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# What do we know about per- or polyfluoroalkyl substances (PFASs) ? Issues, Challenges, Regulations and Possible Alternatives

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## Abstract

Per- or polyfluoroalkyl substances (PFASs) are man-made compounds involved in compositions of many industrial processes and consumer products. They are categorized into two main families based on their molar mass: though low molar mass-products (<1000 Da) are toxic, mobile, bioaccumulable and cross the human membranes, others of much higher molar masses, e.g., fluorinated macromolecules and especially fluoropolymers are safe, reliable, do not face such concerns, do not cross the membranes (hence, they are regarded as Polymers of Low Concern) and are involved in many applications including medical products and high value-added materials and devices. Because the former family has led to a severe global contamination, recent regulating agencies in Europe (REACH) and USA (EPA) have aimed at restricting fluorochemicals. Recently, the consultation from affected organisms and industries have led to more than 5,600 answers and comments. This review supplies an update on the overall situation of PFAS, their limitations, regulations, end of life, degradations and possible alternatives.

Keywords: contamination; degradation; fluoropolymers; per- and polyfluoroalkyl substances (PFAS); polymer of low concern; regulators.

## 1. Introduction

A severe attack on fluorine chemistry has been launched more than one decade ago. Media and activists have been quite busy to denounce the adverse effects of per- or polyfluoroalkyl substances (PFASs) whereas many plaintiffs have sued fluorochemical producers. As a definition from the Organization for Economic Co-operation and Development (OECD),<sup>1-2</sup> PFASs contain multiple C–F bonds, related to the presence in a substance of fully fluorinated methyl (-CF<sub>3</sub>) or methylene (-CF<sub>2</sub>-) groups, with a few exceptions. They represent a group of artificial / anthropogenic chemicals with unique hydrophobic and lipophobic physico-chemical properties and quite different physical, chemical, and biological characteristics.<sup>3-6</sup> « Per » stands for that the compound contains only carbon and fluorine atoms (i.e., all hydrogen atoms are replaced by fluorine ones) while « poly » means that the product contains at least two fluorine atoms. Hence, humans, animals, mammals and plants have been exposed to PFASs through air, dust, soil, drinking water and wastewater. Some PFASs have been identified as substances of very high concern by public health authorities. The number of PFAS molecules is huge (>14,000<sup>7</sup>) and most of them are perfluorocarboxylic acids and perfluorosulfonic acids, represented by perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have been involved in many applications in different areas.<sup>6,8-11</sup> Thus, all these PFASs have recently been under heavy pressure from regulators, press and media.

The objectives of this review focus on educating, listing, categorizing (i.e., to distinguish various F-compounds which are hazardous from others of essential use, matching the

stringent requirements in term of safety, reliability, and integrity of parts), informing on both the PFAS productions and recent regulations and industrial processes to overcome such severe issues. Finally, the end of the review suggests various possible alternatives.

## 2. Various Families of PFAS

The history of fluorochemicals is very rich and started in the late 30-ies.<sup>12</sup> Among these halogenated compounds, PFASs are composed of various families, basically divided according to the molar masses (Figure 1). They are falling into two main families: i) the low molar-mass PFASs (including fluorinated telomers<sup>13</sup>, perfluorocarboxylic acids, oligomers (the molar masses of which are lower than 10,000 g.mol<sup>-1</sup>) and surfactants,<sup>7,14-15</sup> left part of Figure 1) which are bioaccumulable, mobile toxic, persistent, and are under severe restricted and drastic regulations ; ii) the second one encompasses the fluorinated macromolecules. Low molar mass-derivatives are totally different from polymers related to their properties and applications.

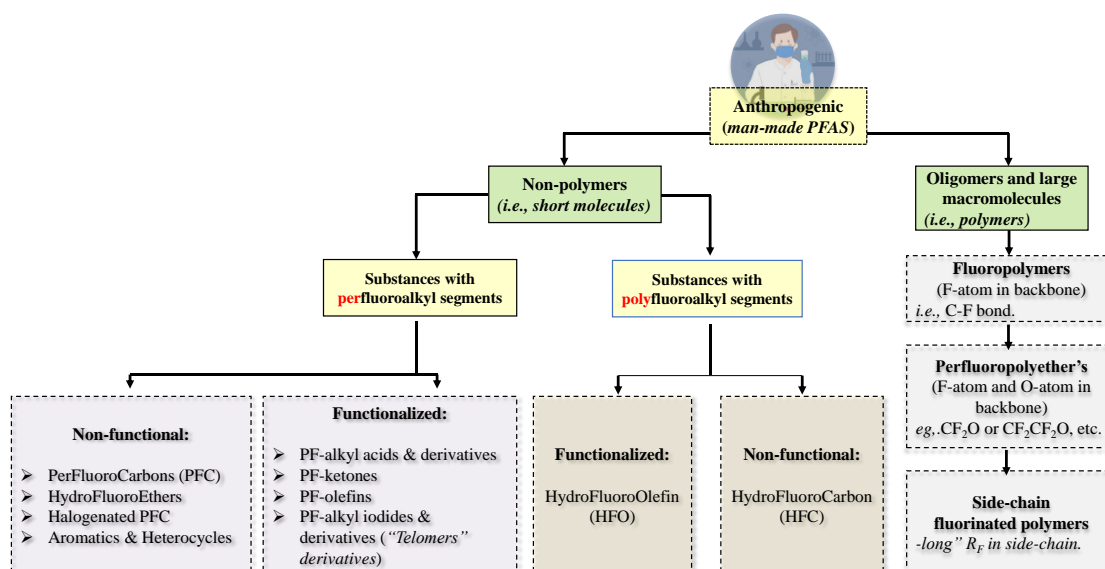


Figure 1: Overview and categorization of man-made per- or polyfluoroalkyl substances (PFAS). PFC, HFE, HFC and HFO stand for perfluorocarbon, hydrofluoro ether, hydrofluorocarbon and hydrofluoroolefin, respectively (ammended from Buck et al.<sup>3</sup>).

### 2.1 Low molar mass-PFASs

The first family deals with organic molecules, the molar masses of which are lower than 1000 Da. They can be either perfluorinated (i.e., containing only carbon and fluorine atoms) or polyfluorinated, both of them been able to be functional or not. Monomers, as precursors of polymers, are mostly gaseous for C2 and C3, and have not been grouped as fluorinated gases because there is no reporting obligation for the monomers under EC regulation no. 166/2006.<sup>16</sup> As noted in Figure 2, the PFAS definition leads to overlaps with those of monomers and fluorinated gases, but several of them are not considered as PFAS. For example, difluorochloromethane, R-22, precursor of TFE (that further makes PTFE) and F-113 are not regarded as a PFAS according to OECD definition.

Besides refrigerents and air conditioning gases,<sup>17</sup> a wide variety of fluorochemicals have found many applications just as fluorinated drugs<sup>18-19</sup> and agrochemicals<sup>20</sup> accounting for *quasi* half of agrochemicals.<sup>20</sup> Presently, the fluorinated pharmaceutical products represent 25% of efficient molecules and are emerged among the most prescribed and top-selling drugs.<sup>21</sup> A featuring example, perfluorohexyloctane, C<sub>6</sub>F<sub>13</sub>C<sub>8</sub>H<sub>17</sub> small block co-oligomer

(under the Miebo® tradename) was approved by the Food and Drug Administration (FDA) in 2023 as a single-component preservative-free eye drop to reduce tear evaporation in the dry eye-treatment.<sup>21</sup> Actually, active principles in pharmaceuticals, biocides, and plant protection products are controlled by agencies different from Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH, vide infra) and, so far, benefit from time-unlimited derogations in the EU restriction proposal. In view of the risk associated to emission (particularly in the case of plant protection products), the derogation comes with a recommendation to the EU to address these concerns in the respective regulations to reduce the use and emissions of PFAS.

Other fluorochemicals of interest are used various areas as contrast agents,<sup>21</sup> in MRI imaging<sup>22-23</sup> and labeled molecules with <sup>18</sup>F for positron emission tomography.<sup>24</sup> Another group is composed of fluorinated surfactants. These surface active compounds have the remarkable facility to form big supramolecular self-assemblies in aqueous solutions,<sup>14-15</sup> at liquid interfaces and on solid surfaces. These valuable surfactants can be involved in more than 200 applications (including aqueous film-forming foams (A<sub>3</sub>F)<sup>25</sup> used to extinguish fires, comfort products, such as for waterproofing and as stain-repellent treatment of furniture, clothes, fabrics, carpets, leather, metal plating, anti-reflective, antifogging or antistatic coatings, and papers for fast food packaging,<sup>26-27</sup> taking advantage of their unparalleled aqueous surface tension-lowering properties. Moreover, such surfactants can also be used as processing aids (or emulsifiers) for fluoropolymer manufacture, yielding micelles in which the reaction occurs and also stabilizing the resulting latex, section 3).

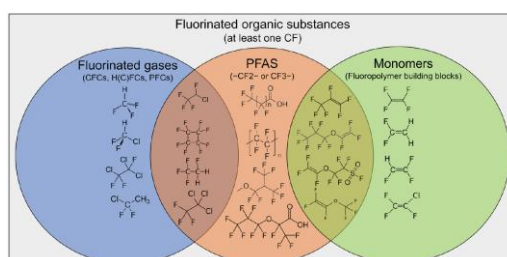


Figure 2: Overview in grouping fluorinated organic compounds and their overlap.<sup>16</sup> Some derivatives are included to illustrate to which category these substances would be assigned. Reproduced with permission from RSC.

As a matter of fact, the essential use concept<sup>16</sup> distinguishes the uses for which PFASs hardly find any replacement product(s) able to fulfill the searched requirements, from those for which lesser performances are sufficient and attainable otherwise. The need for discerning, eco-responsible use of PFASs has to be enhanced while features of PFASs should be maintained without showing poor performances. Indeed, to be regarded as “essential”, the utilization must be “*necessary for health, safety or is critical for the functioning of society*” and “*there are no available technically and economically feasible alternatives*” as defined under the Montreal Protocol (Decision IV/25.19).

In 2022, the global market for fluorinated compounds was estimated to ca. 25 billion USD,<sup>28</sup> with a yearly production of about 4-5 million-ton. Refrigeration and air conditioning are the biggest growing markets,<sup>17</sup> followed by transportation, pharmaceuticals,<sup>18-19,21</sup> agrochemicals,<sup>20</sup> aluminum production, construction, semiconductor and electronic industries. Major commercial manufacturers are the 3F and 3M companies, AGC (formerly Asahi Glass Company), Arkema, Daikin, Chemours (formerly Du Pont de Nemours), Dongyue Group,

Gujarat Fluorochemicals Limited, Halopolymer, Honeywell, Juhua Group Corp., Mitsubishi, Syensqo (formerly Solvay-Specialty Polymers), Sinochem Lantian Co, The Linde Group, Orbia. Asia Pacific dominates the organofluorine market.

Actually, soluble PFASs (including surfactants) can travel for long distances through air, creeks, streams, rivers, seas and strongly adsorb to rocks and sediments.<sup>15-16</sup> They are globally distributed, environmentally persistent, bioaccumulative,<sup>28</sup> toxic and cross the cellular membrane,<sup>1-3,14-15</sup> thus rising many issues.<sup>1-2,29-30</sup> Moreover, PFASs also affect ecosystems because of teratogenicity, immunization damage, and oxidative stress.<sup>31</sup> As an example, in plants, these substances induce apoptosis, modifying the growth-decay cycle. PFASs also cause exudation in plants, intensive rhizosphere defense, harm dissolved organic matter (DOM) morphologies and characteristics, while their spatiotemporal distributions are *quasi* the same as those of DOM in *in-situ* environments. DOM affects the PFAS fate in many compartments.

However, many PFAS are not inert. On the contrary, toxicological and ecotoxicological data, especially of the most intensively studied perfluorinated carboxylic and sulfonic acids, show that adverse health effects occur even at very low doses or concentrations. Hence, in 2006, EPA brokered an agreement for voluntary phase out of PFOA and PFOS in the USA. A 2022 report alerted on PFAS pollution in the USA, with about 50,000 plants either producing or using PFAS, over 4,000 contaminated water treatment stations, 3,500 polluted military bases, and more than 500 airports contaminated.<sup>32</sup> Moreover, from data reported by the National Health and Nutrition Examination Survey (NHANES), the centers for disease control and prevention alarmed that PFASs were detected in the blood of 97% of Americans.<sup>33</sup> The French newspaper *Le Monde* proposed the map of Europe that identified the widespread PFAS contamination sites.<sup>34-35</sup>

Moreover, from many articles, Mancini et al.<sup>36</sup> carefully reported that PFOA was classified as carcinogenic to humans based on « sufficient » evidences for cancer in experimental animals and strong mechanistic evidence in exposed humans while PFOS was classified as « possibly carcinogenic to humans » based on « strong » mechanistic mechanism.<sup>36</sup> Unfortunately, though many studies were developed to find out alternatives, several products were potentially analyzed more toxic than PFOA.<sup>37</sup> Thus, examples of « regrettable substitutions » should be avoided in the future. More generally, pharmacokinetics and (eco)toxicological profiles of PFASs are characterized by still poorly understood species, gender and other variations.

As a matter of fact, the modern detection tools have been so accurate and powerful that ppb<sup>38-39</sup> (and even ppt) can be detected (knowing that one ppb represents a drop of water in an Olympic swimming pool). Nevertheless, the FDA has no evidence that PFASs, at levels found in the samplings, induce some human health concerns.<sup>38</sup> Actually, persistent organic pollutant (POP) regulations launched from the Stockholm Convention has banned PFOS since 2009, PFOA since July 2020 and perfluorohexanesulfonic acid (PFHxS) since June 2022 while restrictions on perfluoroalkane carboxylic acids (PFCAs) are under scrutiny<sup>40</sup> while the dossier is progressing. Furthermore, the restrictions directed by the POP regulations may also look after substances when they are alone or are components of formulations above certain thresholds.

In addition, on February, 23<sup>rd</sup> 2022, the European Chemical Agency (ECHA) published a restriction on all PFAS in firefighting foams (A3F).<sup>41</sup> This agency estimated that ca. 4.4 million metric tons of PFAS “*would end up in the environment over the next 30 years unless action is taken*”.<sup>42</sup>

The «*Forever Pollution Project*» (FPP)<sup>35</sup> listed 22,934 known contamination places, including 20 PFAS production sites, and 21,426 “presumptive contamination sites”, including 13,745 zones presumably contaminated with A3F discharge, 2911 industrial manufacturing

facilities, and 4752 places containing PFAS waste. However, the authors reported that « *the true extent of contamination in Europe remains significantly underestimated due to a lack of comprehensive geolocation, sampling, and publicly available data* ».

Indeed, from January 2026, U.S. companies manufacturing PFAS in the USA or imported PFAS, or finished or semi-finished compounds and formulations containing PFAS between 2011 and 2022 will be subjected to a reporting rule.<sup>43</sup> Several states (e.g., Maine, Minnesota Vermont and others<sup>44</sup>) have already started to restrict the utilization of PFAS or require reporting while the scope and schedules vary significantly from one state to one another.

## 2.2 High molar mass-PFASs

Fluorinated polymers<sup>45-48</sup> are niche specialty, reliable and bio-inert<sup>49-51</sup> polymers. Thanks to their strong C-F bonds and high molar masses (and thus do not cross the membrane), they are endowed with outstanding properties. Indeed, under their conditions of uses, they are stable thermally, chemically, electrochemically and against UV and aging offering them to be involved in many applications (vide infra).<sup>52</sup> Thirty-eight fluorinated polymers are commercially available.

Basically, they can be divided into three major sub-groups (Figure 1) : perfluoropolyethers (PFPEs),<sup>53</sup> polymers bearing fluorinated side groups<sup>54</sup> and fluoropolymers (FPs)<sup>55-57</sup> which contain a (per)fluorinated backbone. Indeed, FPs are completely different from other fluorinated polymers which may degrade to small PFAS during their cycle life.<sup>8,11</sup>

Though the two first families display some failures (PFPEs may contain some oligomers while the other one, mainly based on poly[fluoro(meth)acrylate]s which possess  $\omega$ -perfluorinated dangling moieties might release 6:2 or 8:2 fluorotelomeric alcohols<sup>58</sup> from hydrolytic degradation (i.e., saponification). The last group, the FPs exhibit remarkable above features, are solid substances, insoluble in water, non-bioavailable, non-bioaccumulative, non-toxic and resistant to degradation<sup>59-60</sup> having been proven to be biologically stable<sup>49-51</sup>, their molar masses being able to reach several million  $\text{g}\cdot\text{mol}^{-1}$  (e.g. for polytetrafluoroethylene, PTFE<sup>57</sup>).

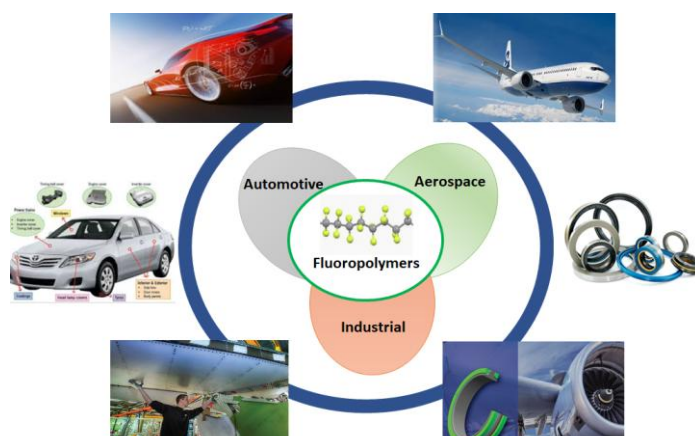


Figure 3. Application fields of fluoropolymers including automotive and aerospace (reproduced with permission from Wiley<sup>65</sup>)

FPs are high value materials that enable the adequate functioning of a number of key industrial sectors. In addition, they fulfill the 13 Polymer of Low Concern (PLC) criteria<sup>59-60</sup> (vide infra) and, in contrast to organic molecules, they overcome such above hazardous issues. The outcomes of both reviews indicate that 96% of global commercially available FP satisfies such globally accepted OECD PLC criteria.

Presently, these (co)polymers are utilised in numerous high-tech applications (e.g., Energy-as for binders for batteries<sup>61</sup>, fuel cell membranes,<sup>62-64</sup> backsheets for photovoltaic panels, and lubricants and mold release agents for wind mills-<sup>53</sup> electronics (additives to photoresist formulations),<sup>65</sup> aerospace (e.g., brakes and hydraulic fluids in aircrafts,<sup>65-66</sup> automotive,<sup>66-67</sup> (tele)communication (e.g. internet of things<sup>52,68</sup>) and biomedical industries, as excellent examples of « essential use » products.<sup>49-51</sup>

In addition and advantageously, the FluoropolymerGroup, FPG, composed of AGC, Arkema, Chemours, Daikin Chemical Europe, W. L. Gore & Associates and Syensqo (formerly Solvay) lauched the Manufacturing Programme anchored on stringent commitments for industrial productions of FPs. It has recently implemented abatment technologies<sup>69-70</sup> making «sustainable» the manufacturing of FPs by drastically reducing emissions of non-polymeric PFAS residues, as both the fluorinated gas and aqueous emissions (lower than 0.009% by the end of 2024 and lower than 0.003% by 2030<sup>71</sup>) as well as in improving their manufacturing processes without using any fluorinated surfactants.<sup>72</sup> A commitment to inform downstream users of FPs on their safe handling and utilization in the guide for the *Safe Handling of Fluoropolymer Resins*, under procedure.

However, in the production of PTFE, the Chemours company has identified a few by-products probably released from transfer reactions<sup>73</sup> from hydrocarbon polymerization aids onto growing oligo(TFE) radicals.

### 3. Concept of PLC

FPs are regarded as polymers of low concern (PLC) following definitions by the OECD.<sup>59-60</sup> They fulfill the 13 criteria in terms of molar mass, oligomer content, dispersity, charge, thermal chemical and UV stability, etc.. While a focus on FP applications has been traditionally looked from the perspective of users by consumers, Sales et al.<sup>69</sup> highlighted how the benefits of FPs use stand out more clearly when linked to industrial sectors, on the basis of their contribution to safety, reliability, decarbonisation, circularity, non-obsolescence and outstanding overall performance. This has also well-being summarized by Conversio<sup>74</sup> which studied a set of comprehensive case studies showing that their persistency does not pose any risk to human health. Actually, FPs are extremely stable as one of the main reasons on extending life of many products, part of Circularity definition.

Moreover, Wang et al.<sup>61</sup> recently extensively reviewed the importance of fluorochemicals involved as components in rechargeable batteries and highlighted breakthrough progress. Though conventional lithium-ion batteries have maintained a leading position in overall performance for years, other alternative batteries also demonstrate significant advantages in specific aspects and it is expected that such fluorinated compounds will also play a pivotal role in these devices.

### 4. Elimination and trapping low molar mass-PFASs

Many reviews and articles report the degradation and trapping of PFAS<sup>9,70,75</sup> and this present manuscript does not aim at recalling them again.

Though PFAS removal from water can be usually acheived from adsorption techniques involving conventional sorption materials such as granulated activated carbons (GACs) or ion exchange resins, more recent studies for efficient adsorbent materials as biological-based materials: proteins, advanced materials like nanocomposites and cyclodextrins as organic frameworks including nano(ligno)cellulosic-based materials and layered double hydroxides led to the best results<sup>75</sup> by increasing their selectivity, the adsorption capacity and faster uptake kinetics on PFOA, PFBA and ammonium 3-oxa-perfluorohexanoate, GenX. These authors also mentioned that the presence of fluorine- and amine-counterparts in the derivatives may improve both the PFAS uptake and selectivity.

More recently, Monsky et al.<sup>76</sup> mineralized five fluorinated telomers bearing at least one C–H bond and a sulfonate end-group under relatively mild conditions in the presence of NaOH. These telomers underwent deprotonation and subsequent fluoride elimination as a starting point of the degradation. These authors reported that the degradation was complete within 24 h, monitoring such a degradation by means of <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopy, hence evidencing various intermediates (formate, carbonate, oxalate and glycolate as well as higher 3–4 carbon carboxylic and sulfonic acid telomers). This study was confirmed by DFT simulations and suggested a degradation mechanism.

## 5. Regulations

On 7 February 2023, the European Chemicals Agency (ECHA) published a restriction proposal on PFAS under the REACH Regulation, as submitted by five European Member States, Denmark, Germany, the Netherlands, Norway and Sweden. This was regarded as a quite complex initiative in the history of the EU, to restrict the production, use and placing fluorinated chemicals on the market. The proposal now follows the regulatory procedure established under REACH, articles 69 through 73 to adopt restrictions or suggest derogations<sup>77</sup>. Following a 6-month public consultation (ended September, 25<sup>th</sup>, 2023), the affected organisations and companies had the opportunity to contribute to this consultation by submitting comments on the potential scientific and socio-economic impacts of such a legislation. Indeed, industrials, academics and individual people answered more than 5,600 comments and additional information (leading to >100,000 pages).<sup>78</sup> The answers (top 3 countries were Sweden, Germany and Japan) arised from 4400 stakeholders, 3313 companies, 1543 individuals (many of them from Scandinavia), 552 associations, 61 NGOs, from 30 countries and 70% at least concerned the FPs.

The Risk Assessment Committee (RAC) and the Socio-Economic Assessment Committee (SEAC) of ECHA also suggested their opinons. Then, the European Commission plans to supply a draft amendment to the list of restrictions in Annex XVII of REACH. The final decision will be taken in comitology procedure with scrutiny involving the Member States and the European Parliament.

Various fluorinated compounds are already banned (e.g., PFOA and PFOS) and continuous procedures from the competent authorities are pursuing their pressure to impose drastic restrictions.

The justification to launch a restriction on PFAS as a group is based on ‘persistency and other concerns’ related to these chemicals. Previous initiatives to regulate PFAS chemicals individually has resulted in substitution of one PFAS by another molecule, that also matches the PFAS definition,<sup>79</sup> and being also able to exhibit similar toxicological properties.

Thomas et al.<sup>80</sup> summarized various regulatory actions launched both in Europe and in the USA, including federal and state-level recent initiatives. These authors supplied an exhaustive list of different texts of legislation and described in detail to demonstrate how competent authorities approached the issues on PFAS from different perspectives.

## 6. Recycling

The global market of fluoropolymers in recent years was estimated at 330,000 tons in 2021<sup>74</sup> and 346,970 tons in 2023<sup>81-82</sup>, although the exact figures vary on the source. These volumes are much lower (< 0.1%) than the global plastics production, estimated at 390.7 million tons in 2021.<sup>83-84</sup> Nevertheless, the consumption of FPs has been increasing<sup>85</sup> because they are crucial components in chemical, electronics, automobile, petroleum, building, textile, aerospace, and other manufacturing industries.

Regarding polymers and plastics, 9% has been recycled,<sup>86-87</sup> while that percentage was only 3.4% for FPs in 2021.<sup>84</sup> Although major efforts must be developped to increase the

recyclability of FPs *versus* 13.1% landfill and 83.5% incineration,<sup>84</sup> the circular economy is lower than that of hydrocarbon polymers.

Besides chemical or thermal degradations (e.g. pyrolysis of PTFE at 550 °C<sup>88</sup>), other recycling ways of specific FPs have been reported. First, Schuster et al.<sup>89</sup> reviewed the recycling of fluorinated elastomers and summarized that only two major methods enabled to achieve the recycling of poly(VDF-*co*-HFP) copolymers or poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers (FKM, Figure 4) in an industrially suitable process: i) milling FKM to release a fine powder mixed with virgin FKM and ii) mechanical FKM devulcanization followed by successive compounding with virgin rubber.

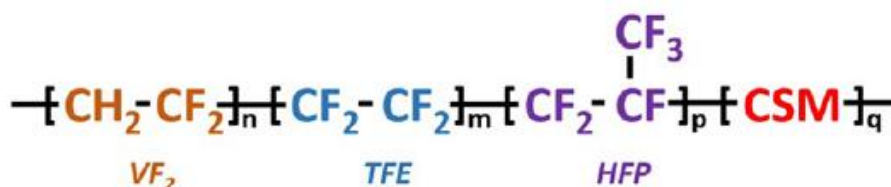


Figure 4: chemical structure of FKM elastomers (where VF2, TFE, HFP and CSM stand for vinylidene fluoride, tetrafluoroethylene, hexafluoropropylene, and cure site monomer, respectively)<sup>46-48,89</sup>

The Arkema Company has launched a completely recycled PVDF (called Agitech™ High Performance PVDF<sup>90</sup>) with excellent mechanical and high chemical resistance to fuel and hydrolysis along with its high flame resistance for various applications. A second example deals with recycling of perfluorosulfonic acid (PFSA), the best candidates being -Nafion, Flemion, Aquivion, 3M membranes<sup>64</sup> - which are of growing interest for green energy. Several studies report suitable solvents to recover and further reprocess membranes<sup>62-64</sup> with sometimes some loss in performances as lower conductivity.

Recycling poly(2,2,2-trifluoroethyl methacrylate) into 2,2,2-trifluoroethyl methacrylate monomer could be achieved from 185 °C from poly(2,2,2-trifluoroethyl methacrylate) bearing a trithiocarbonate end-group prepared by RAFT polymerization.<sup>91</sup>

The 3M/Dyneon company implemented the depolymerization of FPs (especially PTFE, FEP and PFA) in a pilot plant,<sup>92</sup> releasing TFE *via* unzipping further using it in (co)polymerization.

While several methods have been reported to safely dispose various PFAS waste, particularly end-of-life FPs in materials,<sup>93</sup> more information on recycling of FPs has been *quasi* exhaustively summarized in a recent review.<sup>94</sup>

## 7. Mineralization and End of Life of FPs

Hori's group<sup>95-99</sup> developed a relevant process to mineralize PFOS<sup>96</sup> and FPs (PVDF<sup>97</sup> and various VDF<sup>98</sup> and TFE copolymers<sup>99</sup>) in subcritical water. This releases fluoride anions, and, in presence to calcium hydroxide, they led to calcium fluoride as the starting point of the fluorine Chemistry.<sup>6,11,15,27,46,57,60</sup>

Materials	Mass Fraction (wt %)
PTFE Tubes	63

PTFE Tapes	7
PVDF	18
PFA	6
FKM Rubber	6

Table 1: mixture of various FPs in treatment of Brenda (where PFA and FKM stand for poly(TFE-*co*-perfluoroalkyl vinyl ether) and poly(VDF-*co*-HFP) or poly(VDF-*ter*-HFP-*ter*-TFE), respectively).<sup>100</sup>

By using a *BRENNkammer mit DAmfessel* (Brenda) pilot plant, Aleksandrov et al.<sup>100</sup> successfully degraded FPs waste (containing a mixture of various FPs, Table 1) which converted into inorganic fluorides, HF and CO<sub>2</sub>. That efficient process requires high temperatures (850-1000 °C) to yield no residual PFAS (< 1 ng/m<sup>3</sup>) in only 2 seconds.

The same German team<sup>101</sup> revisited the incineration of FPs at their end-of-life and supplied data to support mineralization of FP waste. They noted negligible PFAS release as products of incomplete combustion. These authors burnt a mixed sample of FPs representing 80% of commercially available FPs incinerated at conditions representative of municipal and industrial waste incinerators operating in Europe. They used state-of-the-art emission sampling and Ultra-high Performance Liquid Chromatography coupled with tandem Mass Spectrometry and GC-MS to identify and quantify released PFAS, the standards of which were available. Statistical analysis of the results confirmed non-detected to insignificant PFAS amounts which highlight an efficient FP mineralization.

## 8. Alternatives

Searching alternatives to PFAS is quite challenging. For low molar mass products, several attempts in short fluorochain surfactants have been reported<sup>102</sup> while fluorinated surfactants used in emulsion radical polymerization of fluoroalkenes have been replaced by hydrocarbon ones.<sup>72</sup> For FPs, the difficult task to propose substitutes is not easy since there are many types of well-designed FPs for specific applications, which must fulfill stringent requirements. Actually, perfluoropolymers are required for optical fibers to avoid any loss of signal intensity usually observed from fibers made from polymers containing hydrogen atoms which absorb some signal.<sup>103</sup> This is a nice example of « essential use ». In contrast, in 1986, the NASA experienced the tragic accident of the Challenger shuttle that exploded 77 seconds after launching, the seals (or gaskets) being not made of fluoropolymers (their Tg were not low enough).<sup>104</sup> Another relevant items of « essential use » deals with perfluorosulfonic acid (PFSA) membranes for fuel cells (section 6) which display a combination of remarkable features as chemical, thermal, oxidative and mechanical properties, high proton conductivity and perm-selectivity that other sulfonic acid polymers (e.g., polyimide, polysulfone, PEEK, polystyrene, etc) do not have.<sup>64,105</sup> A recent study by Artificial Intelligence (AI<sup>106</sup>) was suggested by Lang-Koetz and Hutschek<sup>107</sup> who used the AI tool "CumulusAI" in conjunction with the extensive data pool: a total of 420 materials were identified which have the potential to replace PFAS in various industrial applications. These materials were carefully analyzed and structured into 32 material categories to better

understand their diversity and range of applications (optical photolithography for the production of microchips, automotive industry, medical as resectoscope for invasive prostate operations, pharmaceuticals (treatment of severe dry eye). Among them, only two were selected but the final (experimental) tests indicated poor properties and thus failure, evidencing that, so far, no alternative enables to compete with fluorochemicals or FPs.

However, Sherrell et al.<sup>108</sup> reviewed mechanical-to-electrical energy harvesting polymers and suggested alternative fluoropolymer energy harvesters (especially to PVDF) as well as alternative technologies including non-fluoropolymer piezoelectric polymers, triboelectric nanogenerators, ferroelectric elastomers, and flexoelectric polymers. They also compared and listed the advantages and limitations of the materials. However, from natural polymers (as globular proteins, modified chitosan, aerogels of oxidized cellulose, silk fibroin nanofibers, etc...<sup>108</sup>) the piezoelectric performances of such biopolymers were much worse than those of PVDF and copolymers.<sup>65</sup> Thus, it is assumed that much research is needed to boost their performance close to at least 30 pC/N.

More recently, Joudan et al.<sup>39</sup> studied eventual alternative(s) of FPs and suggested poly(ether ether ketone), PEEK, as a possible replacement in laboratory chromatography. However, analysis of such a PEEK also revealed fluorinated chemicals (trifluoroacetic acid and other fluoroalkyl carboxylic acids). Their presence may be related to their synthetic production such as processing aids, residuals and inhibitors used.

Keyte et al.<sup>109</sup> identified PFAS alternatives in more challenging sectors such as medical devices, green energy, transport (wires and cables insulation) and industrial uses and they proposed PEEK, polyamides and ultra high molar mass polyethylene. However, such materials were convenient in only limited domain (e.g., balloon catheters made of PEEK) but such alternatives are not suitable for all uses across this sub-sector of medical uses (especially for purity and biocompatibility), in redox flow batteries because of the susceptible aryl-oxy bonds undergoing oxidative deterioration at each charging cycle (in presence of  $\text{VO}_2^+$ ).<sup>110</sup> and display poor performance (lower strain at break and density).

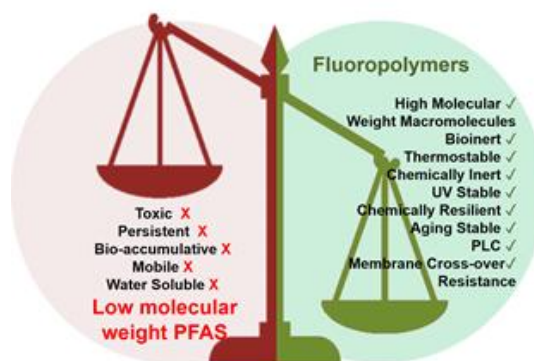


Figure 5: drawbacks of low molar mass (MW) PFAS in contrast to advantages of high MW ones (Fluoropolymers) (reproduced with permission from MDPI<sup>70</sup>)

## 9. Conclusion

Man-made PFAS are numerous and separated into 2 families.<sup>5,8</sup> Named as “forever chemicals” because they are characterized by a very high persistency over decades,<sup>111-112</sup> even indefinite lifetime,<sup>113</sup> some are modified or evolved in the environment, while a (per)fluorinated residue may remain. A recent report on reshuffling a revised definition may further supply<sup>2</sup> (i) an explanation of how PFASs relate to other organofluorine compounds, (ii) a comprehensive overview of known PFAS groups and their structures, including

examples on whether common names and acronyms exist, and (iii) some common synthesis routes of individual or groups of PFASs.

The first restriction actions to ban PFAS involved those in the composition of ski wax, food packaging, cosmetics<sup>114</sup> while sectors and elements recently discussed in the next three committee meetings are textiles, upholstery, leather, apparels, carpets, food contact materials and packaging, petroleum and mining.

The “essential use”<sup>16</sup> concept should help sorting out specific high performance-demanding uses for which no non-fluorinated alternatives have yet been identified from utilizations for which possible substitutes have become available to fulfill stringent requirements, and from convenience uses which are definitely not essential and hence should help phase out non-essential uses. European Union’s upcoming revision of the REACH scheduled for 2025,<sup>115</sup> is looking for strengthening chemical safety by tightening restrictions on dangerous substances, mainly on PFAS, to reduce administrative burdens, and streamline regulatory processes to support public health and environmental protection, reducing the need for individual authorizations, and addressing critical information gaps. More recently, ECHA suggested to favor some derogations, allowing the continued manufacture, placing on the market or use of PFAS<sup>116</sup> instead of a ban specific items useful for batteries, membranes for fuel cell and electrolizers made from fluoropolymers.

In addition, the growing development of fluorine chemistry is bringing many scientific and technical challenges, leaving substantial investigation room for its future applications. Thus, researchers are highly encouraged to unlock the fundamental role of fluorine chemistry in overcoming the hurdles for various types of materials, thus promoting the widespread effectuation of fluorine chemistry in many sectors. For example, in battery applications,<sup>61</sup> it has been recently noted that most PVDF producers have extended their capacity of production because of the high demand as chemically, thermally, and electrochemically stable binders for cathodes.

Indeed, FPs offer a combination of functionalities and are used when the material fails to satisfy minimum performance criteria as per global standards, and are usually a higher cost option. Hence, they represent a distinct family of fluorinated polymers, which can be clearly differentiated from other substances typically included in the PFAS group of chemicals (Figure 5). Moreover, the main limitations linked to the industrial productions of FPs have been addressed showing that these high value-added polymers must be separated from conventional PFASs and are irreplaceable materials. In contrast to low molar oligomers, the benefice/risk ratio is much higher for FPs and they do not degrade under standard conditions of intended use.

It is quite difficult to provide alternatives to PFAS able to match the harsh and stringent requirements since previous attempts led to poor<sup>105,109</sup> or catastrophic consequences (as the Challenger shuttle<sup>104</sup>). Though PEEK seems to be a possible alternative,<sup>109</sup> it does not match with all sectors covered by PTFE and PVDF, for examples. In addition, during the REACH restriction process, it is required that possible alternative(s) must be assessed for their risks to human health and the environment, their availability, but also their technical and economic feasibility.

While their annual growth rate is 6-8%,<sup>84</sup>, among all plastics, FPs represent a rather small volume production/tonnage since the FP production reached ca. 347,000 tons in 2023 (compared to >460 million tons for all polymers<sup>83-84</sup>), i.e. less than 0.1 % of conventional plastics.<sup>69,83,85</sup> In addition, the annual benefits of fluoropolymers in semiconductor manufacturing are substantial, estimated at approximately €10 billion per year.<sup>68</sup>

The circular economy should not only be driven by efforts in commodity plastics. Recycling advanced materials has also to be taken into account and growing developments are under way.

## Conflict of interest

There is not conflict of interest to declare.

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