatory attention. PFOS has been restricted and PFOA has been banned under the EU Regulation on Persistent Organic Pollutants. This article highlights the progress that industry has made over the last years in relation to control of PFAS emissions due to their use in fluoropolymer production. Such a progress is based on the improvement of abatement techniques, but more importantly, on the removal of PFAS polymerization aids, introducing alternative technologies that do not require using such chemicals. It is expected that most of the fluoropolymer production will be developed completely free from PFAS polymerization aids in a relatively short time frame. Thus, it appears reasonable to claim that fluoropolymers that are manufactured without the use of PFAS polymerization aids should be exempted from any regulatory initiative, and that their uses should be allowed without any unjustified restriction.

I. Introduction

The PFAS family of chemicals is currently under strong regulatory scrutiny globally. Some of the substances covered by this group are known for being highly harmful to the environment and human health, due to their persistency, bioaccumulation/mobility and other toxic effects. However, the broad definition that is frequently used to describe PFAS, which was not originally introduced to be used for regulatory purposes[2], results in a very large number of substances covered jointly in this family of chemicals, more than 4,700 according to the OECD[3] as being present on the global market. There have been significant efforts to group and classify the different substances that can be regarded as meeting the definition of PFAS (Figure 1). One such group is that of fluoropolymers.[4]

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1 ECHA, 'Registry of restriction intentions until outcome - Per- and polyfluoroalkyl substances (PFAS)' (2023).

2 J K Anderson, R W Brecher, I T Cousins, J DeWitt, H Fiedler, K Kannan, C R Kirman, J Lipscomb, B Priestly, R Schoeny, J Seed, M Verner, S M Hays, 'Grouping of PFAS for human health risk assessment: Findings from an independent panel of experts' (2022) Regulatory Toxicology and Phamacology, 134.

3 OECD, 'Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs)' (2018) Series on Risk Management No. 39. Organisation for Economic Co-operation and Development.

4 Bruno Ameduri, 'Fluoropolymers: A special class of per- and polfluoroyalkyl substances (PFASs) essential for our daily life' (2023) Journal of Fluorine Chemistry 267, 110117.

One of the key features of fluoropolymers is that they fulfil the conditions set out by the OECD to meet the definition of Polymers of Low Concern (PLC). This has been demonstrated for the vast majority of these substances, accounting for >96% of global production.[5] This means that fluoropolymers are not toxic, mobile or bioaccumulative. While they are persistent, the lack of degradability during normal conditions of use and at end of life makes fluoropolymers completely inert and not hazardous to human health and the environment.

Due to their intrinsic nature based on the carbon-fluorine bond, fluoropolymers offer a combination of various properties of interest that render them highly valuable products in different industrial sectors such as renewable energy, in applications such as back sheets for photovoltaic panels and lubricants in wind turbines, binders and separators for lithium-ion batteries and proton exchange membranes and frame gaskets for hydrogen production and fuel cells. Fluoropolymers are also valuable in industries such as semiconductors, food and water processing, automotive, aerospace, chemical processing, electrical, electronics, and construction. It is to be noted that the broad applications of fluoropolymers, which are virtually irreplaceable in critical industrial sectors needed by modern society is not in scope of this paper, and significant information on this can be found in literature.[6]

II. Historical Concerns Related to Manufacture of Fluoropolymers

The manufacture of fluoropolymers has been flagged by researchers as a source of environmental damage in different locations in Europe (Italy, France, the Netherlands), the USA and China.[7] However, it needs to be stressed that this concern is not related to the fluoropolymers as individual substances, but to the use of non-polymeric PFAS that have been frequently used as polymerization aids. These Fluorinated Polymerization Aids (FPAs), also referred to as surfactants, facilitate the development and completion of the polymerization reaction. In the past, this use has led to specific situations of uncontrolled emissions of these surfactants, which are known to pose an environmental hazard.[8]

In terms of global production, fluoropolymers represent a very small share compared to the total amount of plastics, with estimated 320,000 tonnes of fluoropolymers in 2019[9] in front of 460 million tonnes of total plastics.[10] It is estimated that only 50% of fluoropolymer production requires the use of FPAs, based on standard manufacturing practices by industry to this date;[11] while manufacture of fluoropolymers via suspension process normally does not require the use of surfactants, these have traditionally been required to achieve high molecular weight polymer emulsions.[12]

5 Barbara J Henry, Joseph P Carlin, Jon A Hammerschmidt, Robert C Buck, L William Buxton, Heidelore Fiedler, Jennifer Seed and Oscar Hernandez, 'A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers' (2022) 14 Integrated Environmental Assessment and Management 13, 316–334; Stephen H. Korzeniowski, Robert C. Buck, Robin M. Newkold, Ahmed El kassmi, Evan Laganis, Yasuhiko Matsuoka, Bertrand Dinelli, Severine Beauchet, Frank Adamsky, Karl Weilandt, Vijay Kumar Soni, Deepak Kapoor, Priyanga Gunasekar, Marco Malvasi, Giulio Brinati, Stefana Musio, 'A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers' (2022) Integrated Environmental Assessment and Management.

6 Bruno Ameduri and Sergey Fomin, *Fascinating Fluoropolymers and Applications* (Elsevier, 2020); Bruno Ameduri, 'The Promising Future of Fluoropolymers' (2020) Macromol Chem Phys 221, 1900573; Bruno Ameduri, *Issues, Challenges, Regulations and Applications of Perfluoroalkyl Substances* (Oxford University Press, 2022).

7 Wouter A Gebbink, Laura van Asseldonk and Stefan P J van Leeuwen, 'Presence of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in River and Drinking Water near a Fluorochemical Production Plant in the Netherlands' (2017) 51 Environ Sci Technol 19, 11057–11065; Rainer Lohmann, Ian T. Cousins, Jamie C. DeWitt, Juliane Glüge, Gretta Goldenman, Dorte Herzke, Andrew B. Lindstrom, Mark F. Miller, Carla A. Ng, Sharyle Patton, Martin Scheringer, Xenia Trier, and Zhanyun Wang, 'Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?' (2022) Environ Sci Technol 54, 12820–12828; Xuan Jia, Hongyan Guan, Zhongbao Guo, Chengjing Qian, Yali Shi and Yaqi Cai, 'Occurrence of Legacy and Emerging Poly- and Perfluoroalkyl Substances in Fluorocarbon Paint and Their Implications for Emissions in China' (2021) 8 Environ Sci Technol Lett 11, 968-974.

8 Rob Bonta, Superior Court of the State of California, County of Alameda 10 November 2022.

9 ETC/WMGE Consortium Partners, 'Fluorinated polymers in a low carbon, circular and toxic-free economy - Technical report' <https://www.eionet.europa.eu/etcs/etc-wmge/products/etc-wmge-reports/fluorinated-polymers-in-a-low-carbon-circular-and-toxic-free-economy> accessed 1 May 2023.

10 OECD, 2022. Plastic pollution is growing relentlessly as waste management and recycling fall short, says OECD. Available at: https://www.oecd.org/environment/plastic-pollution-is-growing-relentlessly-as-waste-management-and-recycling-fall-short.htm. Last access December 2022.

11 Jaime Sales, Francisco Hernández, Deepak Kapoor, Marcel van den Noort, 'Fluoropolymers: The Safe Science That Society Needs' (2022) 5 International Chemical Regulatory and Law Review 1, 13-23.

12 Ebnesajjad, *Fluoroplastics, Volume 1: Non-Melt Processible Fluoropolymers - The Definitive User's Guide and Data Book* (Elsevier, 2014).

Aqueous emulsions are required to produce high performance grades of some fluoropolymers.[13] Surfactants are highly soluble in water, but the final fluoropolymer substances are not; hence after separation, the residual water contains amounts of dissolved surfactant, which may lead to PFAS emissions when FPAs are used.[14]

Another consequence of the use of these surfactants is that sometimes the final fluoropolymer product may carry residuals of such non-polymeric PFAS, which can be also emitted to the environment during the life cycle of fluoropolymers. Again, in this case there is an indirect pollution associated to fluoropolymers, not related to the intrinsic specific properties of these substances.

As a final step in the life cycle of fluoropolymers, disposal and waste treatment has been frequently flagged as a reason for concern of these products. However, recent studies have demonstrated that the waste generation of fluoropolymers is insignificant compared to that of other plastics,[15] and that the most common waste treatment technique for fluoropolymers - incineration - will not result in any PFAS species of concern.[16] In addition to this, fluoropolymers do not degrade during normal use or environmental conditions[17] and do not pose any significant risk if they are landfilled.[18]

In summary, it can be established that the only real source of concern for human health or the environment related to fluoropolymers is the use of PFAS as polymerization aids in the manufacture of these polymers of low concern. Providing efficient solutions that would completely neutralize such concerns would result in completely safe manufacture, use and disposal of fluoropolymers.

III. How to Avoid PFAS Emissions (Polymerization Aids) from the Fluoropolymer Value Chain?

For many years, industry has placed significant efforts to reduce emissions of PFAS from the manufacturing process of fluoropolymers. In order to achieve this goal, there are basically two options available:

1. To improve the abatement techniques and recovery of PFAS surfactants from the manufacture of fluoropolymers.
2. To develop alternative processes that do not require the use of such PFAS polymerization aids for the production of fluoropolymers.

In the case of item 1 above, significant improvements have occurred over the last years that have allowed for reduction of 99% of emissions of fluorinated surfactants since the 1990s.[19] More recent research brings that value as high as 99.99%.[20] Extensive literature exists in relation to control and treatment of emitted PFAS from industrial processes.[21] The strategies of containment involve the recovery, removal, purification, sorption techniques, microbial degradability and recyclability of the polymerization aids

13 Oleg N. Primachenko, Alexey S. Odinoko, Elena A. Marinenko, Yuri V. Kulvelis, Valerij G. Barabanov and Svetlana V. Kononova, 'Influence of sulfonyl fluoride monomers on the mechanism of emulsion copolymerization with the preparation of proton-conducting membrane precursors' (2021) Journal of Fluorine Chemistry 244, 109736.

14 Ebnesajjad, *Fluoroplastics, Volume 1: Non-Melt Processible Fluoropolymers - The Definitive User's Guide and Data Book* (Elsevier, 2014).

15 Conversio, 'Fluoropolymer waste in Europe 2020 – End-of-life (EOL) analysis of fluoropolymer applications, products and associated waste streams' (2022).

16 Krasimir Aleksandrov, Hans-Joachim Gehrmann, Manuela Hauser, Hartmut Mätzing, Daniel Pigeon, Dieter Stapf and Manuela Wexler, 'Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas' (2019) 226 Chemosphere; RIVM, 'Per- and polyfluorinated substances in waste incinerator flue gases. Rijksinstituut voor Volksgezondheid en Milieu' (2021).

17 Danish EPA, 'Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances. The Danish Environment Protection Agency' (2013) LOUS Review, Environmental Project No. 1475, 2013.

18 Stephen H. Korzeniowski, Robert C. Buck, Robin M. Newkold, Ahmed El kassmi, Evan Laganis, Yasuhiko Matsuoka, Bertrand Dinelli, Severine Beauchet, Frank Adamsky, Karl Weilandt, Vijay Kumar Soni, Deepak Kapoor, Priyanga Gunasekar, Marco Malvasi, Giulio Brinati and Stefana Musio, 'A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers' (2022) Integrated Environmental Assessment and Management.

19 Daikin Chemicals, 'Measures concerning environment emission of PFAS' (2022) <https://www.daikinchemicals.com/company/sustainability/pfas.html> accessed 1 May 2023. Chemours, 'Our Commitment to Responsible Chemistry' <https://www.chemours.com/en/corporate-responsibility/sustainability-safety/our-commitment-to-pfas-stewardship> accessed 1 May 2023.

20 Rebecca DiStefano, Tony Feliciano, Richard A. Mimna, Adam M. Redding and John Matthis, 'Thermal destruction of PFAS during full-scale reactivation of PFAS-laden granular activated carbon' (2022) Remediation 32, 231–238.

21 ITRC, 'PFAS Technical and Regulatory Guidance Document and Fact Sheets: 12. Treatment Technologies' (2022) Interstate Technology and Regulatory Council; Jinxia Liu and Sandra Mejia Avendaño, 'Microbial degradation of polyfluoroalkyl chemicals in the environment: A review' (2013) Environment International 61, 98-114.

from off-gases, waste-water streams, aqueous dispersions, and final products. The recovery/recycling techniques of the polymerization aids depend on the final form of the fluoropolymer product: they can be removed when the aqueous emulsion is dried for sale as a solid (in the case of powder), or they can be thermally destroyed at high temperatures during the curing process (in the case of aqueous dispersion). Such techniques, including ion exchange technology for removal of FPAs from aqueous emulsions, have been applied for more than 20 years, and at present time, they are installed in most of the fluoropolymer manufacturing facilities around the world.

However, it needs to be acknowledged that achieving an absolute zero value of emissions in processes where PFAS are used is technically impossible. Frequently industry operates with the concepts of As Low As Reasonably Practicable/Achievable.[22] From that point, developing improved technologies becomes complex and significantly resource intensive for industry. Furthermore, with the development of ever more sophisticated analytical techniques, the possibility that (low) PFAS concentrations in the vicinity of industrial sites where these chemicals are used will be detected will continue to increase as well. This is certainly a positive development, due to the properties of the most dangerous PFAS as persistent, bio-accumulative, mobile and toxic. However, if the goal is to ensure zero emissions, it is highly unlikely that continued improvement of abatement techniques (which is nevertheless a clear necessity) will achieve this target.

Instead, option 2 appears to be the only realistic possibility to ensure that the emission of PFAS surfactants will be completely removed; if no PFAS surfactants are used in the manufacturing process of fluoropolymers, then no emissions will occur. Thus, the use of Non-Fluorinated Polymerization Aids (NFPA) can be considered as the most direct path forward to respond to the societal concern related to PFAS pollution associated to fluoropolymers.

However, it needs to be noted that both options are not mutually exclusive. The switch to fluoropolymer manufacture with the use of NFPA will also require the implementation of the most efficient abatement techniques, such as, use of ion exchange resin,[23] filtration[24] or foam fractionation.[25] This is because the process may still lead to small amounts of residual fluorinated by-products coming from side reactions between chemicals involved, such as monomers or the NFPA. Still, an adequate selection of surfactant and process conditions should allow for a minimisation of fluorinated residuals, particularly if compared to the situation where fluorinated surfactants are used.

Indeed, when comparing manufacturing processes of fluoropolymers that may use either FPAs or NFPAs, the whole life-cycle of all the chemicals involved in the process needs to be taken into account. The use of FPAs requires its manufacture, transport, storage and maintenance (e.g., cleaning) of the equipment used in those processes. All these activities will result in potential PFAS emission sources that have to be added to the possible emissions of the FPA (and residuals) that will be generated during the manufacture of the fluoropolymer. In the case of NFPA technology, only the contribution of residuals from the manufacture of fluoropolymer may contribute to emissions. Again, the fact that today such emissions can be adequately controlled via efficient abatement, e.g., by keeping values of fluorinated residuals well below the 250 ppb limit established in the restriction proposal[26] clearly results in favour of the transition to manufacturing processes of fluoropolymers involving NFPA technology.

An overview on the current situation about implementation of NFPA technology and expected future developments is provided next.

1. State of the Art Related to NFPA Technology for the Manufacture of Fluoropolymers and Path Forward

Over the past years, the fluoropolymer industry has undertaken significant efforts in continued attempts

22 HSE, 'ALARP at a glance. Health and Safety Executive' (2022) <https://www.hse.gov.uk/managing/theory/alarpglance.htm> accessed 1 May 2023.

23 Fuhar Dixit, Rahul Dutta, Benoit Barbeau, Pierre Berube and Madjid Mohseni, 'PFAS removal by ion exchange resins: A review' (2021) Chemosphere, 129777.

24 EPA, 'Reducing PFAS in drinking water with treatment technologies' <https://www.epa.gov/sciencematters/reducing-pfas-drinking-water-treatment-technologies> accessed 1 May 2023.

25 Sanne J. Smith, Karin Wiberg, Philip McCleaf and Lutz Ahrens, 'Pilot-Scale Continuous Foam Fractionation for the Removal of Per- and Polyfluoroalkyl Substances (PFAS) from Landfill Leachate' (2022) ACS EST Water 5, 841–851.

26 ECHA, 'Registry of restriction intentions until outcome - Per- and polyfluoroalkyl substances (PFAS)' (2023) <https://echa.europa.eu/es/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b> accessed 1 May 2023.

to introduce NFPA technologies in the manufacture of fluoropolymers. An overview on patents that have been filed on technology based on non-fluorinated surfactants demonstrates that this is an effort that the whole industry has taken in parallel, and not limited to the initiative of one or a reduced group of suppliers. Several manufacturers of fluoropolymers have filed multiple patents on NFPA technology over the past 2 decades. This explains a high focus and investment in this direction by the industry. Table 1 (Appendix) provides a list of identified patents related to the use of NFPA technologies for the manufacture of fluoropolymers as published over the last years. While this is not an exhaustive list of initiatives in this field, it provides a good description of efforts developed by the whole fluoropolymer industry.

It should be noted that, even if Table 1 lists patents filed in the XXI Century, initiatives to introduce NFPA technology in the manufacture of fluoropolymers have been on-going since the 1960s.[27]

2. Commercialization of NFPA Technology and Successful Market Acceptance

As of today, it is assumed that there are technologies available that allow for the manufacture of more than 80% of fluoropolymer global production in volume without the use of FPAs.[28] This includes 100% of the three main fluoropolymers by volume: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and fluoroelastomers (FKM). While progress on PVDF was achieved around 15 years ago[29], and some grades of PTFE and FKM have been traditionally manufactured without the use of FPAs, success with other PTFE grades (aqueous dispersions and fine powders) and other FKM grades has only been possible in the last months. Progress on smaller volume products such as is poly (TFE-co-perfluoroalkoxyvinylether) copolymers or perfluoro(alkoxyvinylether)s (PFA) have also been recently announced, and it is expected that further developments will be confirmed in the next months that will involve other fluoropolymers.

It needs to be noted that, while such technologies are currently available, it is not expected that all the suppliers will be in a position to integrate them in their manufacturing processes at the same time. This means, for example, that while one supplier may have developed a procedure to manufacture all grades of PTFE without the use of FPAs, this may not yet be feasible today for all the suppliers. While sublicensing of rights to a specific technology is possible, full implementation of these procedures by all the suppliers may take some time.

For many years, the fluoropolymer industry has made efforts to develop alternative technologies that do not require the use of FPAs. However, it is in the recent past when different fluoropolymer manufacturers have increased the announcements of different developments to replace technologies based on FPAs, either by introducing NFPAs, or by turning to completely alternative processes that simply remove the use of surfactants.[30]

In order to be considered as a completely viable option for fluoropolymer manufacture, the alternative processes must lead to the production of grades that are accepted by downstream users in terms of quality and performance. This can be confirmed since thousands of metric tonnes of fluoropolymers manufactured without the use of FPAs have already been introduced on the global market and have been well accepted by customers. In recent years, it was only possible to manufacture those fluoropolymers with FPAs, however this situation has changed following recent developments by industry. Furthermore, these grades have to ensure that any water-soluble fluorinated by-products present in the final product are brought to insignificant levels, which can

27 Hoashi Juzaemon, Stabilized, concentrated polytetrafluoroethylene dispersions containing non-ionic surfactants. U.S. Patent No. 3,301,807. 31 Jan. 1967.

28 Jaime Sales, Francisco Hernández, Deepak Kapoor, Marcel van den Noort, 'Fluoropolymers: The Safe Science That Society Needs' (2022) 5 International Chemical Regulatory and Law Review 1, 13-23.

29 PCI, 'Arkema Eliminates Fluorosurfactants from Kynar 500® PVDF' (2008) <https://www.pcimag.com/articles/88876-arkema-eliminates-fluorosurfactants-from-kynar-500-pvdf> accessed 1 May 2028.

30 Chemours, 'Chemours Announces Process Innovation with New Viton™ Fluoroelastomers Advanced Polymer Architecture (APA) Offering' (2022) <https://www.chemours.com/en/news-media-center/all-news/press-releases/2022/chemours-announces-process-innovation-with-new-viton-fluoroelastomers-advanced-polymer-architecture> accessed 1 May 2022: Solvay, 'Producing new fluoropolymers without fluorosurfactants' (2022) <https://www.solvay.com/en/article/eliminating-pfas> accessed 1 May 2023; Gujarat Fluorochemicals, 'Company Announcements' (9 March, 2022) <https://www.gfl.co.in/upload/pages/ebce5fed9030753d0ee651bf1f48d0a0.pdf> accessed 1 May 2023; Gujarat Fluorochemicals Limited, 'Company Annoucement' (27 August, 2022) <https://www.gfl.co.in/assets/pdf/Announcement-on-NFPA-technology-FKM-27-Aug-2022.pdf> accessed 1 May 2023; Gujarat Fluorochemicals Limited, 'Company Annoucement' (30 November, 2022) <https://gfl.co.in/assets/pdf/GFL%20Announcement%2030.11.22_new.pdf> accessed 1 May 2023.

also be guaranteed by some suppliers using known analytical methods.

In the recent past, and mainly in 2022, various fluoropolymer manufacturers have released statements announcing discontinuation of use of FPAs in the manufacturing of specific fluoropolymers. A summary of latest announcements is given in Table 2 (Appendix).

The fluoropolymer user industry has already witnessed the transition when PFOA was substituted by other PFAS polymerization aids, except in China where PFOA is still in use.[31] They have now become sensitive to the potentially negative aspects of FPAs currently in use replacing PFOA.[32] Hence, the user industry is requesting fluoropolymer manufacturers to switch to NFPAs. There is an urgency to qualify new versions of fluoropolymer products produced without the use of fluorinated polymerization aids. The regulatory developments from various authorities are pushing the industry to swiftly move towards sustainable technologies. As a result, fluoropolymers produced with NFPA technology are a commercial success and that further motivates the industry to work harder in this direction.

IV. A Regulatory Proposal for Fluoropolymers

The EU Chemicals Strategy for Sustainability (CSS) towards a Toxic-Free Environment proposes the development of a horizontal essential use concept to apply across chemicals legislation (European Commission, 2020). The CSS commits to "define criteria for essential uses to ensure that the most harmful chemicals are only allowed if their use is necessary for health, safety or is critical for the functioning of society and if there are no alternatives that are acceptable from the standpoint of environment and health".

Most harmful substances as defined in the CSS are chemicals that cause cancers, gene mutations, affect the reproductive or the endocrine system, or are persistent and bioaccumulative. It also covers chemicals affecting the immune, neurological or respiratory systems and chemicals toxic to specific organs. It is clear that fluoropolymers as independent substances do not fall into the category of Most Harmful Chemicals as defined in the CSS, based on[33]:

- Fluoropolymers are Polymers of Low Concern as per well-established OECD criteria
- Fluoropolymers are insoluble, non-mobile, non-bio accumulative and non- toxic

However, the FPAs that have been traditionally used in the manufacture of fluoropolymers are small non-polymeric PFAS substances of low molecular weight such as perfluorooctanoic acid (PFOA), ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, or GenX), ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA), or perfluorohexanesulfonic acid (PFHxS) might fall into the category of Most Harmful Chemicals and they would therefore require regulatory control. It is important to highlight that, as mentioned above, at present between 50 and 80% of fluoropolymers do not require the use of fluorinated polymerization aids (depending on suppliers and implemented technology).

Any regulatory process on fluoropolymers should start by differentiating if the polymer has been manufactured with the use of FPAs. If this is not the case, then the fluoropolymer substance should be excluded from any legislative action, because there is no justification to regulate a chemical that will not pose any concern to human health or the environment.

If FPAs have been used in the manufacturing process, fluoropolymers should only be used in situations where the use can be considered to be essential. While the concept of essential use is still under development[34], this is expected to include situations in which it can be clearly demonstrated that the application is critical to ensure health, safety, and an adequate functioning of society. It is out of the scope of this article to discuss about the conditions under which essential use could be demonstrated. Yet it is

31 Rainer Lohmann, Ian T. Cousins, Jamie C. DeWitt, Juliane Glüge, Gretta Goldenman, Dorte Herzke, Andrew B. Lindstrom, Mark F. Miller, Carla A. Ng, Sharyle Patton, Martin Scheringer, Xenia Trier, and Zhanyun Wang, 'Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?' (2022) Environ Sci Technol 54, 12820–12828.

32 Bruno Ameduri, *Issues, Challenges, Regulations and Applications of Perfluoroalkyl Substances* (Oxford University Press, 2022).

33 (n 5).

34 Cefic, 2022. Regulating Chemicals Based on the Essential Use Concept. Available at: https://cefic.org/policy-matters/defining-europes-essential-chemical-for-society/. Last access November 2022; Wood 2022, prepared for European Commission, DG Environment. Supporting the Commission in developing an essential use concept. Workshop report. Available at: https://environment.ec.europa.eu/system/files/2022-05/Essential%20Use%20Workshop%20Report%20final.pdf . Last access December 2022.

expected that many applications of fluoropolymers would meet these criteria.[35]

The essential use concept will be linked to the availability of alternatives. In cases where viable alternatives are proven to be available for a specific use of fluoropolymers, the use should be restricted so that it can be covered by the alternatives. Again, detailed discussions will be required to demonstrate viability of alternatives, particularly in situations where health and safety parameters (or even adequate functioning of society, depending on the case) will be critical. In such cases, equivalent performance to that provided by fluoropolymers will be necessary since downgrades in performance could have extremely negative impacts for the environment or the population. Likewise, the typical parameters of overall reduced risk and economic availability of the alternative (and in sufficient amount) will have to be carefully evaluated. So, availability of alternatives would have to be evaluated with a broad perspective covering items such as performance, accessibility, resource efficiency, waste generation, cost, availability, stability and lifetime. Where viable alternatives are not found for essential uses of fluoropolymers manufactured with FPAs, derogations from the impact of upcoming regulatory restrictions should be granted. Such derogations would need to be based on the introduction of all existing abatement techniques based on the most modern developments, plus the guarantee of a maximum PFAS content in the final product. For example, 250 ppb as has been included in the restriction proposal.[36] However, such derogations should be time limited to provide incentives to move suppliers to fully implement manufacturing process involving NFPA technology as soon as possible.

Figure 2 displays a schematic overview of the proposed regulatory path for fluoropolymers. In the absence of a definitive definition of "Essential Use Concept", the term 'Critical Use for Society' is used.

V. Conclusions

The manufacture of certain grades of fluoropolymers had traditionally required the use of FPAs (short-chain PFAS) to ensure an optimal production. This practice has resulted in PFAS emissions and pollution of certain areas around manufacturing and processing sites, which has been a reason of major concern for the society. This has also triggered significant regulatory actions globally against PFAS. Fluoropolymers have been impacted by such actions, due to use of non-polymeric PFAS in the manufacturing process and the fact that they meet the very broad definition of PFAS based on structure.

For many years the fluoropolymer industry has been looking for alternative technologies that would help to remove the use of FPAs while ensuring top quality end-products. For this to be assured, not only commercial acceptance is required, but it also needs to be ensured that the final fluoropolymer will not lead to emissions of undesirable PFAS. The fact that industry has placed substantial efforts in such developments is proven by the relatively large number of patents that have been deposited over the last two decades.

Due to the increased regulatory pressure, and also to a better understanding by industry of the increasing constraints in terms of societal acceptance of chemical risk, significant progress has been achieved over the past years on the development of NFPA technology. In fact, only in the year 2022, up to 5 announcements from 3 different fluoropolymer suppliers have been released describing upcoming implementation of different manufacturing methods that will remove the need to continue using FPAs. Such announcements are not only based on achieved technical progress, but also on successful introduction of new fluoropolymer grades on the market, including customer acceptance. This demonstrates that such NFPA technology is not a vague concept or an aspiration, but a reality that should be developed by industry in a relatively short timeframe.

It is possible that not all suppliers will be ready to introduce such changes at the same pace, for every single fluoropolymer grade. Due to the well-established high value of fluoropolymers to many critical applications for society, it is expected that those uses should be allowed to continue, while likely on a time-limited basis. Nevertheless, efforts should be made by industry to ensure that all feasible abatement techniques are in place to guarantee that PFAS emissions from the manufacture of fluoropolymer is kept as low as possible.

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35 Bruno Ameduri, 'The Promising Future of Fluoropolymers' (2020) Macromol Chem Phys, 1900573.

36 ECHA, 'Registry of restriction intentions until outcome - Per- and polyfluoroalkyl substances (PFAS)' (2023).

This article also suggests a regulatory frame for fluoropolymers which is based on the need to exclude fluoropolymers that are manufactured with NFPA technology from any future restriction on their use. This is based on the fact that fluoropolymers are substances that pose no hazard to human health or the environment. Removing FPAs from their manufacture takes away the only real concern associated to fluoropolymers. The lack of degradability and the possibility to effectively destroy them during end-of-life without generating further PFAS emissions supports this principle. The proposal considers the need of other considerations such as uses that are critical for society (pending a final definition of the essential use concept) or the availability of alternatives to provide derogations to continue using fluoropolymers manufactured with FPAs, which should in any case be granted under specific time limits and with the obligation to introduce highly efficient abatement techniques to minimize emissions.

Appendix

Table 1: Summary of identified patents on fluoropolymers and NFPA (in no particular order)

Name of the patent	Company	Application	Reference
Fluoropolymer dispersions containing no or little low molecular weight fluorinated surfactant	3M	United States	Dadalas et al., 2005
Polymerization of Halogen-Containing Monomers Using Siloxane Surfactant and Aqueous Composition	ARKEMA	United States	Wille et al., 2005a
Polymerization of fluoromonomers using 3-ally-loxy-2hydroxy-1propanesulfonic acid salt as surfactant	ARKEMA	United States	Wille et al., 2005b
Emulsifier free aqueous emulsion polymerization to produce copolymers of a fluorinated olefin and hydro-carbon olefin	3M	United States	Kaspar et al., 2006
Process for preparing fluoropolymer dispersions	SOLVAY SPECIALTY POLYMERS ITALY	United States	Kapeliouchko et al., 2007
Process for preparing fluoropolymer	DAIKIN	United States	Otsuka et al., 2009
Preparation and Stabilization of Fluoropolymer Dis-persions by Aqueous Emulsion Polymerization with Carbosilane Surfactants	3M	United States	Bissinger et al., 2010
Aqueous process for making fluoropolymers	ARKEMA	United States	Amin-Sanayei et al., 2011
Polymerization of Fluoropolymers Using Alkyl Phos-phonate Surfactants	ARKEMA	United States	Durali et al., 2012
Aqueous Process for Making a Stable Fluoropolymer Dispersion	ARKEMA	United States	Amin-Sanayei et al., 2012a
Aqueous Process for Making Polyvinylidene Fluoride Dispersion	ARKEMA	United States	Amin-Sanayei et al., 2012b
Polymerization of fluoropolymers using polycaprolac-tone	ARKEMA	European patent specification	Hedhi, 2013
Polymerization of fluoropolymers using non-fluorinat-ed surfactants	ARKEMA	United States	Durali et al., 2014
Synthesis of making 2,3,3,3-tetrafluoropropene con-taining fluoropolymers	ARKEMA	United States	Amin-Sanayei et al., 2014
Method for producing aqueous fluorinated polymer dispersion, aqueous fluorinated polymer dispersion and fluorinated polymer	AGC	United States	Toyoda et al., 2015

Fluoropolymer Compositions Containing a Polyol Compound as Emulsifier and Methods of Making Them	3M	United States	Zipplies et al., 2015
Method of producing fluoropolymers using alkyl sulfate surfactants	ARKEMA	United States	Amin-Sanayei et al., 2016
Method of Producing Fluoropolymers Using Acid-Functionalized Monomers	ARKEMA	United States	Durali et al., 2016
Aqueous polymerization of fluoromonomer using hydrocarbon surfactant	CHEMOURS	European patent specification	Brothers et al., 2016
Employing polyalkylene oxides for nucleation in aqueous polymerization of fluoromonomer	CHEMOURS	United States	Brothers et al., 2019
Fluoropolymer aqueous dispersion production method and fluoropolymer aqueous dispersion	DAIKIN	United States	Hayashi et al., 2020
Method for stabilizing aqueous dispersions of fluorinated polymers	SOLVAY SPECIALTY POLYMERS ITALY	United States	Carella et al., 2020
Peroxide curable fluoropolymers obtainable by polymerization with non-fluorinated emulsifiers	3M	United States	Jochum et al., 2020
Method for producing modified polytetrafluoroethylene, method for producing modified polytetrafluoroethylene powder, and method for producing stretched porous material	AGC	United States	Higuchi et al., 2020
Process for preparing fluoropolymers and fluoroelastomers in presence of a non fluorinated sulfonate type hydrocarbon containing surfactant thereof	GUJARAT FLUOROCHEMICALS	European patent specification	Chauhan et al., 2022

Table 2. Summary of recent announcements by fluoropolymer manufacturers on commercial progress to introduce NFPA technology in the manufacture of fluoropolymers that previously required the use of FPA.

Development of NFPA technology by fluoropolymer manufacturers	
PTFE Aqueous dispersions	Gujarat Fluorochemicals (2022a)
PTFE Fine powders	Gujarat Fluorochemicals (2022c)
PVDF	Arkema (PCI, 2008), Solvay (2022), Gujarat Fluorochemicals (2022c)
FKM	Chemours (2022b), Solvay (2022), Gujarat Fluorochemicals (2022b)
PFA	Gujarat Fluorochemicals (2022c)

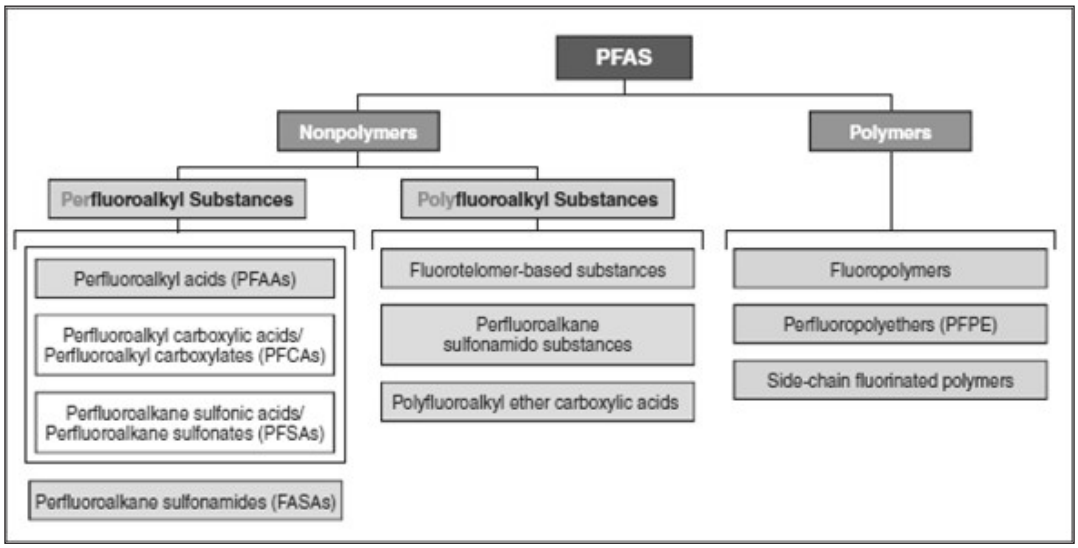


Figure 1: Commonly recognized PFAS groups of substances

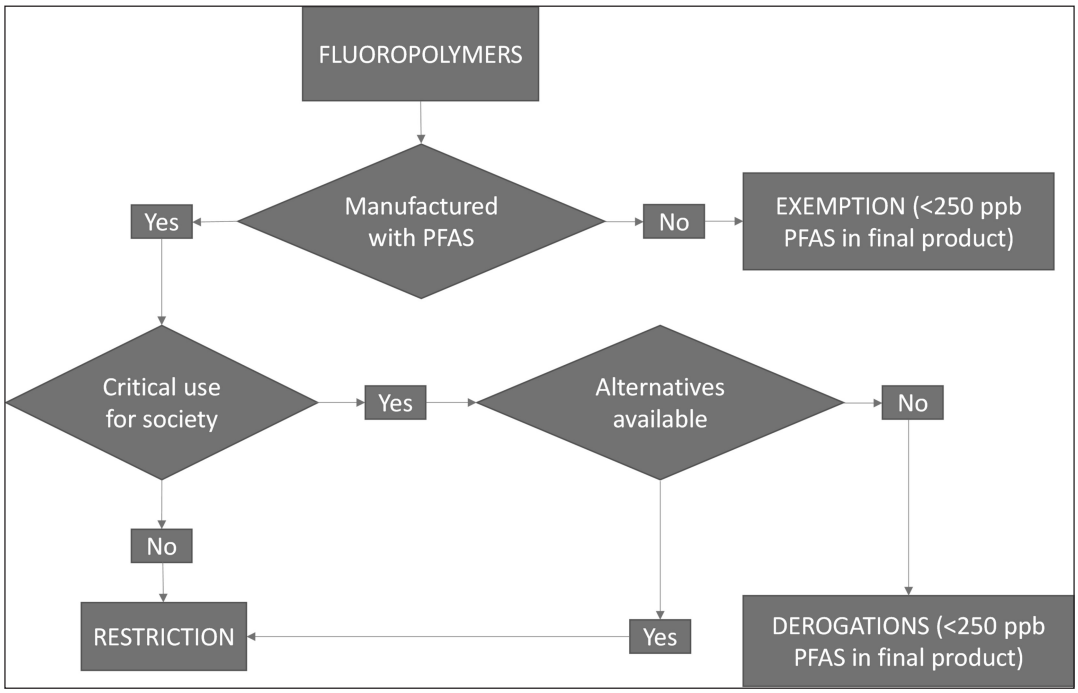


Figure 2: Summary of the regulatory process recommended for fluoropolymers