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PFASs – avoiding the streetlight effect

An overview of the current situation in the EU[1]

Executive summary

PFASs (per- and polyfluoroalkyl substances) are receiving increased regulatory attention because of their persistence and (eco)toxicological profile, as well as their widespread use and resulting ubiquitous presence. It has been said that there are more than 4,700 PFASs, yet most people familiar with the topic can only cite a few.

In this report, we have used REACH registrations of PFASs, independent literature, technical information from producers and general chemical knowledge to sketch the landscape of which types of PFASs are most prevalent in products and likely lead to highest environmental pressures.

We conclude that the types of PFASs one should most care about are: fluorotelomer substances (FTs) and the side-chain fluorinated polymers (SCFPs) they give rise to, as well as fluorinated (poly)ethers. This report is also meant as an introduction to the world and chemistry of PFASs.

Current regulatory initiatives on C6 PFASs and PFASs in the broader sense as welcome and necessary.

This report is neither exhaustive nor perfect, and it may contain errors due to insufficient knowledge or scrutiny. We kindly ask the reader to provide feedback as necessary.

1. The streetlight effect

> *There is a story of a drunkard searching under a street lamp for his house key, which he had dropped some distance away. Asked why he didn't look where he had dropped it, he replied, "It's lighter here!".*

This story[2] illustrates a common fallacy: we focus on familiar elements because we already know them better, while forgetting about those unfamiliar ones that may be more relevant.

The purpose of this report is to shed light on those PFASs that are not in the media spotlight, but that get increasing attention from (eco)toxicologists and regulators.

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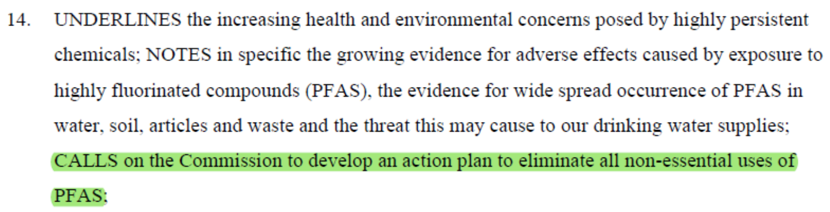
[1] Dr Zhanyun Wang of ETH Zurich (CH) is gratefully acknowledged for critically reading the manuscript.

[2] as related by A. Kaplan in his seminal work *The Conduct of Inquiry* in 1964.

2. We have a PFroblem

The Council's conclusions of June 2019 (Figure 1) describes the most salient environmental and health risks posed by PFASs[3] and calls for drastic action to put a halt to these threats.

Figure 1: Extract from the conclusions of the Council of the European Union, June 2019



14. UNDERLINES the increasing health and environmental concerns posed by highly persistent chemicals; NOTES in specific the growing evidence for adverse effects caused by exposure to highly fluorinated compounds (PFAS), the evidence for wide spread occurrence of PFAS in water, soil, articles and waste and the threat this may cause to our drinking water supplies; CALLS on the Commission to develop an action plan to eliminate all non-essential uses of PFAS;

The focus of such an action plan is on shorter-chain PFASs (C4, C6 and some more complicated cases, see box), as longer-chain PFASs have largely been regulated away. Researchers have proposed differentiation of uses of PFASs[4] based on the definition of essentiality of the Montreal protocol,[5] banning CFCs in 1987.

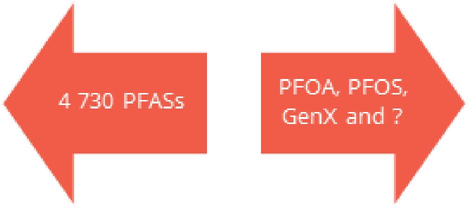
3. Know your PFoe

Effective regulation meeting the ambition of the Council of the EU will rely on a simple yet sufficiently wide and clear definition of PFASs without loopholes for regrettable substitution. For this, it appears useful to describe the current family picture of PFASs, esp. that in the EU.

3.1. A cognitive dissonance

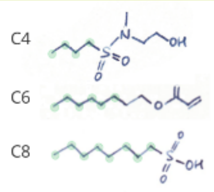
Two contradictory statements are heard often in discussions around PFASs, as illustrated in Figure 2.

Figure 2: Cognitive dissonance of statements on PFASs



On the one hand a dazzling number of different substances[6] have been found in different registries. On the other hand, common knowledge, websites, scientific and newspaper articles tend to revolve around only very few individual

Chain lengths
PFASs are often (unnecessarily) divided into called *longer-* or *shorter-chain* ones, and the separation is often confusing. Shorter-chain ones have fewer than eight perfluorinated carbon atoms (often called C6 and C4). They replaced the longer ones (C8 and upwards) have largely disappeared from the market (but not from the environment) due to action under the Stockholm convention. (Eco)toxicologically speaking, there is no strict cut-off (like with hexane and heptane). It is all a big fuzzy continuum dominated by bioaccumulability for the longer-chain PFASs and by mobility for the shorter-chain PFASs. They are all highly persistent, but some play surprising tricks on top (see section 6.3). A few examples: (the green halo denotes a perfluorinated carbon atom)



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[3] A concise and clear introduction to PFASs is available on the ECHA's dedicated webpage.
* If you count the perfluorinated (PF) carbon atoms, the system will not make sense to you. It is actually NOT logical: the carboxylic carbon atom in PFHxA is counted (to get to a C6), whereas the first non-PF carbon atom in 6:2 FTs is *not*.
[4] I. T. Cousins *et al., Environ. Sci.: Processes Impacts*, 2019, **21**, 1803
[5] Decision IV/25: Essential Uses
[6] OECD ENV/JM/MONO(2018)7, p. 16.

substances – two of the most famous PFASs (PFOA, PFOS) have largely been phased out. In this study, we attempt to resolve this cognitive dissonance.

3.2. REACH registration as a source of information

The REACH regulation[7] requires registration of chemicals manufactured or used at more than 1 t/y (ton/year). Although in many other cases, this threshold is uncomfortably high, it is sufficiently low to give a reliable picture of large-scale industrial uses – and emissions. REACH distinguishes substances, mixtures and articles[8], both manufactured and used outside or within the EU, as shown in Figure 3.

Figure 3: Schematic overview of the obligations to register chemicals under REACH (for volume > 1 t/y)

PFAS present in:

	substance	mixture	article
Manufactured in EU	✓	✓	✓
Imported for use	✓	✓	✗

In the cases denoted by green tick marks, the chemical must be registered under REACH; only for substances included in articles imported into the EU this obligation does not exist[9]. This is of course a data gap, but this should, considering typical uses of PFASs, not distract from existing information on the five other cases.

Polymers (see box) are exempted from registration, but the monomers used to make the polymers are subject to registration.

The ECHA website lists all registered chemicals: PFAS-relevant substances can be extracted, although with substantial manual work.

Monomers and polymers:
A simple analogy: a monomer is to a polymer what a carriage is to a train.
Top to bottom: five different monomers, a homopolymer and three copolymers of increasing complexity and specialisation.

Different monomers can be used to impart manifold properties to the polymer. In the case of (meth)acrylate chemistry, the homopolymer may correspond to PMMA (Plexiglas) or superglue, whereas the copolymers may correspond to polymers used in a latex paint, in superabsorber or in many polymeric PFASs.

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[7] Regulation 1907/2006, description on ECHA's website.

[8] The three icons in Figure 3 illustrate the meaning of the three classes: an article is an object of a determined shape (such as rain jacket impregnated with PFASs); the spray or liquid used to impregnate the jacket is in most cases considered a mixture; the simple PFASs "molecule" on its own is a substance.

[9] One may be tempted to think that substances included in articles manufactured in the EU do not require registration. This is true in principle. However, considering typical PFAS-treated articles sold (outdoor wear, shoes, carpets, table cloths), the impregnation step is likely taking place late in the manufacturing process: this impregnation step is a use of the mixture and requires registration of the substances in the mixture.

3.3. Assumptions and limitations

Throughout this research, we have made the following assumption:

> *Assumption: "Companies are operating legally when it comes to REACH registration of PFASs."*

Essentially, this means information on registration data can be taken at face value. We have not found any evidence against this seemingly bold assumption in this research.

3.4. The toolbox approach

Most so-called *fine chemicals* are not produced in a single step, but through several steps. Those familiar with industrial chemical production techniques can often make educated guesses on earlier or later synthesis steps for each chemical, as well as on likely and unlikely functions and uses. This is important for monomers, for which later products (i.e. polymers) do not require registration. The rationale of these educated guesses may be enquired from the author.

4. The PFASs family picture

4.1. REACH registrations: qualitative aspects

The tedious and largely manual effort[10] to select PFAS from the ECHA database has yielded 67 substances for various annual tonnage bands, as shown in Figure 4.[11] They are registered by many different companies; the most famous PFAS producers hold most registrations.

Figure 4: number of substances registered by tonnage band (left) and by selected registrants (right).

Registered tonnage band		
Min (t/y)	**Max** (t/y)	**Count**
10,000	100,000	3
1,000	10,000	2
100	1,000	12
10	100	17
1	10	26
intermediate only		7
	SUM	**67**

Registrant	**Count**
Chemours	20
3M	23
Solvay	9
Daikin	1
others	32

A few comments:

- only few substances are registered in the top two tonnage bands.
- the tonnage bands >100 t/y cover more than 99% of the registered volume.
- the tonnage is unknown for the 7 substances registered as intermediates only.
- the total tonnage of all fully registered substances is ca. 335 000 t/y.
- most substances are monoconstituent substances (i.e. purity > 80%).

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[10] Substances with two or fewer consecutive perfluorinated carbon atoms were excluded, except where they can serve as monomers for fluoropolymers.

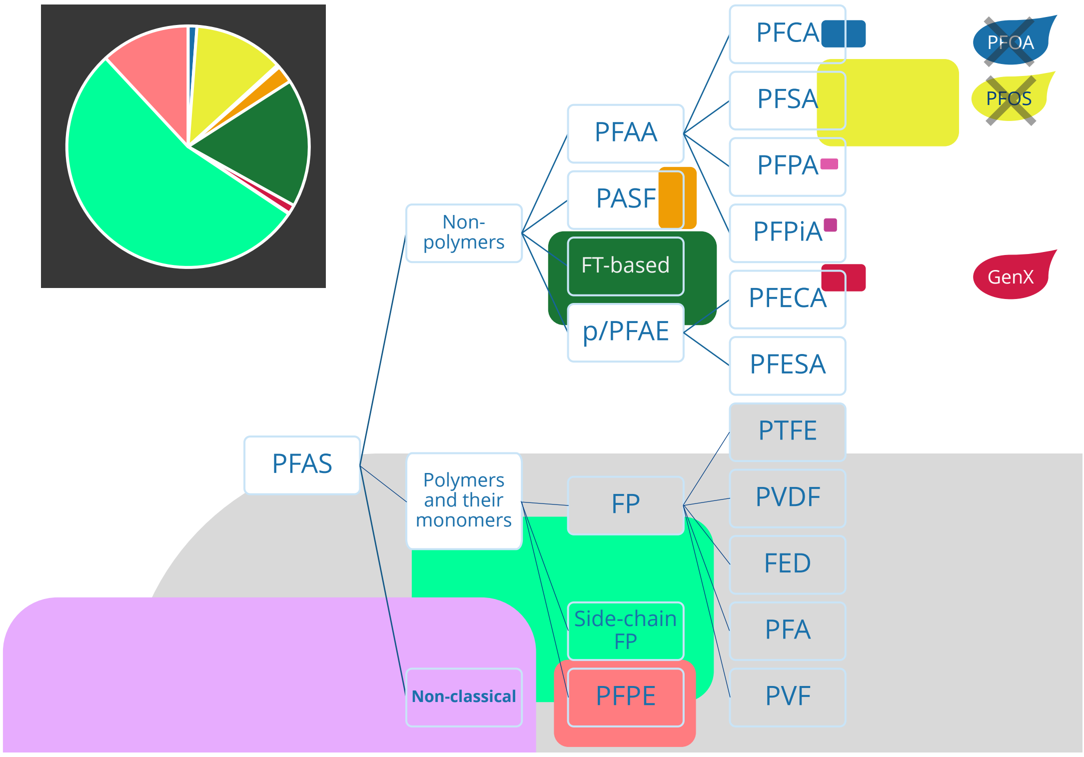
[11] Disclaimer: this number is the result of an individual assessment; many substances are in a grey area and may or may not be PFAS-relevant. Other experts may arrive at slightly different conclusions. Similar caveats are notified in the OECD study cited in footnote 6. The author invites the reader to share any doubts on the relevance or truthfulness of this figure.

4.2. Tidying up the mess

There are various ways to categorise PFASs; we have adopted one scheme proposed by the OECD[12] (Figure 5). This graph is rather busy: take your time to go through it step by step:

- you should not worry now about the meaning of the acronyms.
- types of PFAS used for the further analysis in this study are marked in colour.
- similar colours indicate related chemical structures.
- the types of the three archetypal PFASs (section 3.1), of which two are not registered.
- <u>most importantly</u>: the coloured patches represent the registered tonnage bands; the pie chart gives more detail for the non-dominant PFAS types.

Figure 5: Proposed categorisation scheme of PFASs and relative registered volumes.



What are the important elements?

- monomers for fluoropolymers (FP, grey area, going far beyond the picture) are overwhelmingly dominant (section 5.1).
- the non-classical PFASs are by far the second largest class (purple, section 5.2).
- substantial volumes are found on
    - the FTs and side-chain FPs (greenish hues, sections 5.6 and 6)
    - (poly)ethers (reddish hues, section 5.5)
    - sulphonic acids and derivatives (yellow-orange hues, section 5.4).
- two of the three archetypal PFASs belong to types of minor volumes.

Let's have a look at these types one by one.

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[12] OECD (2013), OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD, p. 7.

5. The most important family members

5.1. Fluoropolymers (FP)

Fluoropolymers (see box) are mostly homopolymers and simple copolymers, or, to use the train image: these are trains made from only one or few fairly normal types of carriages. Of the five polymers marked in Figure 5, PTFE aka Teflon is the most famous one; several applications of FPs are shown in Figure 6.

While FPs represent very high volumes, they are hardly ever the focus of assessments of PFASs. Compared so small-molecule PFASs and side-chain fluorinated polymers (SCFPs, see sections 5.6 and 6), they have negligible solubility, low mobility, large physical size, low biological uptake and, hence, lower (eco)toxicological concern. This is obviously not to say they do not need (eco)toxicological or regulatory attention!

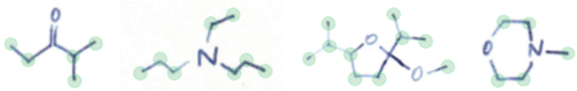
Main chain or side-chain?
Most polymers look either like a train or like a comb. Both the "shaft" and the "teeth" can be fully or partially fluorinated or not fluorinated.
The fluoropolymers in section 5.1 mostly have a "shaft" (or backbone or main chain) which is fully or partially fluorinated.
The perfluoropolyethers (section 5.5) are fully fluorinated. Some only have a backbone, some have side-chains.
Side-chain fluoropolymers are the real comb-like polymers. They have a non-fluorinated backbone and, most importantly, (some) fluorinated teeth.

Figure 6: examples of applications of fluoropolymers (FP): tape for joints, cable insulation, non-stick cookware, tubing in water treatment, ball bearings, medical tubing.

5.2. Non-classical PFASs

These are some substances that are fully fluorinated, but they have very different chemical structures and properties from the more usual PFASs. A few examples of chemical structures are shown in Figure 7; they are used as solvents, heat transfer fluids and dielectrics.[13]

Figure 7: Structures of selected non-classical PFASs



5.3. Intermezzo: remaining uses

So far, PFASs for mostly technical, and somewhat obscure uses have been mentioned and identified. Let's look at some of the remaining, more well-known uses of PFASs (Figure 8).

The following sections (5.4 to 6) will shed light on these applications. Keep in mind that fire-fighting foams have high potential to end up in the environment. Surface treatments (stone, textiles, leather) also easily release PFAS fragments when in use, because of the high surface area exposed to the elements and the partial degradability of FTs (section 6.3).

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[13] probably as substitutes for polychlorinated biphenyls (PCBs).

Figure 8: some uses of PFASs not explained yet in this report, from left to right: fire-fighting foams for mineral oil fires, chrome-plating, water and oil repellence (for concrete or stone surfaces, carpets and tablecloths, outdoor wear, bags and tents), as an auxiliary in making fluoropolymers such as PTFE.

5.4. Sulphonyl fluoride derivatives

The most famous representative of this class is the now-defunct PFOS (C8)[14]; the remaining chemistry is C4-based. It includes PFBS[15] (newly identified as an SVHC), as well as two other derivatives[16] registered 100-1000 t/y.

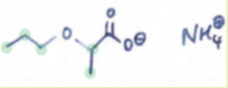
5.5. (Poly)ethers

A full 15 substances are used as small-molecule ethers (of which GenX, see box) and monomers for polyether-based polymers. These substances are often used as lubricants and surfactants. The reader is referred to a comprehensive recent review[17] on these substances.

The famous GenX

GenX is used by Chemours (formerly DuPont, among others in their Dordrecht, NL plant) as a surfactant to carry out the polymerisation of PTFE. It replaced PFOA in this role in 2012, and has been replaced successfully (but not fully yet) by P1010, a fluorine-free surfactant based on $FeSO_4$, a non-ionic (PPG) and a fatty-acid based surfactant.

GenX is a "kind of C6.5" substance and is registered as its ammonium salt (EC 700-242-3). The term "GenX technology" refers to GenX (in the free acid and ammonium salt form) and a volatile degradation product, a fluorinated ether.



5.6. Fluorotelomer substances (FTs)

The remaining 26 fully registered substances,[18] totalling 6 000 t/y, are likely the most interesting ones, and they have recently been getting increased regulatory attention: two CoRAP evaluations and a proposal for a broad REACH restriction on C6 substances. These are what is usually referred to as "C6 technology", yet it is not the logical middle of the C4 and C8 technologies. The C6 technology is, above all, extraordinarily versatile in the types of building blocks and monomers it can provide. This versatility is, together with a little metabolic subterfuge (see section 6.3), a key to the success and pervasiveness of this type of chemistry.

These fluorotelomer substances (FTs) are the basis of most water-, oil- and stain-repellents as well as fire-fighting foams. What are they?

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[14] Once pervasively used as such in chrome plating or derivatised for multifarious purposes.

[15] Registered as its potassium salt (EC 249-616-3), as well as low tonnages of two alkylammonium salts EC 700-536-1 and EC 444-440-5. There is also an FTS sulphonic acid, counted with FTSs (EC 248-850-6), see annex 8.2.

[16] These substances show the limits of this classification model. Substances EC 252-043-1 and EC 252-044-7 are alcohol-functional C4-sulphonamides that can be used as monomers e.g. to make SCFPs by condensation polymerisation, e.g. polyurethanes or polyoxetanes. There is also a methacrylate monomer based on a C4-sulphonamide (EC 266-737-7), which has been counted with the monomers for SCFPs, as it fulfils similar functions.

[17] Z. Wang *et al.* (2020): Per- and polyfluoroalkyl ether substances: identity, production and use, Nordic Council of Ministers.

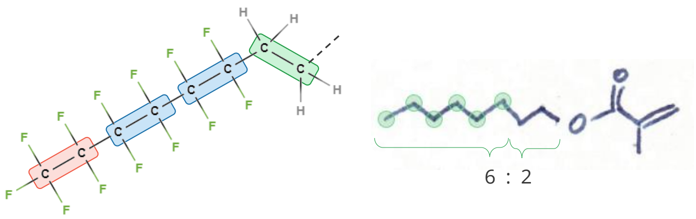
[18] Strictly speaking, two of these substances (EC 807-113-1 and 246-791-8) are not FTSs, but they are nevertheless likely building blocks for SCFPs or PFAEs (polyethers).

6. Fluorotelomer substances: good to know

6.1. A little fluorochemistry

PFASs can be produced by either the electrofluorination or by the telomerisation reaction (see box), which produces fluorotelomer substances. These substances are not *per*fluorinated (i.e. fully fluorinated), as in most cases two carbon atoms bear hydrogen atoms (Figure 9). This structure can then be continued by an oxygen, sulphur or, less commonly, a carbon atom, leading to countless possibilities to add other functionalities to the fluorotelomer.

Figure 9: typical fluorotelomer (6:2) structure (left) and 6:2 fluorotelomer-derived monomer for SCFPs (right)



Telomerisation

The technique as used e.g. in by Chemours: extension pieces (the blue units in Figure 9, left) are added to a starter (red), and the substance is finished off with a non-fluorinated bit (green).

Impurities may have one or three extension pieces, e.g. 4:2 or 8:2.

Odd-numbered units are possible, but currently uncommon – regrettable substitution with 5:3 or 7:2 lurks around the corner!

Electrofluorination

The older technique, as used e.g. in the 3M plant in Zwijndrecht, BE: a “normal” substance is reacted in an electrolytic bath with HF (an acid) and transformed into a fluorinated substance.

Impurities will result from incomplete reaction, impurities in the starting material, and from chain breakages and branching.

6.2. Examples of FTs

Of the many popular applications listed in section 5.3, REACH-registered FTs (detailed list in annexes 8.1 and 8.2) cover most. The situation is surprisingly consistent: the substances can be linked to specific application, and no major application is left void.[19]

6.3. A cuckoo’s tale

The 6:2 fluorotelomer unit is a sneaky one once it reaches the environment (Figure 10): the non-fluorinated “2” part of 6:2 units can be degraded microbially or abiotically in the environment, leading to PFHxA.[20]

PFHxA being a PFAS (and which does not degrade at all) on its own, soil or water analyses detecting PFHxA may blame its presence on emissions of PFHxA, whereas it is far likelier that it originates in a 6:2 FT, by volume considerations. It may be useful to think of the FT as a cuckoo, laying its eggs into another bird’s (PFHxA) nest.

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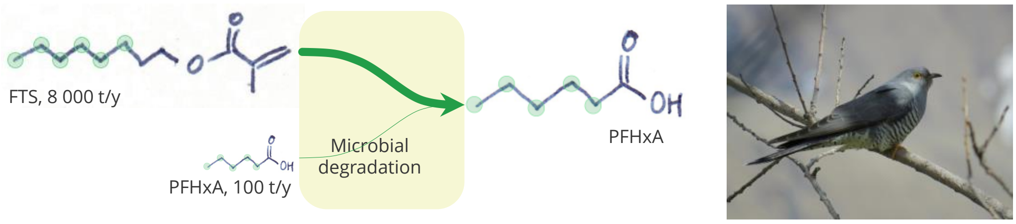
[19] Specific research on these attributions has confirmed them. This and additional information are available upon request from the author.

[20] This mechanism looks implausible at first sight, as it involves breaking two of the very strong C-F bonds. It is correct, however, and convincingly explained in M.J.A. Dinglasan *et al.*, *Environ. Sci. Technol.* 2004, *38(10)*, 2857.

Figure 10: environmental fate of 6:2 FTs and the PFHxA (left) and suggested ecological analogy (right).



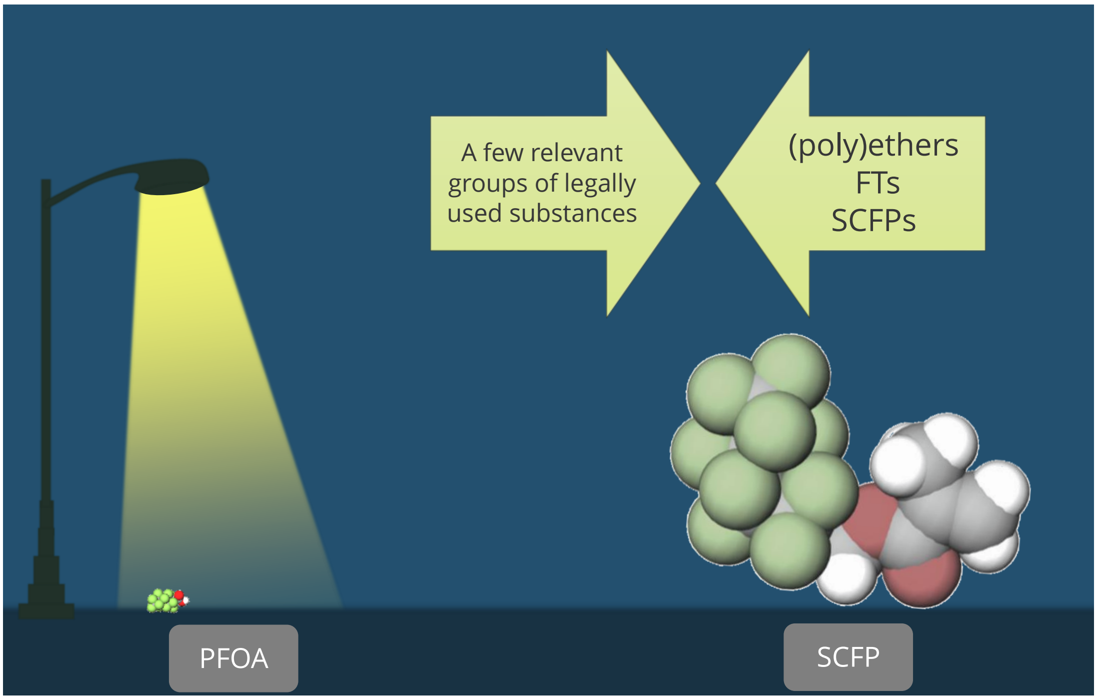
7. Take-home messages

7.1. FT-specific

- There is a handful of relevant FTs (see also section 8). You can make from them manifold, but rather similar SCFPs.
- They have diverse applications, of which many may lead to high emissions in use.
- They may go unnoticed by their degradation products.

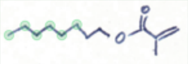
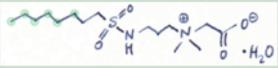
7.2. General

The dissonance in Figure 2 may be resolved like this: please note that the arrows have turned green, point towards each other and have changed text.

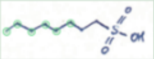
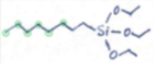
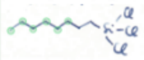
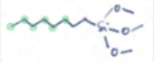
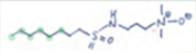
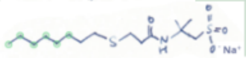
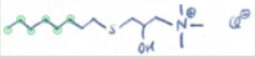


8. Annex

8.1.FTs registered 100 – 1000 t/y and identified uses

Structure	Chemical function	Use	EC
	Methacrylate	in polymers for impregnation and lamination	218-407-9
	Acrylate	in polymers for impregnation and lamination	241-527-8
	Surfactant	Fire-fighting foams	252-046-8

8.2.FTs registered 10 – 100 t/y and identified uses

Structure	Chemical function	Use	EC	Band (t/y)
	Sulphonic acid	Chrome plating (replacement for PFOS)	248-580-6	10-100
  	Silicone monomers	Special rubbers Polymers for impregnation (REACH restriction#73)	257-473-3 278-947-6 288-657-1	10-100
  	Surfactants	Fire-fighting foams	279-481-6 811-522-0 811-523-6	10-100
	Semifluorinated alkane	Ski waxes	432-570-5	10-100

A list of the substances registered 1-10 t/y is available from the author. These substances cover, among others, additional monomers (thiols and alcohols) that can be used to make SCFP based on polyurethane, rather than poly(meth)acrylate chemistry.

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