The Dark PFAS Hypothesis

Strategies of deception

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Abstract

Per- and polyfluoroalkyl substances (PFAS) have been at the center of numerous toxicological and environmental concerns and regulatory scandals for two decades. Previous research has shown a long history of active obfuscation, misdirection (‘science bending’) and regulatory manipulation by the largest halogenation businesses, related to the depletion of the ozone layer and the toxicity of some fluorinated surfactants (PFOS and PFOA). We screened publications for potential evidence of other strategies of deception and obfuscated information regarding PFAS and fluoropolymers. A directed effort was identified to influence the scientific understanding of the environmental source and effects of ultrashort PFAS, especially trifluoroacetic acid (TFA). Critical issues in the current analytical approach to PFAS monitoring were identified, as well as evidence of a silently abandoned “total organofluoride” technique. The non-specific character of the production, incineration and degradation processes is discussed, including the underreported relevance of PFAS congeners to regulation. A critical review of the literature and methodologies used in assessing the toxicology of (ultra)short PFAS resulted in some deeply concerning observations. (Disclaimer: This paper has not been peer-reviewed yet and may be subject to improvements and corrections at any time.)

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Version history

- 2023-09-10: Original (draft) publication
- 2023-09-23: Filtered the correlation matrix in section 'The Chemours transition' by p-value. Added "fit for purpose" assessment of SOF in section 'Total organofluoride (TOP assay, SOF, AOF)'.

Background

Per- and polyfluoroalkyl chemicals (PFAS) have been at the center of controversy since the groundbreaking "Dark Waters" lawsuit in 1998, filed against E.I. du Pont de Nemours & Company. The Tennant case revealed that giants like DuPont and 3M had knowledge of the significant health and environmental effects of PFOA and PFOS as far back as 1976. As the saga unfolded in various PFAS-related legal battles, it became evident that the fluorination industry had not only delayed public knowledge of PFAS toxicity but also stymied environmental regulations and research. A vivid illustration of this approach is captured in "The Weinberg Memo" [1]:

> DUPONT MUST SHAPE THE DEBATE AT ALL LEVELS [...] The outcome of this process will result in the preparation of a multifaceted plan to *take control of the ongoing risk assessment by the EPA*, looming regulatory challenges, likely litigation, and almost certain medical monitoring hurdles. The primary focus of this endeavor is to strive to create the climate and conditions that will obviate, or at the very least, minimize ongoing litigation and contemplated regulation relating to PFOA. This would include facilitating the publication of papers and articles dispelling the alleged nexus between PFOA and teratogenicity as well as other claimed harm. *We would also lay the foundation for creating Daubert precedent to discourage additional lawsuits.*

A large focus in both scientific inquiry and investigative journalism has been on the industry's strategy to "dispel the alleged nexus between PFOA and teratogenicity". Far less attention has been directed at the last sentence. The mentioned "Daubert precedent", refers to a U.S. Supreme Court case (Daubert v. Merrell Dow Pharmaceuticals), described as a landmark decision that redefined *the standard for admitting expert testimony in (U.S.A.) federal courts*. Rather than relying on the "general acceptance" standard from Frye v. United States, the Daubert standard assesses the *reliability* and relevance of the testimony, focusing on the scientific validity and the methodology of the evidence. The ruling empowers judges to act as 'gatekeepers', scrutinizing the scientific merit of potential evidence before allowing it into court. As such, "creating a Daubert precedent" can only be understood as a directed effort to undermine the reliability and relevance of scientific testimony in legal cases.

Such a directed effort does not need to be limited to undermining toxicological

PFAS research, a strategy which has already been extensively studied [2], [3]. In this paper, we investigate the hypothesis that the reliability of and access to analytical methods might also have been actively hindered by the fluorination industry.

The halogenation industry has thus far been involved in at least two well documented scandals revolving scientific influence campaigns. Before the infamous Tennant case and its follow-ups, which focused specifically on “C8” surfactants like PFOS and PFOA, there was also a period from the early 1970ies to the late 1980ies in which the link between the hole in the ozone layer and CFC-gases was vehemently denied using a directed campaign against the unwelcome scientific discoveries at the time [4]. This historical matter and its direct relevance to the current situation is discussed below.

Methodology

Investigating potential “gaps” in analytical research is inherently challenging, as it is a matter of “proving the absence”. Nonetheless, over the years, a small amount of analytical data and insights into PFAS production has trickled out. This data is used to find evidence of suppressed PFAS substances and overlooked analytical techniques.

To complement this, a qualitative analysis using well known industry strategies was applied, based on the work of Hastings and Gaber et al. [3], [5] To search for potential evidence of the purposeful creation of “Daubert precedent”, one must hypothesise on the implementation of these “strategies of deception”. This builds further upon the “Industry Strategies” categorisation described by Gaber et al., expanded to analytical techniques and other critical information that impacts our understanding of the environmental impact of fluororganics. The following techniques were hypothesised:

- Non-disclosure: Actively hiding or refusing to disclose industrial processes and/or chemicals that might critical for targeted environment analytical research.
- Obfuscation: Passive techniques that have the potential to hamper the ability to correlate analytical research.
- Misdirection: Techniques used to (re)direct the attention of analytical research to topics with minimal impact on industrial interests.
- Degradation: Techniques that result in less accurate reporting or that make it difficult to correctly interpret the data.
- Disinformation: Actively spreading false information regarding industrial processes, analytical techniques, etc.

A large number of permit requests, environmental datasets from research papers, patents and public sources, as well as process descriptions were collected and screened for such strategies of deception. Analytical data from a few large industrial companies was investigated, in part due to their historic role in the production of organofluorides and to identify potentially overlooked issues. Source material was tagged with potential strategies of deception and explanations were sought for large knowledge gaps.

Analytical information which might be targeted and/or affected was collected as well. A list was compiled of types of organofluorides and incidents that might show evidence of low or impaired access to analytical techniques and/or deliberate underreporting. A literature search was conducted in scientific publications, legal documents, industry process descriptions and press articles for these (groups of) organofluorides. Available data was reviewed and subjected to statistical analysis where possible.

A second set of qualitative assessments can be derived from McGarity and Wagner's book "Bending Science" [6], in which the authors identify multiple strategies that may be deployed by industry interests to corrupt research:

- Creating/distorting research
- Concealing unwelcome research
- Turning reliable research into "Junk"
- Bullying scientists who produce damaging research
- Assembling an expert group to advance a favoured outcome
- Manipulating public perceptions about credible science

The collected documentation was screened for evidence of these strategies as well.

A common theme in both qualitative approached is the suppression of unwelcome scientific information. Robert R. Kern's "Suppression of Environmental Science" lists some startling statistics regarding this specific issue [7]: Several surveys from the 90ies indicated that scientists and experts were (are) regularly being asked to tailor their research conclusions or resulting advice to suit the preferred outcome, to obtain future contracts, or to discourage publication. Harassment following publication of research on health risks from environmental exposures was also found to be quite common. Of course, suppressed science is non-falsifiable and it is in any case very hard to find or prove. Scientists involved in such a situation are often reluctant to speak out, out of shame and fear of legal/financial risks.

The results were rearranged to fit with the chronological timeline of events.

Part 1: A history of science bending

> "Once is happenstance. Twice is coincidence. Three times is enemy action." - Ian Fleming, Goldfinger

Background: The problem with the ozone layer (1972-1987)

In the early 1970s Dr. Sherwood ("Sherry") Rowland and Mario Molina make the groundbreaking discovery of an anomaly in the ozone layer, following concerns about the potential effects of "supersonic transport" on the stratosphere [4], [8]–[11]. Cicero et al. made a similar discovery within the same context [12]. Both publications suggested that chlorofluorocarbons (CFCs), extensively used in refrigeration and aerosol sprays at the time, were significantly harming the ozone layer. This stratospheric layer plays a pivotal role in shielding life on Earth from the adverse effects of ultraviolet radiation.

This revelation about the disastrous impact of CFC gases posed a significant challenge to the flourishing $2 billion halogenation industry at the time, notably to the inventor and largest producer of ozone depleting chemicals, E. I. du Pont de Nemours. This led to a decade-long effort by the industry to undermine the findings, prominently driven by the well-funded "Alliance for Responsible CFC Policy" [13], [14]. One of the misdirection tactics used, was to (try to) blame the problem on "the 11-year solar cycle" [15], [16], based on a research paper co-authored by a NASA employee. The chair of the board of DuPont was quoted as saying that ozone depletion theory is "a science fiction tale…a load of rubbish…utter nonsense" [13].

However, by the mid-1980s, the severity of the issue and source was already undeniable, with NOAA observations indicating a severe depletion of the ozone layer over Antarctica, a situation even more dire than Rowland had anticipated[17]. The decade long delay between Rowland's discovery and regulation can be viewed as one of the first demonstrations of techniques described McGarity and Wagner [6] from the halogenation industry.

On September 16th, 1987, the Montreal Protocol was signed, implementing a worldwide ban on CFC gases. This political initiative has since been described as one of the most successful initiatives for environmental protection ever [18], [19]. Paul J. Crutzen, Mario J. Molina and F. Sherwood Rowland were awarded the Nobel Prize in Chemistry in 1995 "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone".

The AFEAS/PAFT initiative (1987-current)

Immediately after the signing of the Montreal Protocol a coalition was formed by AlliedSignal, Atochem, DuPont and ICI, all major producers of halogenated gases, to initiate the "Alternative Fluorocarbons Environmental Acceptability Study" (AFEAS) [20], [21]. In November of 1987, an even larger international consortium was formed called "the Program of the Development of Alternative Fluorocarbon Toxicity Testing" (PAFT). The 15 companies that joined the consortium included the four original AFEAS companies, plus Daikin, Hoechst, Solvay and various smaller companies. The stated goal of the AFEAS-PAFT program was quite clearly described by employees of DuPont/Haskell:

> “Chlorofluorocarbon(sCFCs) are currently used in systems for preservation of perishable foods and medical supplies, increasing worker productivity and consumer comfort, conserving energy and increasing product reliability. As use of CFCs is phased out due to concerns of ozone depletion, a variety of new chemicals and technologies will be needed to serve these needs. *In choosing alternatives, industry must balance concerns over safety and environmental acceptability and still meet the performance characteristics of the current CFC-based products.*” - Mack McFarland (E. I. Du Pont de Nemours & Co., Inc, 1992) [20]

> “Therefore, industry needs to create alternatives that are *‘less environmentally stable’* with a low ozone depletion potential, a low global warming potential, and low photochemical reactivity. Such chemicals should still possess, however, a high degree of chemical stability in their end uses, be *relatively low in toxicity*, and also be available at an acceptable cost to users.” - Henry J. Trochimowicz (E. I. Du Pont de Nemours & Co./Haskell Laboratory for Toxicology and industrial Medicine, 1993) [22]

George M. Rusch also played a critical role in the AFEAS-PAFT program and has since claimed the successful ban of CFC on the industry’s efforts [21]. Rusch started his career at Allied Signal Inc., which bought Honeywell in 1999 and subsequently adopted the Honeywell identity. Rusch eventually became the director of “Toxicology and Risk Assessment” within Honeywell. After an industry career of 30 years, he is now a consultant for Veritox, Inc. (a private research company for forensic toxicology).

The PAFT program was estimated to cost approximately three to five million dollars per compound. At least five such (sub)programs were initiated: HCFC-123 and HFC-134a (1987); HCFC-14lb (1988), HCFC-124 and HFC-125 (1989), and HCFC-225 isomers (1990) [22]. The earliest AFEAS/PAFT funded publications indeed showed that HCFC gases would degrade into TFA and PFPrA PFCA’s and be deposited on ocean/land instead of depleting the ozone layer [23].

Frequently cited papers related to the toxicity and environmental issues of fluorinated chemicals often show evidence of AFEAS-PAFT funding. Multiple interconnected lobby groups for the halogenation industry were identified, including the European Chlorinated Solvent Association (ACSA), the Halogenated Solvents Industry Alliance (HSIA) and the European FluoroCarbons Technical Committee (EFCTC, consisting of Koura, Arkema, Chemours, Honeywell and Daikin). These can be considered functionally identical regarding their objectives in this context.

A frequency analysis was made of co-authorship between AFEAS-PAFT connected researchers and others within the PFAS domain. What is evident from the results (appendix B), is the frequent collaboration of industry representatives from the PAFT program (e.g. George M. Rusch of Allied Signal/Honeywell) with researchers from the University of Bayreuth (Hartmut Frank, Melvin W. Anders, Armin Klein aka Armin Jordan, Thomas Colnot and others) and the University of Würzburg (Wolfgang Dekant and others). This (financial) relationship is often acknowledged in the publication, but certainly not always. The University of Würzburg is also structurally sponsored by SKZ (the "German Plastics Center", a lobbying group for chemical companies including those producing fluoropolymers [24].

Wolfgang Dekant specifically was recently named in an EHN investigation on EU lobbying in regards to endocrine disruptors [25]. Dekant has been identified as representing BSEF (the flame retardants industry) and known for actively lobbying against the EU regulation of endocrine disruptors. Dekant now works as an "independent consultant to several REACH consortia, trade organization and individual companies", including 3M [26].

Examples of "scientific bullying" from the AFEAS-PAFT group of researchers were located [27], for example:

> "It is unfortunate that Hoet and coworkers do not cite the extensive published research on the toxicology of these two substances to better understand the nature of the exposure required to elicit an adverse effect in human beings." - George M. Rusch (1997)
>
> "The cases reported by Hoet and colleagues may, in a strict epidemiological sense, qualify as an epidemic, but their title is an overstatement: 'Epidemic of' would better be stated as 'nine cases of liver disease resulting from uncontrolled exposure to'." - M. W. Anders & W. Dekant (1997)

The last couple of years (2015-2023), Wolfgang Dekant has co-authored more than 1100 research papers regarding "RIFM fragrance ingredient safety assessments", equal to one publication every two days.

In 2013 Dekant published a general position paper on endocrine disruptors (funding source not specified):

> "Purported low-dose effects of 'endocrine disruptors' have triggered their inclusion in the EU REACH list of 'substances of very high concern'. Nevertheless, available scientific studies do not allow to unequivocally confirm or refute the existence of non-monotonous dose–effect curves for those substances. To conclusively answer the question of the occurrence of endocrine-mediated low dose effects and, thus, lay at rest the controversial debate that has pervaded toxicology during the last two decades we propose to either perform a high quality toxicological study with a model substance and a mutually agreed study design, or to establish an interlaboratory, endpoint-specific database of historical data. *Until at least one of these proposals intended to overcome the current deadlock have been*

> *implemented, a deviation of the established risk assessment process for thresholded effects is scientifically not warranted.*" - W. Dekant [28]

In 2022 Dekant also commented on the PEQ/PRF approach for PFAS proposed by the Dutch Environmental Services (RIVM), arguing *directly against* such EU regulation. This paper was funded by 3M:

> "In conclusion, deriving a group TDI for PFAS requires a detailed evaluation of the physicochemical information and the available toxicity database on PFAS. *Grouping of a larger number of PFAS of concern into a single assessment group is not supported and separate CAGs should be derived for PFACs and PFASs.* Only potent PFAS with slow rates of elimination should be added to these CAGs." - T. Colnot & W. Dekant [26]

It should be noted that AFEAS/PAFT funded papers are quite influential. They are, for instance, regularly cited in IPCC reports on the potential effects of halogenated gases [29] or to explain the environmental presence of trifluoroacetic acid (TFA) in oceans in reports by the Dutch Environmental Agency (RIVM) [30].

Environmental trifluoroacetic acid (TFA)

A long running scientific debate regarding AFEAS/PAFT associated publications is the source of the apparent high concentrations of trifluoroacetic acid (TFA) in surface waters, especially oceans [23], [31]–[39]. TFA is the lightest possible PFAS with a functional head group, $-COOH$ or carboxylic acid, putting it in the PFAS subclass of PFCA's [40].

In summary: In 1994, AFEAS held a workshop on the environmental fate of TFA in Miami Beach. The topic of interest was the observation that several HFCs and HCFCs were known to degrade in the atmosphere, most notably HFC-134a, HCFC-124, and HCFC-123 [23], [32]. An argument made during this time by AFEAS researchers was that HFC and HCFC cooling gases were superior to CFC gases as they would more quickly degrade in the atmosphere, leading to a significantly lower global warming potential than CFC's [41]. Notably, this report by Wallington et al. already observes that TFA/CF3C(O)OH is a major environmental sink for HFC gases. The final paragraph of this paper concludes:

> There is no known sink for CF3C(O)OH (TFA). *From the available toxicological data concerning CF3C(O)OH, it has been concluded that the formation of this compound from the atmospheric degradation of HFC-134a is of no concern with respect to human health.* High concentrations of CF3C(O)OH ($\geq 5 \times 10^{-4}$ mol) have been reported to adversely impact wheat and tomato seedlings. The concentration of CF3C(O)OH in rainwater expected from the atmospheric degradation of HFCs and HCFCs is $< 10^{-7}$ mol. Research is needed to

> establish the fate of CF3C(O)OH and the environmental impact of low CF3C(O)OH concentrations.

Two years later, in 1996, Harmut Frank and Armin Klein (who later adopted the name Armin Jordan) reported TFA rainwater and river-water concentrations of 25-280 ng/L in Germany, Switzerland and Israel [31]. They also note concentrations of 40-250 ng/L in (Atlantic) ocean surface waters. Based on an estimated HFC/HCFC emissions, Frank et al. suggest additional, unknown sources must be involved.

In 1999 a large AFEAS-PFAT sponsored paper is published called "Environmental Risk Assessment of Trifluoroacetic Acid" [32]. The conclusion is unmistakeable:

> "For the time being, an important question remains concerning the origin of the large present levels of TFA that have been measured in the environment (fresh and marine surface waters, rain, and air) and *cannot be explained by the known industrial sources*."

Armin Jordan and Frank Harmut make a similar claim in February of the same year, namely that based on an emissions inventory of HFC and HCFC gases, the atmospheric deposition rates of TFA could not be explained using the officially reported HFC/HCFC emissions [33]. Interestingly, thermolysis of fluoropolymers was briefly speculated upon as an important source of the environmental TFA burden, but left undeveloped.

In April of 1999, Richard E. Purdy famously resigns his position as Environmental Specialist for 3M [42], over their handling of PFOS and similar chemicals:

> "For more than twenty years 3M's ecotoxicologists have urged the company to allow testing to perform an ecological risk assessment on PFOS and similar chemicals. Since I have been assigned to the problem a year ago, the company has continued its hesitancy. ... 3M told those of us working on the fluorochemical project not to write down our thoughts or have email discussions on issues because of how our speculations could be viewed in a legal discovery process. This has stymied intellectual development on the issue, and stifled discussion on the serious ethical implications of decisions." - Richard E. Purdy (1999) [42]

In May of 1999, Wujick et al confirm evidence of the accumulation of TFA in surface waters in California and Nevada, attributed to HFC and HCFC degradation [43].

Immediately after, Jordan et al. start speculating on an entirely different, non-antropological source: TFA created through vulcanic activity [34], [35]. The study is funded by the EU-Japan Centre for Industrial Cooperation. Simultaneously, Von Sydow et al. "confirm the preindustrial presence of significant background concentrations of trifluoroacetate in historic precipitation samples" in another AFEAS sponsored publication [44]. The theory of a vulcanic origin for halogenated substances is eerily familiar, as the same argument was also made for decades to blame the hole in the ozone layer on non-anthropogenic sources, rather than the well established link to CFC's [4].

The presence of TFA in oceans was subsequently reported in concentrations of > 100 ng/L up to kilometers in depth in the South Atlantic [45]. Estimates of the total amount of TFA in the ocean were made by Harmut Frank et al. to be 268 million tonnes of TFA, *based on a homogenous distribution of 200 ng/L* [46]. The conclusion made by Frank et al. was that "continuous low-level releases from geological or biological sources for a long time may have resulted in present-day levels".

To this day Chemours and an industry lobby group called the European Fluoro-Carbons Technical Committee (EFCTC) maintain this theory on the vulcanic origin of TFA in numerous publications on "the facts of TFA" [49].

Note: If the source of this "ocean TFA" is actually anthropogenic, this could turn out to be one of the largest, long running cases of environmental pollution-denial in history.

A second group of influence (2000-present)

When analysing commonly cited papers on TFA occurrence and toxicity, another group of frequently collaborating authors was noticed, which includes Keith R. Solomon, Brian F. Scott, Mark L. Hanson and others (see appendix). Very few *direct* indications of industrial funding were found, except for a Euro-CHlor (Cefic) funded paper from 2005 co-authored by Brian F. Scott [50]. One paper [51] does mention a program called "Toxic Substances Research Initiative", which links to "Global Change Strategies International Inc." [52]. No further information was found about this organisation.

However, Keith R. Solomon also appears in "The Monsanto Papers" [53]. As Donna Farmer (Bayer) describes the collaboration process between the industry and Solomon:

> "Yes - they are on our side… Organizations/companies work with consultants to address issues in the their proposed programs. For example PSE&G hired *Solomon* and Ritter to help them defend the use of Rodeo[1] in the estuaries near their Nuclear Power Plant for eradication of phragmites." - Donna Farmer (Bayer) [54]

When looking at halogenated substances, specifically TFA, research papers co-authored by Keith R. Solomon are consistent in their overall assessment or harmlessness:

> "These data suggest that *TCA/TFA mixtures* at environmentally relevant concentrations do not pose a significant risk to these aquatic

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[1] Rodeo is the commercial name of glyphosate. The email thread includes the full name: Dr. Keith Solomon.

> macrophytes."- Hanson et al. (2002) [55]

> "The assessment found HAAs (Haloacetic acids) to be of low risk to aquatic macrophytes and the results are described in the second manuscript of this series." - Hanson et al. (2004)[56]

> "Still, HAAs are generally found as mixtures and their potential interactions are not fully understood, rendering this phase of the assessment uncertain and justifying further effects characterization. TCA in some environments poses a slight risk to phytoplankton and future concentrations of TFA and CDFA are likely to increase due to their recalcitrant nature, warranting continued environmental surveillance of HAAs." - Hanson et al. (2004)[57]

> "Based on current projections of future use of HCFCs and HFCs, the amount of TFA formed in the troposphere from substances regulated under the MP is too small to be a risk to the health of humans and environment." - Solomon et al. (2016) [58]

Keith R. Solomon has also co-authored on atrazine [59], another substance implicated in a lobbying scandal [60].

The "Dark Waters" case and PFOA stewardship program

Besides the production of HFC/HCFC gases for refrigeration and similar uses, there are two other major product categories for fluorinated organics: surfactants and fluoropolymers. Fluorinated surfactants are best know for their waterproofing ability, oil resistance and usage in firefighting foam [61], [62].

The focus of the Tennant vs. E.I. du Pont de Nemours & Company case and later cases involving 3M was on very specific surfactants: PFOA and PFOS. Both have eight carbon molecules and were therefore codenamed "C8" by Chemours [3].

However, it seems there is already a misunderstanding or even a misdirection at play here. The patent underlying the production of PFOS [61], which corresponds 1:1 with later process descriptions by 3M [63]–[65] also contains an often ignored aspect:

> "*By-products containing fewer carbon atoms than the starting compound are also formed* due to the cleavage of carbon-carbon bonds in some molecules, and cleavage also results in the formation of non-cyclic by-product compounds when cyclic starting compounds are used." - Brice (1956) [61]

Similarly from a later process description:

> "The electrochemical fluorination process yieIds *about 35%-40% straight chain (normal) POSF*, and a mixture of biproducts and waste of unknown and variable composition comprised of the

> following: 1) higher and lower straight-chain homologs, which comprise about 7% of the process output 2) branched-chain, perfluoroalkylsulfonyl fluorides with various chain lengths, about 18-20% of the output 3) straight-chain, branched, and cyclic (non-functional) perfluoroalkanes and ethers, which comprise about 20-25% of the output 4) “tars” (high molecular weight fluorochemical byproducts) and other byproducts, including molecular hydrogen, which comprise about 10-15% of the output. Because of slight differences in process conditions, raw materials, and equipment, the mixture produced by the electrochemical fluorination process varies somewhat from lot-to-lot and from plant-to-plant. The product that results from electrochemical fluorination is thus not a pure chemical but rather a mix of isomers and homologues. The commercialized POSF derived products are a mixture of approximately 70% linear POSF derivatives and 30% branched POSF derived impurities.” - The Science of Organic Fluorchemistry (3M, 1999) [64]

In other words, there is no such thing as a “pure C8” ECF process. From a 1999 booklet on the use of fluorinated surfactants[62] and from the PFSA patent [61], it is clear that fluorinated acids with eight carbon molecules merely have the “optimal” critical surface tension, where the difference with homologues is not even that large. As will become obvious in part 2, this “misunderstanding” had, for a long time, huge implications on analytical research in the environment.

In 2006, a voluntary “PFOA stewardship program” was initiated by the EPA [66], which can be considered as a direct outcome of the “Dark Waters” lawsuits. All eight companies addressed by the program (Arkema, Asahi, Ciba, Clariant, Daikin, DuPont, 3M/Dyneon, and Solvay Solexis) commit to reducing “PFOA and related chemicals from facility emissions and in product content by 95% no later than 2010, and to work toward eliminating PFOA from emissions and in product content no later than 2015”. However, the scope is notable: “PFOA, PFOA precursor chemicals, and related *higher homologues* from both emissions and product content” (emphasis added). In other words, only “C8” PFAS, their precursors and (rare) longer homologues are considered or reported, not the “by-products containing fewer carbon atoms” reported by Brice in 1956. The companies involved are also allowed to claim some of its available information as “Confidential Business Information”.

As observed a review by Ateia et al. in 2018, this directed most studies towards the fate, transport and remediation of long-chain PFAS ($C > 7$) [67]. In the C1-C3 range, only studies involving TFA were observed.

Evidence of anthropogenic TFA (2020-present)

The first publication to cast doubt on the theory of “naturally occurring TFA” was a study on the distribution of longer PFAS like PFOS, PFOA, PFHxS, PFBS, PFNA and PFOSA in oceanic waters [68]. PFOA was found at levels ranging from several thousands of pg/L in water samples collected from coastal areas in Japan to a few tens of pg/L in the central Pacific Ocean. More troublingly, deep-sea water samples, collected at depths >1000 m in the Pacific Ocean and the Sulu Sea, contained trace levels of PFOS and PFOA.

In 2020, Pickard et al. put the entire discussion on its head, by sampling ice cores from two locations in the High Arctic of Canada[37]. Pickard et al. observe that TFA, PFPrA and PFBA deposition in the Artic increased *significantly* starting around 1990, coinciding with the introduction of HFO's and HCFO's as a result of the Montreal Protocol (fig 1).

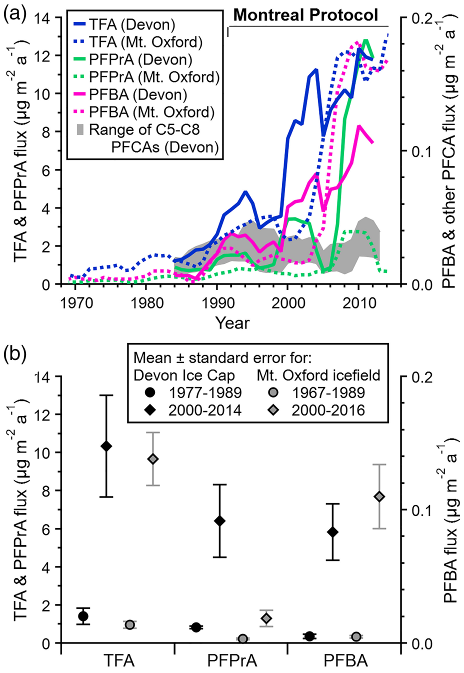

Figure 1: Five-year moving average deposition fluxes comparison of mean fluxes up to Montreal protocol

The models of Muir for the global emissions of C4-C14 PFAS showed a similar increase in global annual PFCA emissions [69]. While this model shows an expected drop in "PFOA-based" emissions after 2002, coinciding with the shift to "C4 chemistry", it doesn't hold into account a (potential) shift to even lower length carbon chains. (See below.)

In a seminal 2021 paper Joudan et al. pointed out numerous issues with the supposed evidence of "naturally occurring TFA" [38]. Only one out of four publications on the presence of TFA in pre-industrial freshwater actually show results above the limit of detection. As for the only counter-claim by Von

Sydow et al. [44], Joudan suggests that “data quality was hampered by modern contamination or that there were problems in the dating methods used to assign age”. One of the core observations by Joudan is that TFA can be released both directly and indirectly (via reactive precursors) as deposition as well as direct surface water discharges. Poor source apportionment, especially when strictly based on industry self-reporting, is not evidence of a natural source.

Misattribution of TFA to “natural sources” can be caused by multiple issues:

- Overestimation of the total amount of PFAS present in the Earth’s oceans [38]. An overestimation by, for example, an order of magnitude, would make source attribution *impossible*.
- Underreporting of emissions by the industry. This is not theoretical. In a 2020 permit request, 3M Belgium in “suddenly realised” that F-gas emissions (HFK-23) were underreported by 120 tons per year, equivalent to 1.78 Mtons of CO_2 [70], [71]. Satellite data from the Advanced Global Atmospheric Gases Experiment (AGAGE) had already indicated a severe underreporting of C2F6 emissions associated with 3M Belgium and/or a nearby and strongly PFAS related industrial process [72].
- Water-based emissions of ultrashort PFAS from production facilities and incineration facilities are currently not publicly monitored, nor reported and may prove to be a significant contributor to both ultrashort PFCA’s and PFSA’s, as well as their precursors. Several PFAS polyethers, including the AFFF, EMSD, Chemours and Solvay clusters described above, as well as numerous Fluoro-Agrichemicals [73] contain fluorinated carbon chains, prompting the obvious question: What happens when they inevitably get disposed (in a landfill or incinerated)? (See section on incineration of PFAS.)
- TFA and PFPrA have also been shown to be stable degradation products of modern PFAS surfactants like HFPO-DA/GenX under UV light in oxidative environments [74].
- Other non-anthropogenic source, such as degrading pesticides.

ToxStrategies

Aside from the already mentioned two “groups of influence”, another name appeared multiple times in critical aspects of the assessment of the toxicity of PFAS: ToxStrategies, a “multidisciplinary scientific consulting firm that strives to develop innovative solutions to address the scientific, technical, and regulatory challenges confronting our clients”. ToxStrategies has previously been implicated in helping stall regulation on Chromium VI (the carcinogenic substance featured in the “Erin Brockovich” story) [75], manganese [76] and aspartame [77]. In the case of Chromium VI, ToxStrategies was hired by the American Chemistry Council, a lobby organisation members of which include 3M, Chemours, DuPont, Daikin, Honeywell and Solvay.

On 25 November 2021, ToxStrategies first submitted a research paper called

“Assessment of the applicability of the threshold of toxicological concern for per- and polyfluoroalkyl substances” to the journal of Regulatory Toxicology and Pharmacology, which was published on 1 June 2022 [78]. The contents of this paper are discussed in the Part 2, Toxicity revisited, Cramer classification. Funding for this paper was provided by The Chemours Company FC, LLC.

On February 9, 2023, ToxStrategies published a report called “Evaluation of Approaches for Assessing PFAS Mixtures”, the contents of which are discussed in Part 2, Toxicity revisited, PFAS mixtures. This ToxStrategies report showed up in the same month (February 2023) as an attachment to 3M Belgium’s permit request for ultrashort PFAS emissions. The report was officially “prepared for Hogan Lovells, LLP”, which is curious as this is a law firm. The method used looks like a simple way to obscure the true beneficiary of this study. Lawyers from Hogan Lovells have previously represented The Chemours Company in court case 5:21-cv-01156, City of Corona et al v. 3M Company et al. [79]. Hogan Lovells has also represented 3M in the case 4:2022cv09001, The People Of The State Of California, Ex Rel. Rob Bonta, Attorney General Of California v. 3M Company et al., the case Golden State Water Company v. 3M Company, 2:20-cv-08897, (C.D. Cal.) and more.

The cost of Science Bending

Based on Lobbyfacts.eu data[2], the lobbying efforts of PFAS producing companies in the EU alone amount to an estimate 12-25 million € per fiscal year in total (fig 2). This seems more than enough for an significant, coordinated effort to “bend” regulation in the preferred direction.

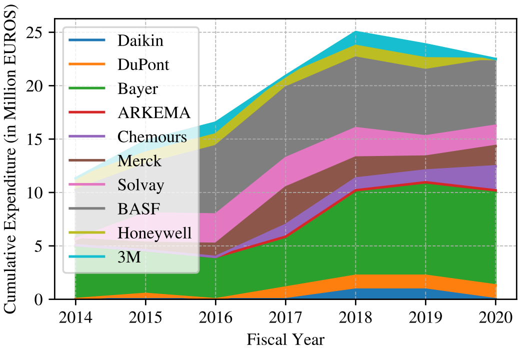

Figure 2: Estimated EU lobbying expenditures fluorochemical companies (source: Lobbyfacts.eu)

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[2] Some fiscal years were missing from the reporting for several companies, linear interpolation was used to fill in those gaps. As such, this should be considered an estimate.

Part 2: PFAS revisited

Background

The evidence found of “Science Bending” beyond CFC, the Tennant case and the controversy surrounding TFA clearly prompts a reconsideration of the potential sources of TFA (and other fluororganics) in the environment, specifically a general reconsideration of the fluorination production process and the environmental fate of perfluorinated products.

There are only a few critical and common production methods known for fluororganics [80], [81], which can be split into two main categories: a) The creation of the perfluorinated base products, in essence relatively short chains of fluorinated carbon atoms with an optional “head group”. b) Assembly of molecules of higher complexity. For the creation of base fluororganics two methods are commonly cited: (Fluoro)telomerisation and electrochemical fluorination (the “Simons process”). For assembly of fluororganics with a higher complexity/molecular weight, esterification and polymerisation are the most commonly used pathways.

However, as Matthias Kotthoff and Mark Bücking pointed out in 2018 [82], the structural diversity of PFAS molecules can lead to a high versatility of unknown target molecules, posing significant analytical challenges. As suggested by Kotthoff & Bücking, understanding the *amount, identity, mobility, toxicity, formation pathways and transformation dynamics of polymers and PFAS precursors* is critical if an attempt would be made to assess *the full environmental impact of this industry.*

3M’s ECF process

To create (sulfonic) surfactants, starting on a pilot scale in 1949, 3M has typically used the Simons Electro-Chemical Fluorination (ECF) process wherein organic feedstocks (hydrocarbons) are dispersed in liquid hydrogen fluoride, after which an electrical current is passed through the solution, causing the hydrogens atoms in de hydrocarbons to be replaced with fluoride. The ECF process was issued a patent in 1951[83]. Four 3M sites were using the ECF process in 1999: Cordova (Minnesota), Decatur (Alabama), Antwerp (Belgium) and the Cottage Grove pilot plant (Minnesota) [63].

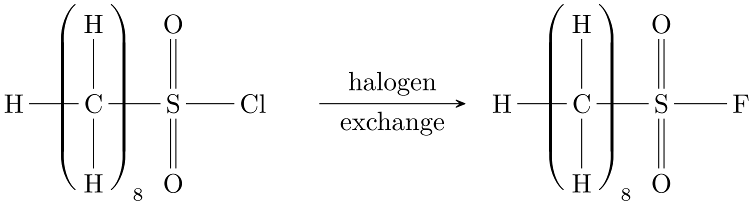
For 3M, two distinct phases merit attention: the era before 2002-2003 and the subsequent period, which marked a significant shift in their primary fluorination process.

The public and environmental focus predominantly centered around the “C8” PFAS, namely PFOS and PFOA, emerging from this process. Upon closely examining the elusive documentation and patents detailing 3M’s chemical processes, some significant details have eluded public and environmental oversight.

The underlying 1956 patent [61] describes the proces as follows:

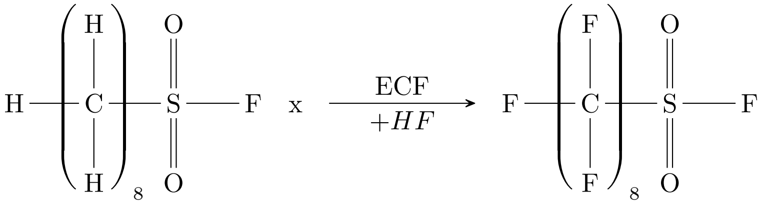
> "The key to this preparatory route is the electrolyzing of a mixture of anhydrous liquid hydrogen fluoride (HF) and an appropriate hydrocarbon sulfonyl halide starting compound (saturated or unsaturated) to provide a perfluorinated product having a saturated fluorocarbon group bonded to a sulfonylfluoride group in the molecule. The starting compound is soluble in the liquid HF and pro vides adequate conductivity."

Using 3M's (1999) process [63], [84], the "basic building block" is described to be 1-Octanesulfonyl Fluoride, obtained through a halogen exchange in a 1:1 ratio:



$$\mathrm{H}-\left(\mathrm{C}H_2\right)_8-\mathrm{S}(=\mathrm{O})_2-\mathrm{Cl} \xrightarrow[\text{exchange}]{\text{halogen}} \mathrm{H}-\left(\mathrm{C}H_2\right)_8-\mathrm{S}(=\mathrm{O})_2-\mathrm{F}$$

The next step in the proces is electro-fluorination itself, commonly described as follows:



$$\mathrm{H}-\left(\mathrm{C}H_2\right)_8-\mathrm{S}(=\mathrm{O})_2-\mathrm{F} \quad x \xrightarrow[+HF]{\text{ECF}} \mathrm{F}-\left(\mathrm{C}F_2\right)_8-\mathrm{S}(=\mathrm{O})_2-\mathrm{F}$$

As is clear from the molecular structures and confirmed in the 3M patent [61], this basic process would also work with longer or shorter sulfonyl chlorides. The reason for the focus on the "C8" length can be found in its use as a water repelling surfactant:

> "Once seven outermost carbon atoms are fully fluorinated, the wettability approaches that of the corresponding perfluorocarboxylic acid, 10dynes/cm. *A terminal perfluoroalkylchain of seven carbons is sufficiently long* to shield non-fluorinated segments beneath the fluorinated segments." - Chemistry & Technology of Fabric Preparation & Finishing (1992) [62]

In other words, C8 simply is the shortest perfluoroalkylchain with the desired physical characteristics. However, in accordance to this common process description, most environmental and toxicological research as well as legal cases in this period also focused on the so-called "C8" PFAS: PFOS, with the "O" indicating octane (8).

However, when the process description is further scrutinized, a more troubling picture emerges. As per 3M's records, merely 35-40% of the 1-Octanesulfonyl

Fluoride undergoes conversion to POSF. The rest (60-65%) results in a variety of *higher and lower straight-chain homologs*, essentially “shorter” or “longer” alkane structured PFAS, as well as *branched-chain isomers*, even *cyclic perfluoroalkanes.* The 1956 patent already mentions this issue:

> “By-products containing fewer carbon atoms than the starting compound are also formed due to the cleavage of carbon-carbon bonds in some molecules, and cleavage also results in the formation of non-cyclic by-product compounds when cyclic starting compounds are used.”

3M’s publication, authored by Tomasino, on the use of fluororganics in fabric preparation & finishing [62] also shows the fluorination industry is and was well aware of the relative insignifance of the carbon chain length in the context of fabric protectors. Tomasino describes both fiber surface application and monomer synthesis with generic PFAS chain lengths (fig 3 and 4). The difference in the critical surface tension of C3 PFCA/PFPrA and C8 PFCA/PFOA is described as differing only by about 1 Dynes/cm. The same (pre 1992) 3M documentation shows a difference in oil repellency of about 25-30% between C3 and C8 (unit unclear).

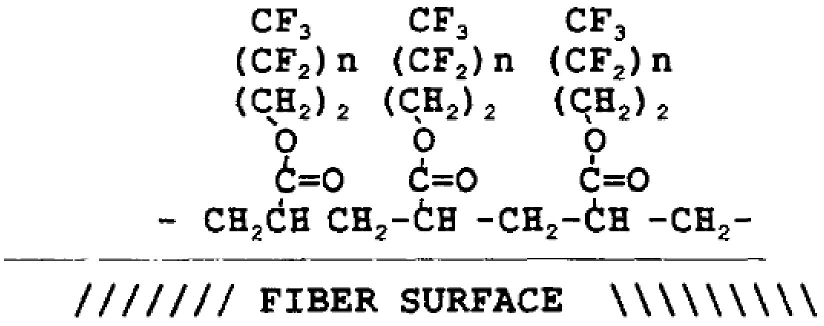
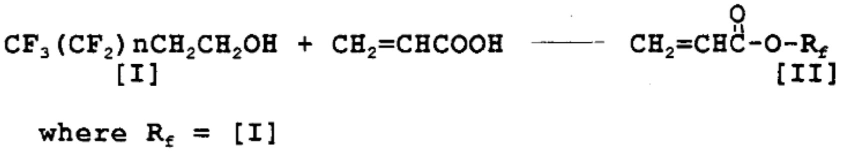


Figure 3: An generic fiber surface model of PFAS surfactants as applied to synthetic fibers (Tomasino, 1992)

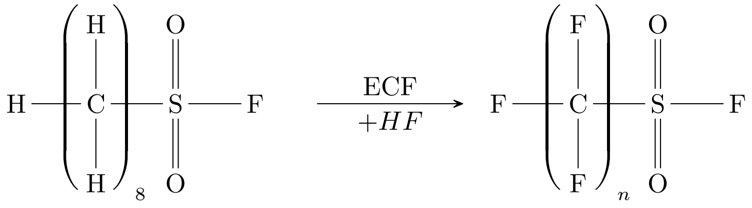


$$\underset{[I]}{CF_3(CF_2)nCH_2CH_2OH} + CH_2{=}CHCOOH \longrightarrow \underset{[II]}{CH_2{=}CH\overset{\overset{O}{\|}}{C}{-}O{-}R_f}$$

where R_f = [I]

Figure 4: Monomer synthesis (Tomasino, 1992)

A generalised chemical description of the ECF/Simons process would look like this (where $n \leq 8$), where both branched and cyclic perfluoroalkenes are *also* amongst the possible outcomes:



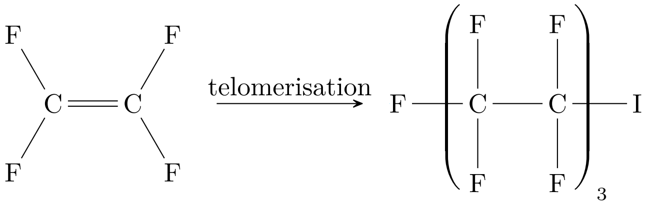
$$\mathrm{H{-}(CH_2)_8{-}S(=O)_2{-}F} \xrightarrow[+HF]{\text{ECF}} \mathrm{F{-}(CF_2)_n{-}S(=O)_2{-}F}$$

This explains the need for an extensive distillation step after the ECF process [85]. The first separation step in this "fractioning" process is quite imprecise, with only three separation stages (fractions) available: the "pre-fraction" ("low boiling"), "main fraction" and "post-fraction" ("high boiling"). These "high" and "low" fractions are fed back into the process. The ECF process continues until all that remains is "product", undesirably "short" perfluorinated molecules and heavy (long chain) perfluorinated "tar", further processed as waste. This observation negates the idea of a "pure C8" chemistry, which is in fact never literally described as such.

This non-specific production process was (re)discovered by Velayutham et al. in 2002 while fluorinating tripropylamine [86], supporting the view that the ECF process occurs mainly through a free radical pathway, resulting in the formation of all manner of byproducts.

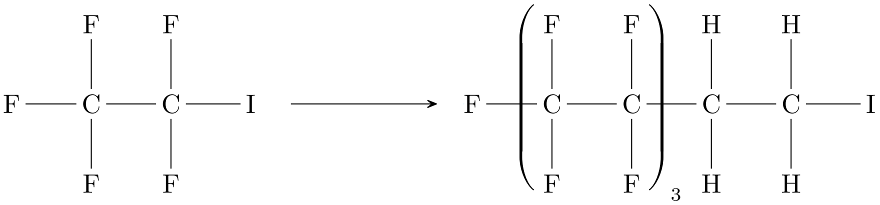
(Fluoro)telomerisation

Where 3M's original ECF process starts from a relatively large (C8) alkene, it is also possible to construct fluororganics using a feedstock composed of (short) fluorinated alkenes. The process is commonly depicted as follows:



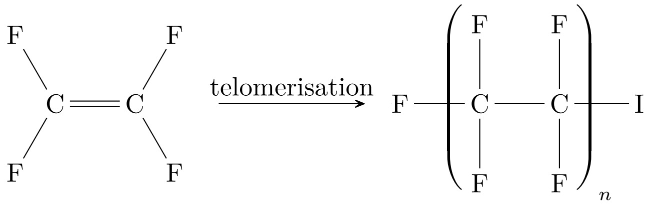
$$\mathrm{F_2C{=}CF_2} \xrightarrow{\text{telomerisation}} \mathrm{F{-}(CF_2{-}CF_2)_3{-}I}$$

and the following creation of the 6:2 FTS fluorotelomer:



$$\mathrm{F{-}CF_2{-}CF_2{-}I} \longrightarrow \mathrm{F{-}(CF_2{-}CF_2)_3{-}CH_2{-}CH_2{-}I}$$

However, it should once more be noted that this is not a deterministic process with only one fluorotelomer species as outcome. A more realistic description would be as follows:



And even this is not the entire picture, as there is an equivalent fluorotelomerisation pathway starting from HFP, which results in 5:3/7:3/… fluorotelomers.

Fluororganic production reconsidered

3M Belgium groundwater pollution

The PFAS pollution underneath 3M Belgium's facilities, available from publicly accessible environmental monitoring data from the years 2000 and 2022[^scatter], demonstrates the general principles of the ECF process (fig 5, fig 6, fig 6).

Groundwater tests were conducted in 2000 at 77 different locations on 3M factory grounds, years before a sanitation program was initiated. One significant outlier was omitted from figure 5 for readability, a sample which contained 257000 µg/L PFOS, 48000 µg/L n-PFHxA and 25200 µg/L PFOA. A scatter plot was chosen because of a large difference in LOQ between the ultrashort PFAS and the rest. This approach avoids having to assign substitute values to samples < LOQ.

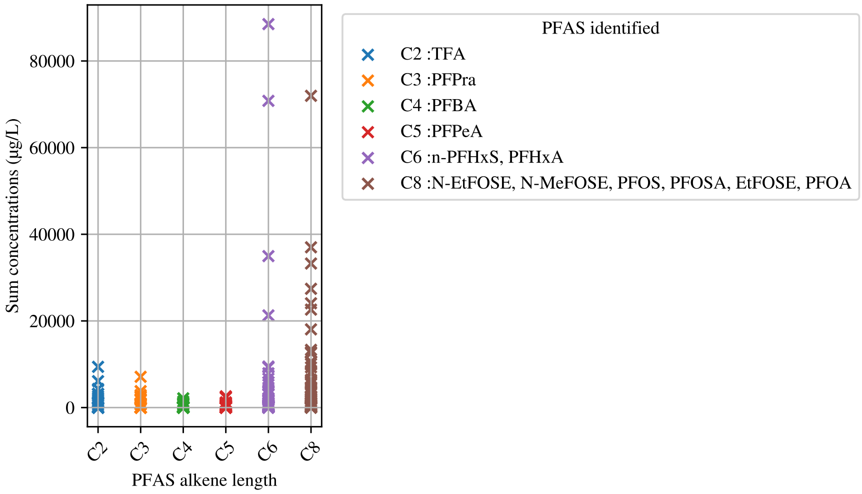


Figure 5: Concentrations of organofluorides in groundwater (2000)

As expected, the length of perfluorinated carbon chains found largely conforms to $n \leq 8$, with the “target length” C8 as dominant.

However, the groundwater testing conducted in 2000 also included two ultrashort PFAS (TFA and PFPrA) in a pattern that does not conform to what might be expected from Simon’s process. A different source must be assumed, possibly this is a degradation product of TFE/HFP based processes or a byproduct of incineration. Note that these groundwater measurements predate 3M’s shift to ‘C4’ chemistry in 2002, see section below where a more recent source of ultrashort PFAS is identified.

The differences between selected PFAS parameters in 2000 vs 2022 are also quite notable. First of all there is the complete absence of ultrashort PFAS in later monitoring data, where C4 (PFBS/PFBA) is used as the shortest organofluoride of interest. This confirms the concerns raised in part 1 regarding an industy-influenced misdirection away from these ultrashort PFAS. On the other hand longer carbon chains ($n > 8$) are also analysed and detected in 2022, which were not included in the 2000 monitoring. Note a slight preference for even numbered sulfonic acids (PFSA’s) is visible (C6 and C8), which does not appear in the carboxylic acids (PFCA’s).

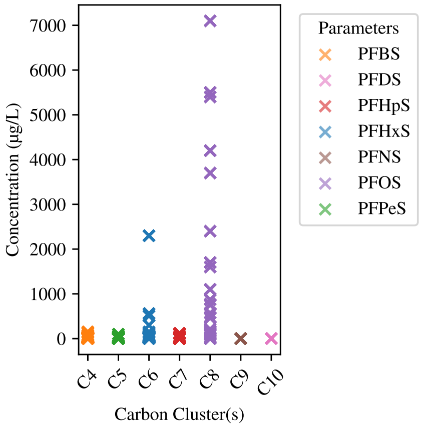


Figure 6: Concentrations of PFSA's in groundwater (2022)

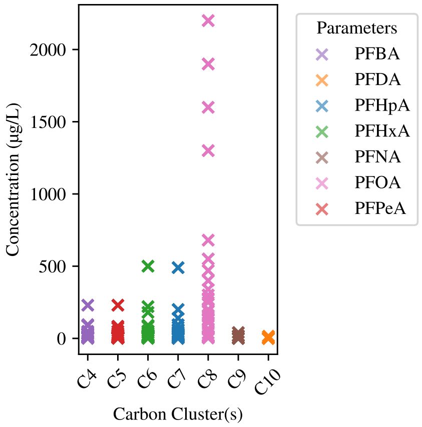


Figure 7: Concentrations of PFCA's in groundwater (2022)

C8-era surfactants in products

In 2009 EPA commissioned report that looked for C5 to C12 PFCA's in "116 articles of commerce", including carpet-care and similar households liquids, apparel and food wrapping paper. The results show a consistent distribution centered around C7-C8 PFCA for most consumer products (fig 8). For non-woven medical garments, the results suggest that "C4" chemistry might already be showing up as a replacement. The only real exceptions are thread seal tape and dental floss, where a distinct "C8-only" pattern can be found.

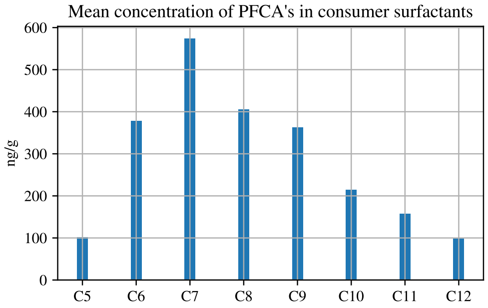


Figure 8: Mean concentrations in consumer products with PFCA surfactants

This pattern matches remarks made by Hoechst, DuPont, 3M and Merck experts in section "Fluorine Compounds, Organic" of the Encyclopedia of industrial chemistry [80]:

> Impurities are usually removed from organic fluorine compounds by fractional distillation, fractional crystallization, or chromatographic methods. This does not apply to fluoropolymers and high-boiling perfluorinated oils, which require special measures, i.e., the use of extremely pure starting materials.
>
> Long-chain perfluoroalkanecarboxylic acids and their salts are surface-active chemicals (surfactants), which greatly reduce the surface tension (surface energy) of water, aqueous solutions, and organic liquids even at low concentrations. These acids (*C6–C12*) and derivatives are used as wetting, dispersing, emulsifying, and foaming agents.

As a general rule, it would appear PFCA-based surface-active products (often called surfactants or "protectives") are the result of a *minimally* fractionated (electro)fluorination output, consisting of a distribution around the "target" carbon chain length. Only when applied to (fluoro)polymers or other specialised applications are further measures taken. Understanding this fundamental aspect quite obviously changes subsequent environmental exposure, as there is, in most scenario's, simply no such thing as "C8-only" exposure, simply due to this production process.

Unfortunately, as the "116 articles of commerce" study demonstrates once more, analysis of PFAS chains of either the PFCA or PFSA variety limit the shortest carbon chain at C4 or up, in this case, even at > C5/C6.

The C4 transition (3M)

Under the pressure of various lawsuits, both 3M and eventually Chemours changed their PFAS chemistry. 3M Belgium did so in the period by the end of

2001 [84], by officially switching to “C4 chemistry”. The presumption here is that these shorter chains have a lower potential for bio-accumulation and (therefore) lower toxicity profiles. However, this transition to shorter PFAS alkanes did not appear to coincide with a matching shift in environmental monitoring of towards “ultrashort” analytical PFAS parameters. As demonstrated in the groundwater measurements at 3M Belgium in 2022, most governmental environmental monitoring data is limited to “C4 and above”. In fact, ultrashort C1-C3 PFAS are sometimes not even mentioned in general overviews like naming conventions [40].

However, one internal 3M laboratory test labeled “amine washing waters” was discovered from this period [87]. When analysed for alkene chain length, a non-specific distribution emerges (fig 9).

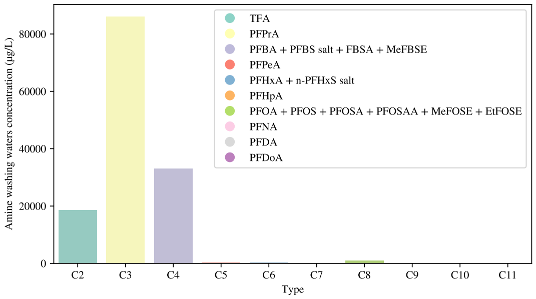


Figure 9: Concentrations of alkenes in amine washing waters

It should be noted that these particular concentrations were present in process water that has not passed 3M’s waste water filtration system (yet). Both PFPrA (C3) and TFA (C2) are clearly significant components of the “C4” amine production process. The reporting limits for TFA and PFPrA are listed as 0.5 mg/L.

Not until a complaint was made by the author to environmental services regarding the fact that 3M did not have an emission permit for these “ultrashort PFAS” (TFA and PFPrA specifically), was this discrepancy noticed and handled. This complaint resulted in environmental permit request for these ‘missing parameters’ with quite a bit more information (and confirmation) regarding these ultrashort parameters [88]–[90]. Notably:

- 3M has in fact developed and had access to its own analytical (LC/MS)-based method for determining ultrashort PFAS since 2000 or even earlier.
- Ultrashort PFAS are indeed present in high concentrations in process water. Based on 38 samples, the following mean concentrations were reported for previously undisclosed PFAS in process water: 23 µg/L TFA (max 78 µg/L), 769 µg/L PFPrA (max: 6770 µg/L), 72 µg/L PFBSi (max: 250

µg/L), confirming the relative dominance of “C3” (PFPrA).[3]

- Ultrashort PFAS are *also* present in 3M’s rainwater effluent, with mean concentrations of 22 µg/L for TFA and 15 µg/L for PFPrA (not TFMS was reported). (See the section on TFA below.)
- The permit request splits PFPrA from its isomers 2333-TFPrA and 2233-TFPrA, reporting separate analytical results and requesting a separate emission norm from PFPrA.

3M also provides an explanation on the origins of these ultrashort PFAS[4], essentially confirming the above theory regarding non-specific PFAS production, while simultaneously putting PFAS-based liquids used in electronics on the map.

> “Wastewater streams contaminated with PFAS are mainly derived from EMSD[5] production and the production of C4-based protectives and advanced materials.”

After grouping the reported mean concentrations of PFAS monoethers in reported production water, a familiar pattern emerges (fig 10).

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[3] Since it is easy to arbitrarily dilute process water, the absolute concentrations are not useful for analysis.

[4] Original Dutch language sentence: “Met PFAS vervuilde afvalwaterstromen zijn voornamelijk afkomstig van de EMSD-productie en de productie van *C4-gebaseerde protectives en geavanceerde materialen*.”

[5] Inert liquids for applications in electronics (Electronic Materials Solutions Division, EMSD)

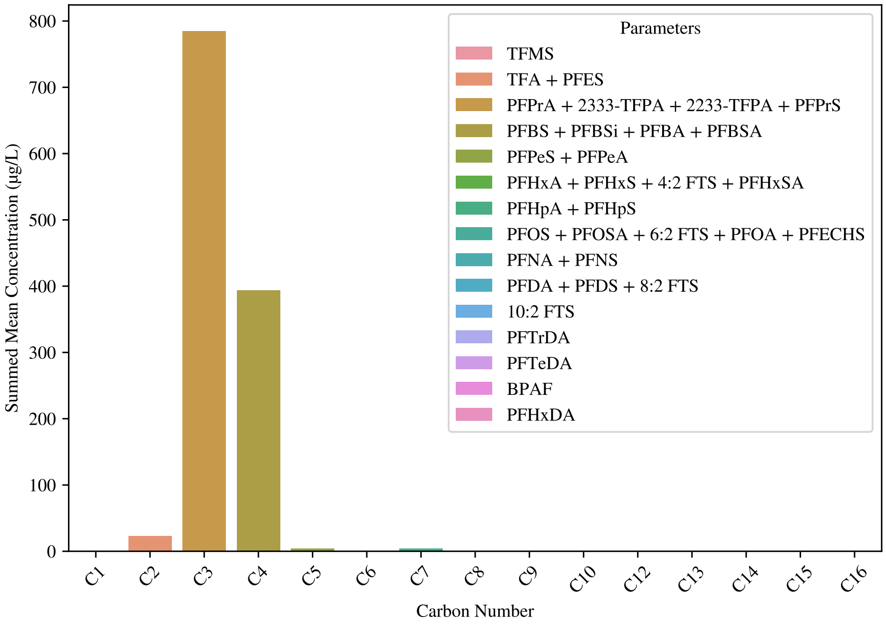


Figure 10: Summed mean concentrations of monoethers grouped by carbon number in EMSD production water

The report also, interestingly, reports concentrations of a series of polyethers which are most likely the “EMSD and/or C4-based protectives and advanced materials” products referred to (fig 11).

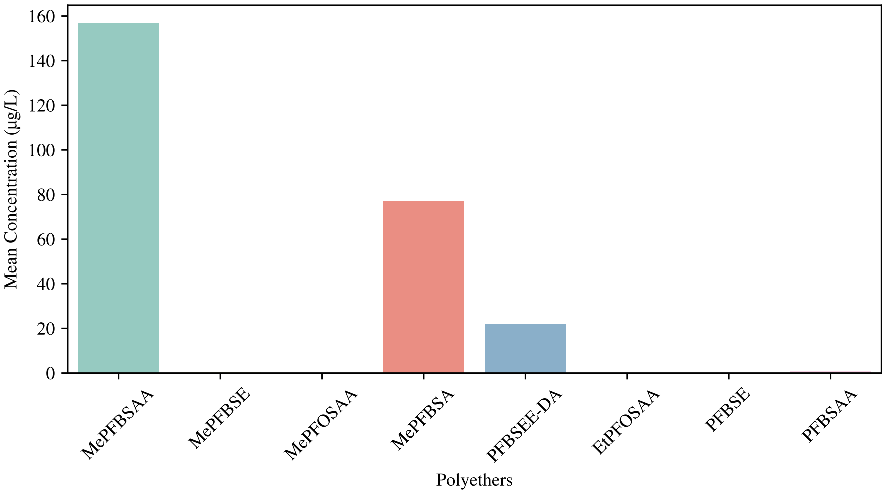
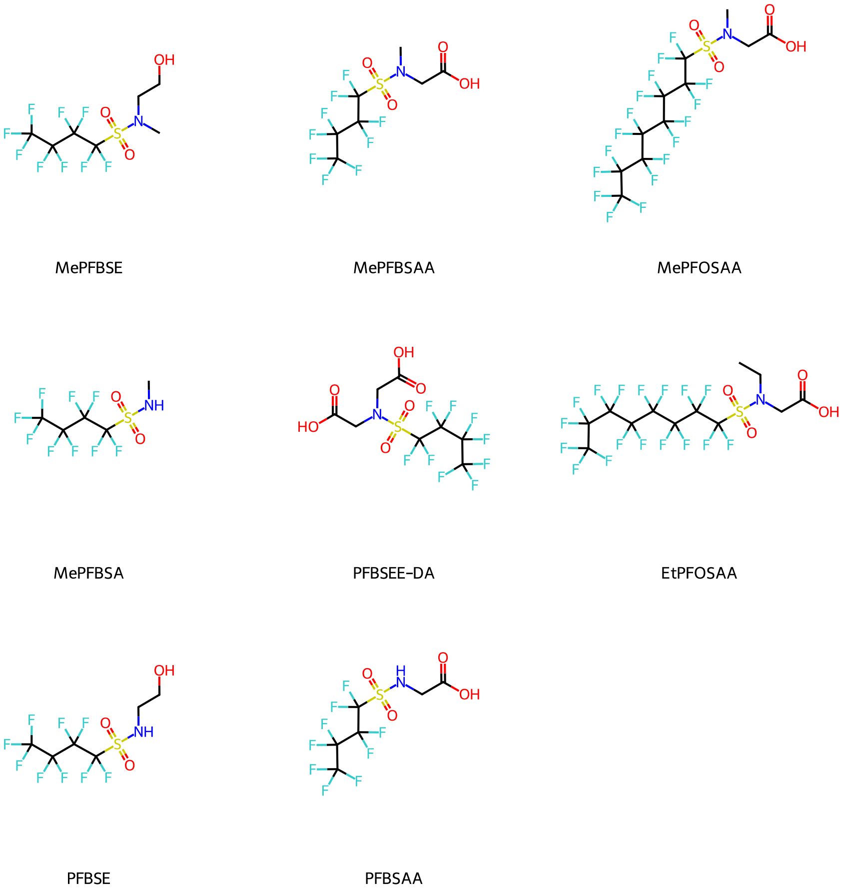


Figure 11: Mean concentrations of polyethers in EMSD production water

Some of the molecules in question are indeed “C4-based”, combined with traces of C8-based polyethers, possibly legacy products (fig 12).



MePFBSE

MePFBSAA

MePFOSAA

MePFBSA

PFBSEE-DA

EtPFOSAA

PFBSE

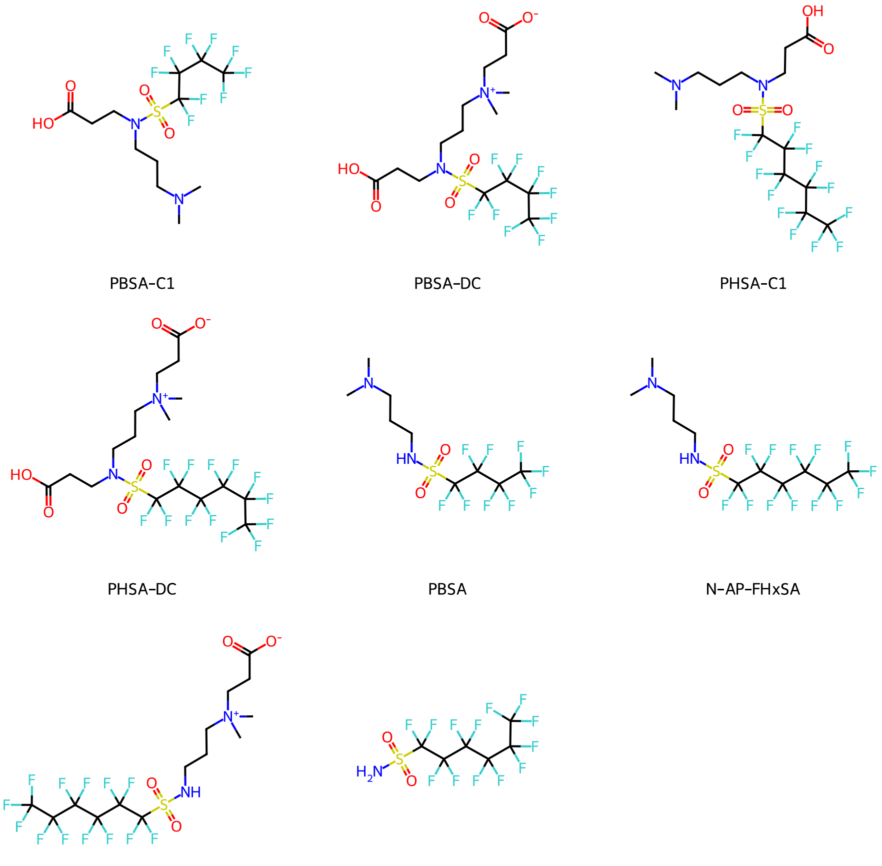
PFBSAA

Figure 12: EMSD related polyethers

In the evaluation of the efficiency of 3M's filtration systems, it is noted that one of the "corner stones" in the production of EMSD Novec 1230 is a substance codenamed "C3AF" [90], which is described as "a volatile compound that degrades to PFPrA when it comes into contact with water". This appears to confirm the idea that these products are made with more than just "C4". The use of such a codename to obscure a critical element in the production process falls within a repeated pattern of behaviour.

The permit request also contained a paper called "Evaluation of Approaches for Assessing PFAS Mixtures" by ToxStrategies and analytical information on "Soluble Organic Fluoride" (SOF), both of which will be discussed separately.

For completion, 3M also produces a series of molecules associated with "historical" AFFF[6] (fig 13). These were not part of the available environmental monitoring. They consist of both recent "C4-based" PFAS chemistry as well as "C6", making the term "historical" a potential misnomer.



PBSA–C1 PBSA–DC PHSA–C1

PHSA–DC PBSA N–AP–FHxSA

PHSA–C2 FHxSA

Figure 13: AFFF related polyethers

The Chemours transition

> "DuPont developed a new polymerization aid to replace the use of PFOA in the manufacture of fluoropolymers. DuPont stopped manufacturing and using PFOA in 2013, well ahead of the schedule to which it had committed." - "Teflon education" from the current Chemours website [91]

---

[6] Fire Fighthing Foams. These molecules were listed as the ingredients of "3M Fluorocarbon Analytical Standard #1 for quantitative analysis of PFAS related to historical AFFF".

Following 3M's switch to "C4 chemistry" as outlined above, Chemours (formerly DuPont) announced a similar change away from "C8 chemistry". As a result of a consent order in 2019 between the State of Carolina, Cape Fear River Watch (a local NGO) and Chemours, monitoring information became available on the presence of PFAS and other Chemours products in the Cape Fear river [92]. One of the more interesting datasets to come out of this involves the monitoring of "raw" (river) water by the Cape Fear Public Utility Authority (CFPUA) at their Sweeney drinking water facility, which sits downstream of the Chemours "Fayetteville Works" production facility. Many of the monitored parameters appear to have been discovered by Hopkins, Sun, DeWitt and Knappe in 2018 [93].

Building on a methodology used by Hartz et al. ([94]), we computed a correlation matrix across the diverse parameters in the CFPUA data. Four clusters could be identified using this method[7]. A clear PFCA (lineair PFAS with a carboxylic acid head group) cluster can be identified with a distinct "PFAS soup" signature around C5-C6. The high correlation can only really be explained if there is a common (industrial) source[8].

---

[7] It should be noted that some parameter correlations are false positives, mainly due to missing or extremely sparse analytical data. These were removed from the analysis. Unfortunately, PFPrA was only monitored starting in 2023, which yields insufficiently strong correlations with various other molecules. Other typical ultrashort PFAS (TFA, TFMS, PFEtS and PFPrS) are simply not monitored at all. (See section below.)

[8] PFOA has a higher concentration than expected, which may be due to a secondary source for this particular molecule, which still has a high correlation with the other (hypothesized) PFCA source.

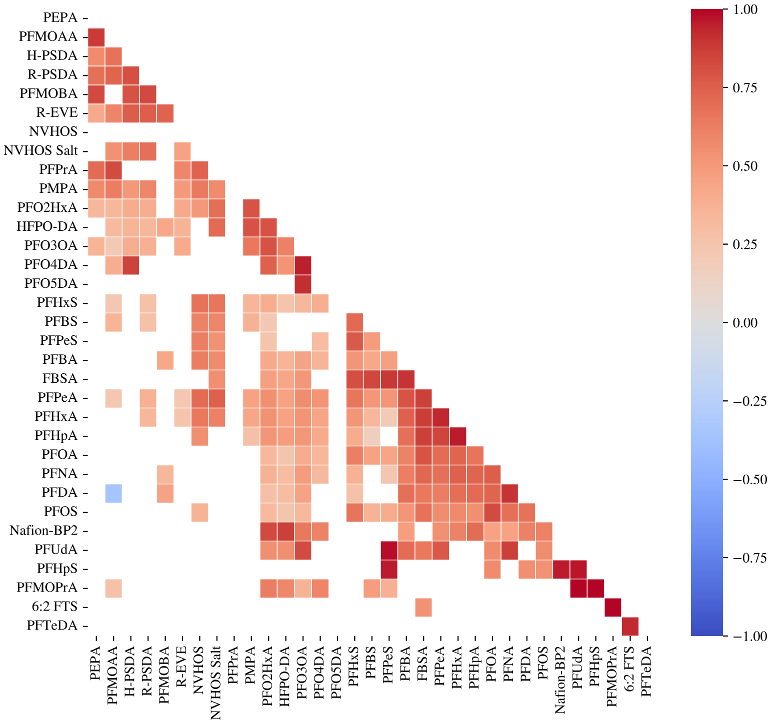


Figure 14: Correlation matrix “Sweeney raw” (filtered for $p < 0.01$)

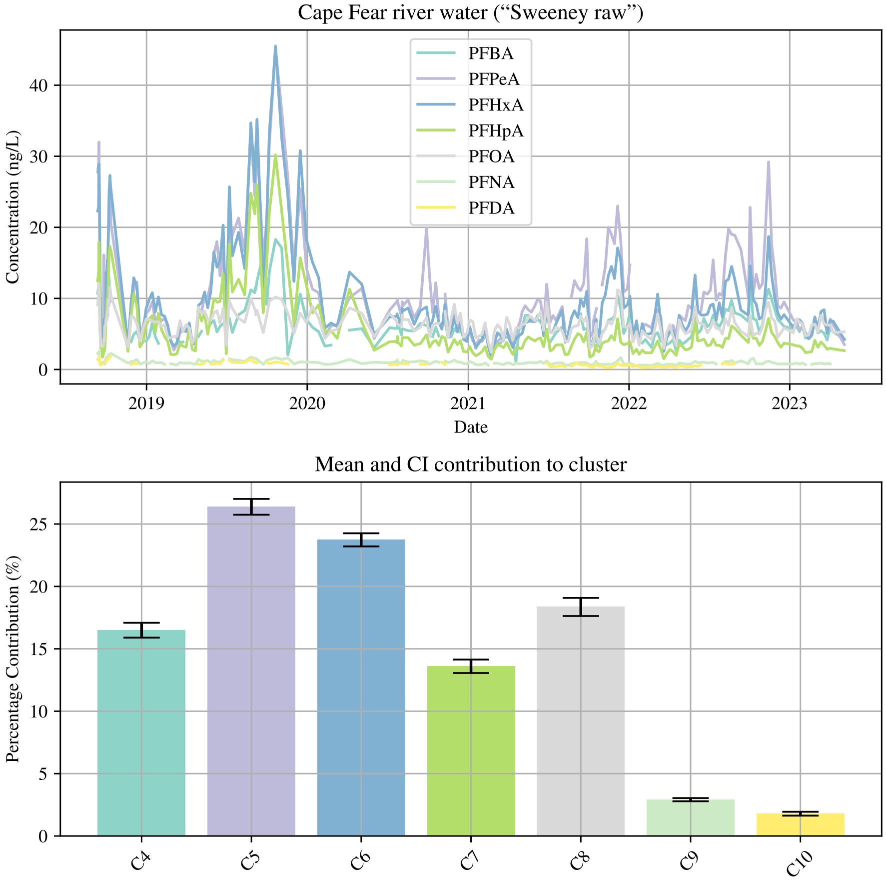
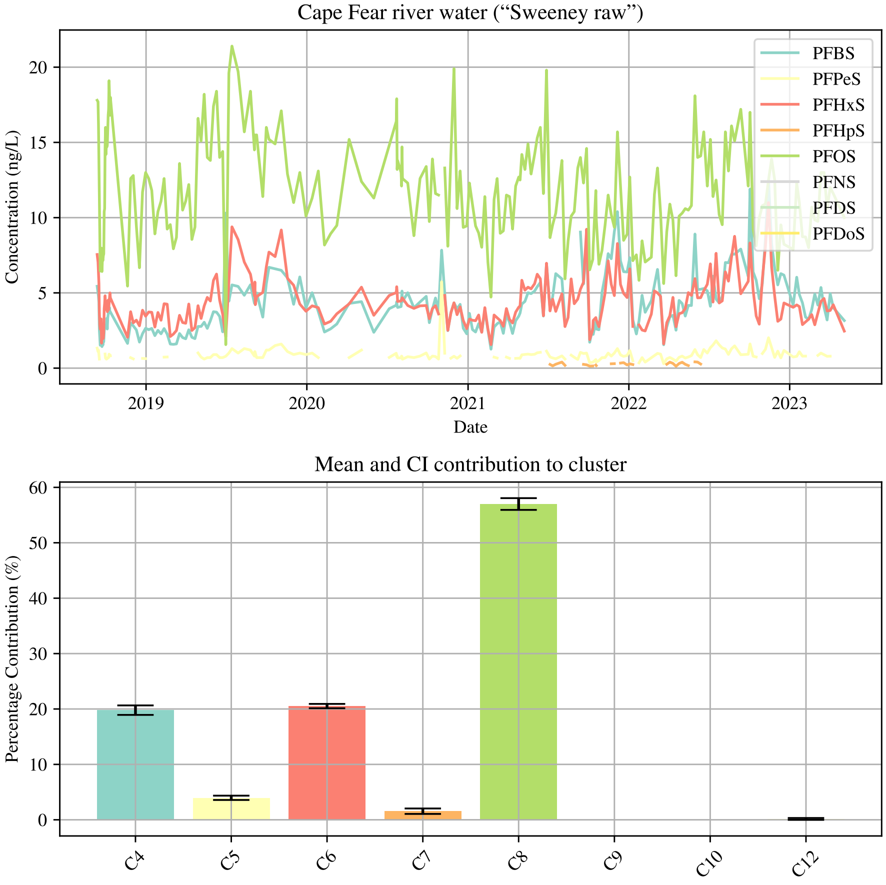


Figure 15: PFCA cluster in "Sweeney raw"

The PFCA cluster immediately points to problems similar to those of 3M's C4 chemistry: Environmental exposure to a single PFCA seems highly unlikely, prompting questions about the cumulative toxicity of these particular PFAS soups. It is also obvious that ultrashort PFAS (TFA and PFPrA) are likely a part of the Chemours "C6 soup".

Additional Cape Fear clusters

The PFSA (lineair PFAS with a sulfonamide head group) cluster is just as pronounced as the PFCA cluster. The "evenness" of PFSA parameters suggests (fluoro)telomerisation as the origin (fig 16).

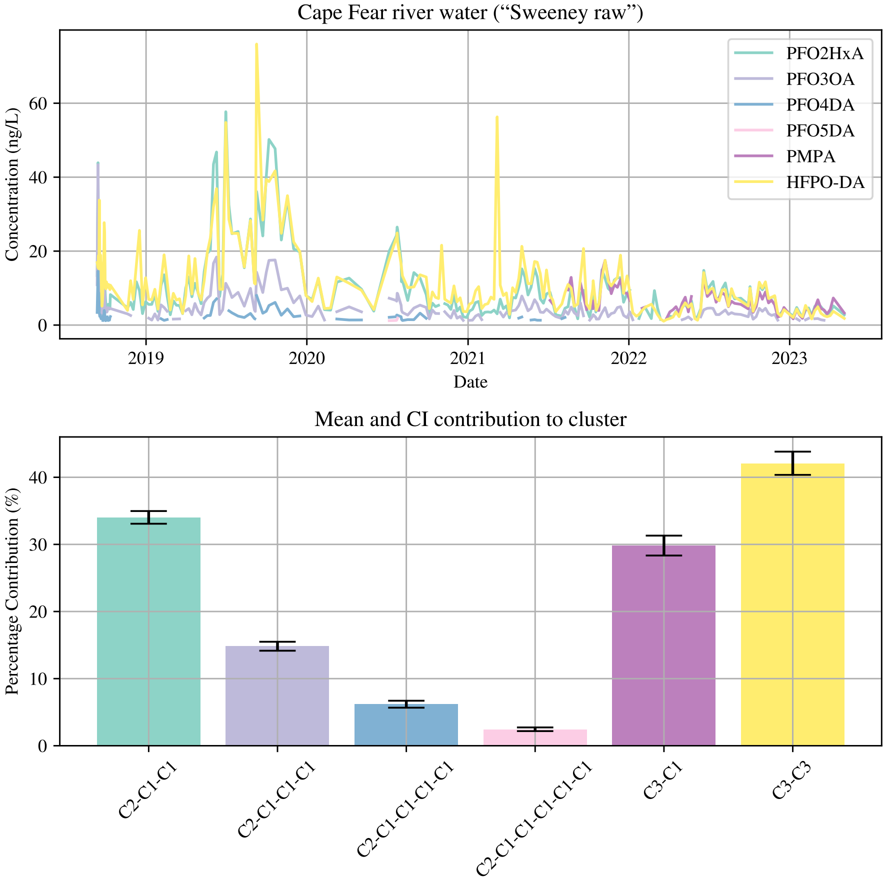


Cape Fear river water (“Sweeney raw”)

Mean and CI contribution to cluster

Figure 16: PFSA cluster in “Sweeney raw”

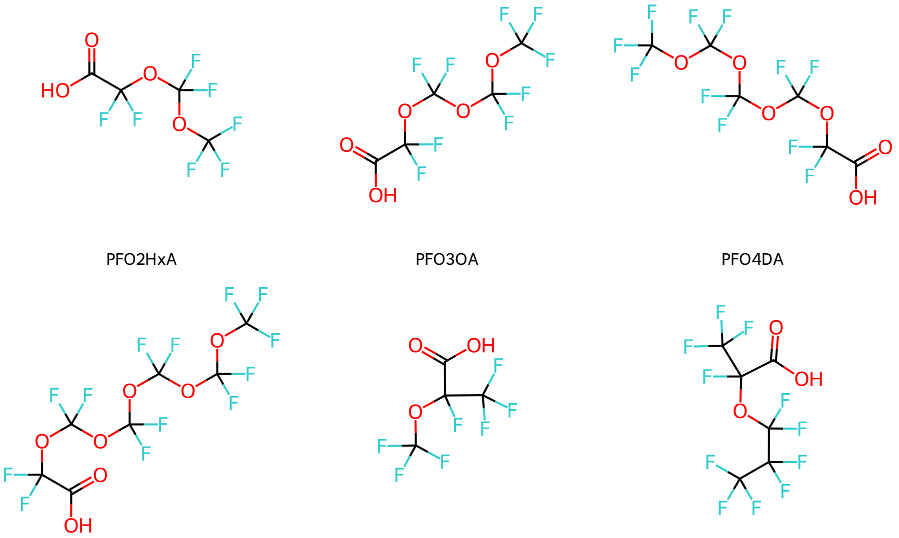
A cluster of polyether PFCA’s was also identified (fig 17), consisting of PFAS composed from multiple alkenes (fig 18), including HFPO-DA (better known as “GenX”) and PMPA (quite similar to HFPO-DA). These polyether PFCA’s were first discovered in the Cape Fear river in 2015 by Strynar et al, which may explain how they ended up in the 2019 consent order and in eventual monitoring by the CFPUA. Although more research would be needed for a definite conclusion, the obvious explanation for this cluster would be a *non-specific* second stage production process. If this is indeed the case, one way to confirm this theory would be to do targeted analysis on polyethers with other combinations of ultrashort monoether PFECAs (C1-C3).



Cape Fear river water ("Sweeney raw")

Mean and CI contribution to cluster

Figure 17: Cluster of polyether PFCA's in "Sweeney raw"



PFO2HxA PFO3OA PFO4DA

PFO5DA PMPA HFPO-DA

Figure 18: Polyether PFCA's

A similar cluster of polyether PFSAs, composed with monoether PFSA's (fig 20), was also discovered (fig 19), which correlate strongly with "R-EVE". The available data here is however quite sparse compared to the other clusters.

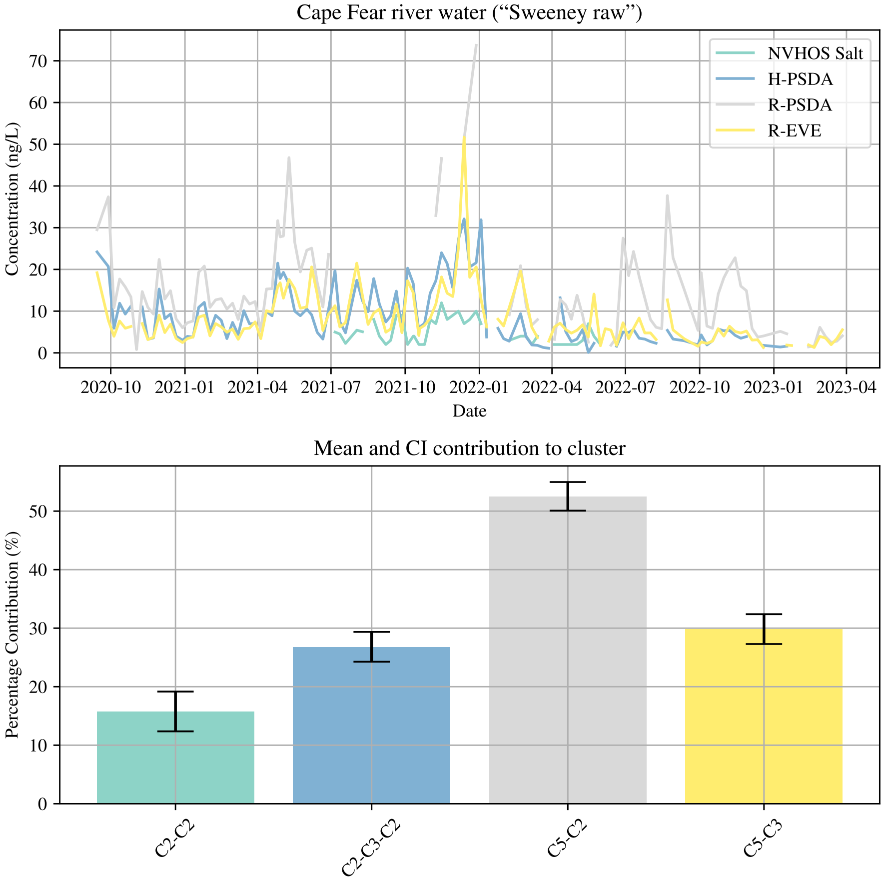
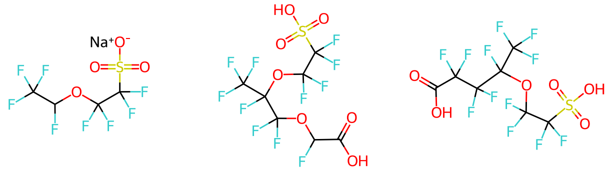


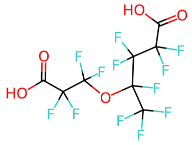
Figure 19: Cluster of polyether PFSA's in "Sweeney raw"



NVHOS Salt

Hydrolyzed PSDA

R-PSDA

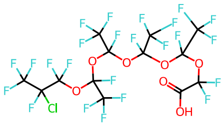


R-EVE

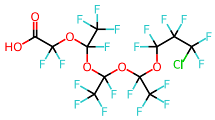
Figure 20: Polyether PFSA's

The Solvay ClPFPECA cluster

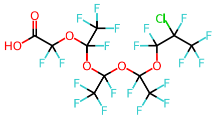
In 2020, Washington et al. [95] employed a method similar to Strynar et al. [96] to detect undisclosed PFAS released by Solvay in New Jersey soil. As the group had no access to analytical standards, which Solvay refused to provide, they started from the tentative identification of one Solvay product congener. Based on literature and specific patterns found in mass spectrometry (split peaks with a distance equal to a molecular fragment, as suggested by Strynar), they detected a wide cluster of chloroperfluoropolyether carboxylates. As is clear from figure 21, these molecules are all based on a Fluorinated C3 mono-ether with a single Chloor atom, estherized with perfluorinated C2-C3 (ethyl-propyl) clusters, including one carboxylic acid. This finding again points directly to a non-specific production method that allows for the creation of a wide range of (regio)isomers and (regio)homologs. This is more of a combinatorial problem than a classic chemical reaction formula.



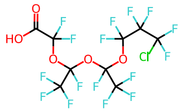
ClPFPECA congener 4,0



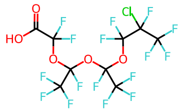
1–ClPFPECA 3,0



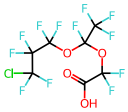
ClPFPECA congener 3,0



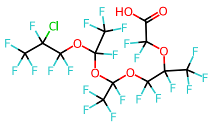
1–ClPFPECA 2,0



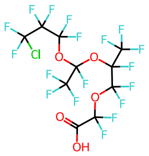
ClPFPECA congener 2,0



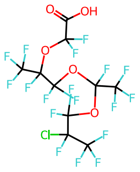
1–ClPFPECA 1,0



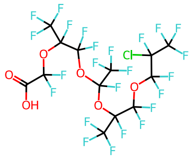
ClPFPECA congener 2,1



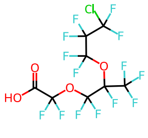
1–ClPFPECA 1,1



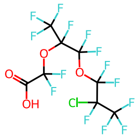
2–ClPFPECA 1,1



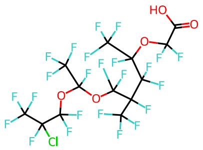
ClPFPECA congener 1,2



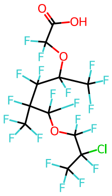
1–ClPFPECA 0,1



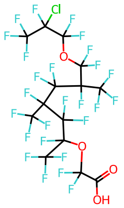
2–ClPFPECA 0,1



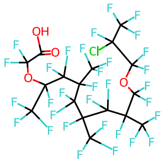
2–ClPFPECA 1,2



2–ClPFPECA 0,2



2–ClPFPECA 0,3



2–ClPFPECA 0,4

Figure 21: Group of chloroperfluorinated polyethers (Solvay)

Incineration and degradation

While many organofluorides are chemically and thermodynamically *quite* stable, they are not completely indestructible. What then is the environmental fate of (per)fluoropolymers, perfluoromonoethers and perfluoropolyethers? It must be assumed they eventually end up either directly in the environment as waste (landfills, direct emissions in water/air, etc) or in a waste incinerator. In 2015 Gardiner already reported a worldwide yearly demand for fluoropolymers of 200 000 tonnes, which has only grown since [97]. This most likely makes fluoropolymers the largest segment in the fluorination industry by mass, of which the environmental fate will be largely similar to that of regular plastics.

3M was already well aware of the effect of high temperatures on PTFE (Teflon), starting somewhere between 200 and 400°C. Figure 22 shows that the transition found by Bryce from an hourly weight-loss of 0.0002% to almost 0.1% per hour is extremely rapid between 316 and 420°C, indicating critical failure.

> "This fact should be carefully borne in mind in considering the properties of the polymer of tetrafluoroethylene. It will be recalled that the energy required to break a carbon-to-carbon bond in a fluorocarbon is about 83 kcal per mole and that of the carbon-fluorine bond is approximately 116 kcal per mole. It is then not surprising that the polymer of tetrafluoroethylene is less stable to high temperatures or high energy radiation sources than a simple fluorocarbon such as $C8F18$, since the energy of formation of the polymer from the monomer is much lower than that of either the $C-C$ or $C-F$ bonds. These points will be considered further in the light of some of the properties of fluorocarbon polymers in a later section.
>
> Of course, these same energy relationships also exist among hydrocarbon polymers as compared to true hydrocarbon molecules, at least so far as thermal or radiation degradation are concerned, but are often masked due to the presence of the highly reactive $-C-H$ bond as contrasted to the very inert $-C-F$ bond.
>
> The data in Table XLVIII illustrates the fact that there are definite, though small, changes occurring in the polytetrafluoroethylene molecules even at temperatures as low as 200°C. It has been determined that these weight losses are associated with the evolution of gaseous decomposition products and at least at temperatures below 400°C may be due to structural defects introduced during polymerization with energies of formation lower than either the $-C-C-$ or $-C-F$ bonds. The principal product formed is the monomer, C_2F_4, with trace amounts of products such as CF_4, C_3F_6, C_4F_8."
> - "Industrial and Utilitarian Aspects of Fluorine Chemistry" H.G. Bryce (1962) [98]

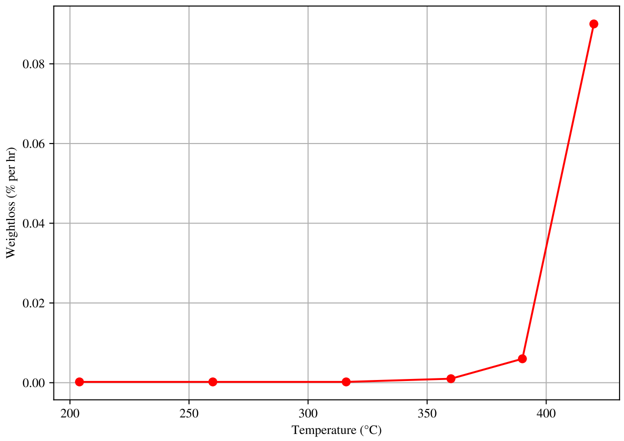


Figure 22: Table XLVIII: degradation of PTFE (Bryce, 1962)

This problem was experimentally confirmed in 1975 by R.S. Waritz, an employee of Haskell/DuPont [99]. Waritz reports a 4% weight loss per hour of PTFE at a temperature of 450°C. Figure 23 shows the rapidly rising concentration of TFE, HFP and - from a temperature of 475°C - of PFIB (perfluoroisobutylene). Waritz also reports how overheating a Teflon (PTFE) coated pan is known to be lethal for nearby pet birds, confirmed in 2016 by Caekebeke et al [100]. Exposure to the gases coming off of an overheated PTFE product is also known by Waritz and DuPont to cause a condition colloquially called "teflon flu". The report claims this isn't a real hazard in home and commercial kitchens, yet precisely such as scenario was reported in 2015 by Hamaya et al. and other cases, lung damage has sometimes been observed [101].

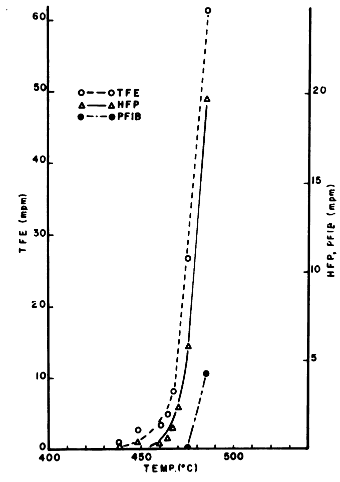


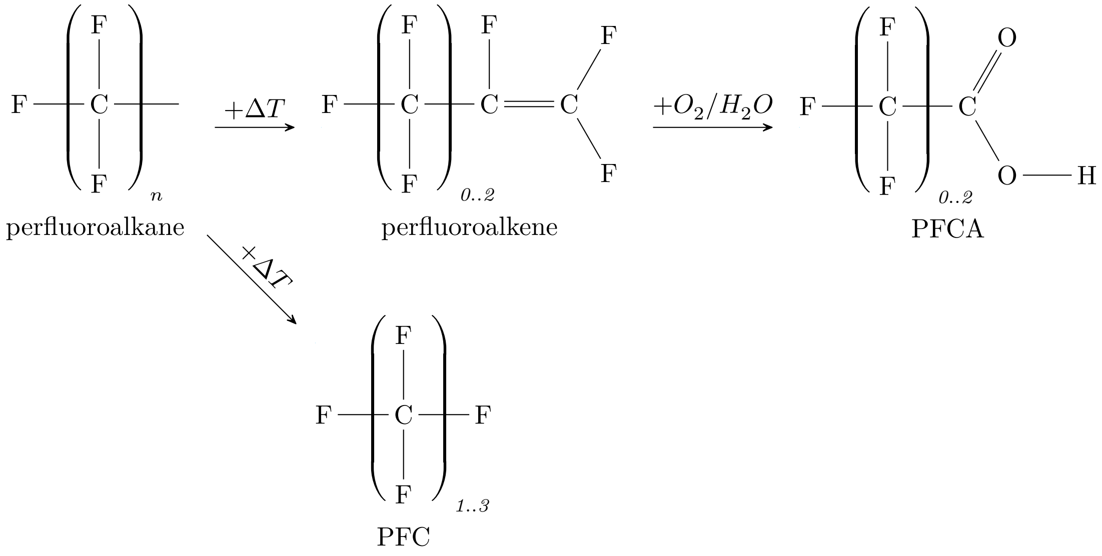
Figure 1. Evolution of (○) tetrafluoroethylene, (△) hexafluoropropylene, and (●) perfluoroisobutylene from polytetrafluoroethylene resin as a function of temperature.

Figure 23: Degradation of PTFE als reported by DuPont/Waritz (1975)

The production of greenhouse gases PFC-14 and PFC-116 by fuel-rich combustion of PTFE was confirmed experimentally by Garcia et al in 2007 [102]. However, where Garitz detected unsaturated fluorinated gases (C_2F_4, C_3F_6 and C_4F_8), Waritz's experiments mostly show saturated greenhouse gases (CF_4, C_2F_6) as the product of the thermal destruction of PTFE. Following theoretical frameworks provided by Burgess [103] and Ellis [104], a simplified general mechanism can be conceptualised where “fragments” of the fluorinated chain break off in the form of highly reactive radicals. These radicals create “unsaturated” alkenes (fluorinated carbon molecules with a double C=C bond) as well as “saturated” fluoroalkanes.

As evidenced by Waritz, there is a predisposition towards ultrashort fragments with carbon length distribution increasing with heat. The saturated fluoroalkenes correspond with the greenhouse gases CF_4 (PFC-14), C_2F6 (PFC-116) and - less often studied - C_3F8 (PFC-218). The unsaturated fluorocarbons are not stable and will preferably degrade into PFCA in atmospheric conditions (availability of oxygen and water), as modelled by Adi and Altwarawneh [105]. The expected emission of PFCA's from water-to-energy plants was experimentally confirmed by Björklund et al. [106], where PFBA was found to be dominant in flue gas emissions. Note that Björklund et al. unfortunately did not consider PFCA's $< C4$, possibly due to a the lack of available standards from Wellington Laboratories. PFHxA was found to be dominant in treated process water. The systematic investigation by Awad et al. into PFAS from water residuals in Swedish incineration plants suffers from the same “C4” limitation [107]. Yang et al. observed the degradation of PFOA into short(er) chain PFCA after electro-oxidation, with a preference for shorter chains (PFPrA) rather than longer homologues (PFHpA) [108].

In summary, the incineration of fluoropolymers or PFAS surfactants can be represented by a fairly simple process diagram:



Not only does this match the description by Bryce, it can also explain the discrepancies between different studies (e.g. Garcia vs Waritz), simply by considering both the effects of temperature, the availability of O_2 and H_2O and which parameters were actually monitored. This can very well explain the wide range of reported main degradation products of PTFE at different incineration temperatures in the 2009 NILU literature survey [109]. While n can be very large (in the case of Teflon/PFTE style fluoropolymers), this model theoretically also covers molecules typically found in surfactants ($C6 - C12$). It is also easy to see that the alkane-alkene transformation is inverse to the same proces used in the creation of fluoropolymers. Due to the polarity of PFCA's, their environmental fate will typically be water emissions and/or deposition [23]. Perfluorinated alkenes (TFE, HFP), which will degrade to PFPrA and TFA, are reported to occur in incineration processes involving various fluoropolymers up to 850°C [102], [109] and may occur at higher temperatures as well. In fact, the complete destruction of CF_4, the smallest saturated fluorocarbon is widely reported to only occur at temperature above 1400°C [103], [110], [111].

PFC's will mostly end up as atmospheric greenhouse gases with extreme atmospheric lifetimes and high warming potentials [72]. The background (Mauna Loa) atmospheric concentrations of (saturated) PFC-14 (CF_4) and PFC-116 (C_2F6) show a very distinct linear (fig 24) growth rate (PFC-218 was not available in the AGAGE/NOAA dataset). The growth rates are 0.7382 ppt per year (95% CI [0.7322-0.7442]) for PFC-14 and 0.08317 ppt per year(95% CI [0.0829-0.0835]) for PFC-116.

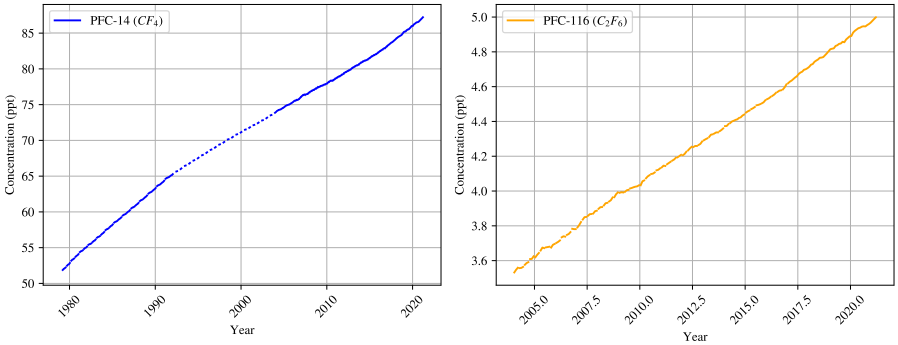
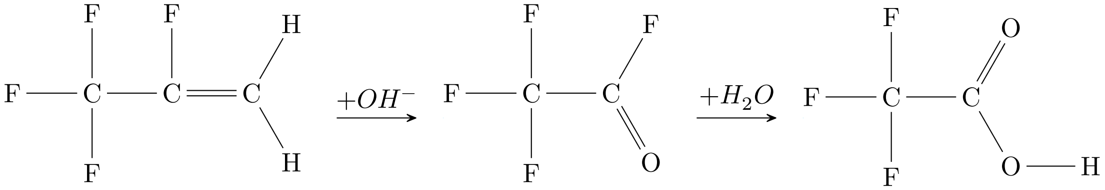


Figure 24: Atmospheric concentration of PFC's at Mauna Loa

Similar pathways to PFCA's also exist for partially fluorinated compounds. An example can be found in the environmental degradation of HFO-1234yf, a commonly used cooling gas sold as "Opteon"[112]. Wang et al. estimate an upper limit deposition of 59.71 Gg yr-1 for TFA from HFO-1234yf, based on the following degradation path:



HFO-1234yf / Opteon

TFF (trifluoroacetyl fluoride)

TFA

Research into the effects of incineration and environmental degradation of "modern" perfluoropolyethers is relatively limited, where GenX/HFPO-DA is most often studied. Bao et al. posited that the degradation of HFPO-DA/GenX under UV light is centered on the cleavage of the oxygen-bridge between the different monoethers[74]. This was confirmed by Yang et al. who reported a nearly direct conversion of GenX to PFPrA and TFA under electro-oxidative pressure [108]. As modeled by Zhang et al., sufficient electrical or thermal energy needs to be available for this degradation process to occur [113]. Ding et al. report degradation of HFPO-DA starting around 40°C and rapidly accelerating at 70°C in thermally activated persulfate (TAP) system [114].

As observed by Wickersham et al., this degradation pathway can also be found in other industrial processes involving fluoropolymers, PFAS surfactants and heat [115]. They also report TFE as a decomposition product from the thermal application of fluoropolymer coatings dispersion to fibers and fabrics.

Landfills can be direct sources of TFA and other (ultra)short PFAS as well, which has been attributed to the presence of AFFF's:

> "We detected relatively high concentrations of TFA in all landfill samples prior to oxidation, with concentrations ranging from 43,300 to 260,000 ng/L. Short and ultrashort PFCA precursor products, particularly TFA, were high in two of the five landfill leachate samples (i.e., 25,900 and 29,900 ng/L, respectively), significantly higher than PFBA, which was the most prominent precursor observed in the standard TOP assay". - Tsou et al. (2023) [116]

Removal of ultrashort PFAS from waste streams

Considering the environmental fate of most PFAS (water), the question arises if these substances can effectively be filtered, especially the "newly discovered" ultrashort PFAS that appear so interconnected with fluoropolymers. 3M Belgium's June 2023 permit request provides insight into the effectiveness of an extensive water filtration plant [88]–[90]. 3M's water filtration plant consists of various stages including sand filters, a dissolved air flotation unit, ultrafiltration, reverse osmosis, ionic exchange and active carbon filters, some of which are applied multiple times in various stages.

The active carbon filters play the most critical role for most PFAS, especially longer carbon chains, with a reported 99.88% reduction efficiency for PFOS with three consecutive carbon filters, 99.9% for PFBS, 99,97% for PFBA/PFBSi and near complete removal of MePFBSAA (a polyether). For PFPrA, the reported efficiency of the first three carbon filters drops to an average of 93% (with a range of 69% - 99%). Reverse osmosis can increase this number to 99.5%. Removal of TFA with carbon filters is significantly less efficient, with a reported efficiency of only 8.7% over the first three carbon filters. Reverse osmosis is reported to have a removal efficiency of 83.3% for TFA. Total removal efficiency for TFA is only 71% on average.

Obfuscation

Various examples were found of potential interferences with the ability to analytically detect or report on PFAS in environmental samples.

As already discussed above, there are stunning gaps in the environmental data available on PFAS. A combination of factors has contributed to this situation:

- An assumption of toxicological harmlessness, which can often simply be reduced to differences in estimated bio-accumulation factors.
- Difficulty of obtaining analytical standards and/or suitable (uncontaminated) blanks [117].

- Absence of certified analytical laboratory methods. (This mostly affects governmental environmental monitoring and reporting of industrial emissions, as university labs are not bound by such restrictions.)
- Not knowing what to look for, or even having an idea of the amount of "missing organofluorides".

Suppressed environmental data

One confirmed case of the direct suppression of PFAS research occurred in 2011, when 3M Belgium funded research at the University of Antwerp into the presence of PFAS in eggs of the Great Tit near their Antwerp based production facilities [118]. This followed an earlier study from 2004 wherein University of Antwerp had found extremely high concentrations of PFOS in local field mice ([119]). However, when the results were ready in 2013, including the highest reported concentration of PFOS in eggs ever (10380 ng/g), 3M invoked a clause in the funding contract which stipulated that publication of any results was only possible with their permission. Permission which was never given. The researchers eventually published the result without permission, without any press release, in 2017 [120]. The primary author of the field mice study, Philippe Hoff, went to work for 3M after 2004 and is alleged to have successfully sabotaged a doctorate research project into environmental PFOS while employed there [121].

It should be reiterated here that researchers may be incredibly reluctant to communicate openly about this type of research suppression, due to non-disclosure agreements and/or other financial and legal risks involved.

Missing Chemours monitoring parameters

Even though PFPrA was listed in the original "Table 3+" belonging to the Chemours consent order, it was largely absent in the reported analytical data. The CFPUA only started monitoring PFPrA in the beginning of 2023, which makes the data too sparse for inclusion in the (correlation) analysis. Documentation from the consent order process was searched as an explanation, which came in the form of a memorandum from the Director of Technical Services at Eurofins for Chemours, labeled "LC/MS/MS Method Performance for DFSA, MMF, MTP, and PPF Acid":

> "Field parameter data are provided in Appendix A. Appendix B includes a letter from Chemours to DEQ dated June 18, 2019 along with supporting technical summaries from TestAmerica and Lancaster. The letter describes why *Difluoro-sulfo-acetic acid (DFSA), Difluoromalonic acid (MMF), Perfluoro-2-methoxypropanoic acid (MTP), and Pentafluoropentionic acid (PPF Acid) were removed from the Table 3+ list of analytes. While these four compounds are included in the TestAmerica analytical reports*, they are not included in the evaluation for this Quarterly Report since their data

> are not considered accurate or reliable using the currently available analytical methods. The TestAmerica analytical reports and the data review narrative whitebook are provided in Appendix C.
>
> The combination of multiple properties that can adversely impact analytical performance means that current 'Table 3+' analytical procedures will generate variable and potentially unreliable results for DFSA, MMF, MTP, and PPF Acid in samples. Analytical performance for DFSA, MMF, MTP, and PPF Acid has been demonstrated to be reliable in the absence of matrix interferences, but a growing body of empirical evidence including sample duplicate and matrix spike results indicates that matrix effects have a significant adverse impact in field samples."

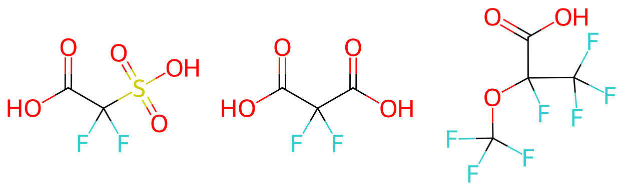
This contrasts sharply with the observation that 3M has been monitoring PFPrA (aka "PPF Acid") in its production waters for at least twenty years by this point and was able to measure both TFA and PFPrA in the Scheldt river (Antwerp) in 2022.

In October 2020, the same Eurofins Environment Testing laboratory in Knoxville, Tennessee, was awarded the "2020 Catalyst for Better" recognition from The Chemours Company, for accomplishments in "excellent PFAS technical innovation."

TFA is simply not part of the Table3+ monitoring program, despite clear indications of its relevance. In fact, the presence of TFA in emissions was already the focus of a 1992 report by DuPont labeled "Ecological testing of an industrial wastestream that contains trifluoroacetate", including site effluent measurements at a level of *3 mg/L*[32]. The report itself could not be located. Boutonnet et al. also mention reports on TFA concentrations in drinking water (with a LOQ of 10 ng/L), rain and air.

Chemours also has no issues identifying TFA using "PFAS NonTargeted Analysis and Methods" in its 2020 interim report (see section on partial fluorination). However, this report only includes ion abundance, not a concentration, which would have merely required a proper calibration based on an analytical standard.

The other parameters that were eliminated from monitoring due to the Eurofins letter are interesting as well (fig 25), as they could easily be products associated with the aforementioned polyethers found in Cape Fear river.



DFSA MMF MTP

Figure 25: Dipole molecules eliminated from Table 3+

Partial fluorination

A 3M process description from 2019 also mentions *partially* fluorinated organic byproducts. According to the documentation, these byproducts are "eliminated" during the "stabilisation" phase, using a strong solvent and a strong base followed by a high pressure+temperature distillation process. Both KOH and LiOH can be found in 3M documentation as bases that have been used for stabilisation.

Environmental monitoring of partially fluorinated PFAS is extremely rare, except perhaps for certain molecules typically classified as F-gases. However, due to the consent order involving the Chemours Fayetteville Works plant, a non-targeted analysis was conducted in 2019-2020 on various samples including process wastewater, stormwater discharge, etc. [122]

Since no standards were available for these molecules, a quantification beyond ionic abundance was not available. No attempt was made to identify the molecular structure either, making the resulting data quite difficult to analyse or interpret. However, a quick screening for (candidate) partially perfluorinated PFCA's, PFSA's and the "telomeric variants" can be performed using the rules (fig 26 and fig 27):

- $N_O = 2$ AND $(N_C - 1) * 2 = N_F + N_H - 2$ (for carboxylic acids)
- $N_O = 2$ AND $N_S = 1$ AND $N_C * 2 = N_F + N_H - 2$

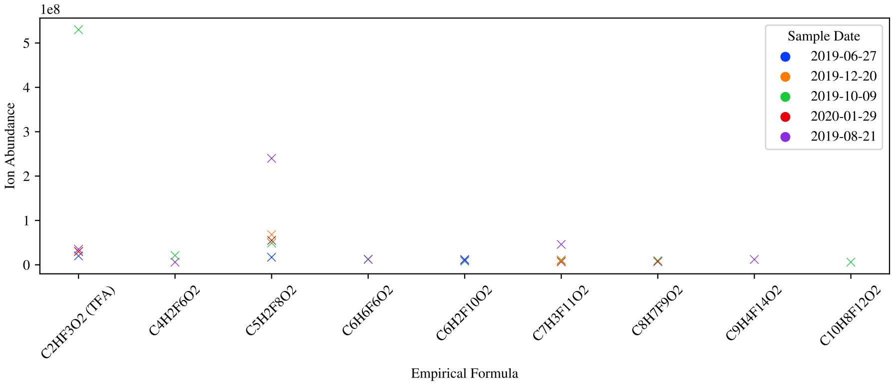


Figure 26: Candidate partially fluorinated carboxylic acids

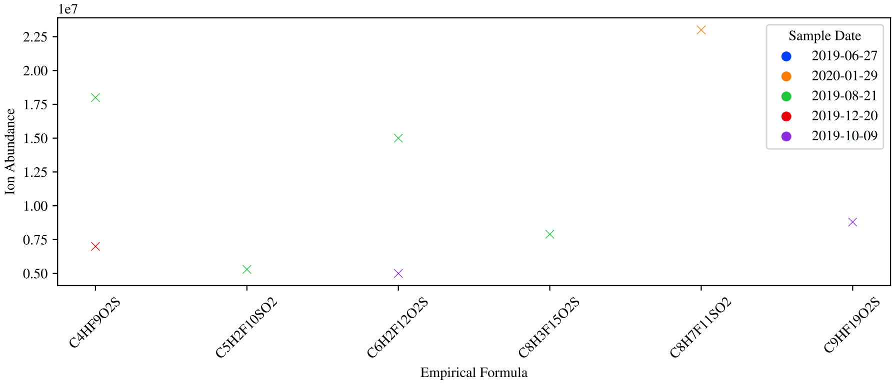


Figure 27: Candidate partially fluorinated sulfonic acids

Proprietary molecules and undisclosed emissions

Examples were found where commercial interests were used as a pretext to hide information critical for analytical techniques or emissions were simply not reported.

In 2019, it was found that Solvay [123] was polluting the Po river and associated Veneto region near its Miteni plant with a fluorosurfactant meant for use as a polymerisation aid, labeled “C604”. Early in 2021, Solvay ordered Wellington Laboratories to cease selling an analytical standard for C604, a novel legal strategy at the time. Later that year Solvay relented somewhat, by offering their own version of the analytical standard [124]. C604 (aka F-DIOX acid) is strongly reminiscent of Chemours’ PFO2HxA, which was found in the Cape Fear river (fig 28). This immediately prompts the suggestion that longer clusters may exist here as well.

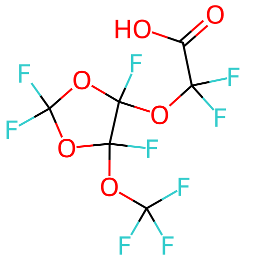


Figure 28: Solvay's "C604" surfactant, found near Miteni, Italy

Meanwhile, in 2020, it was discovered that Solvay Specialty Polymers was using an undisclosed "process aid" at its West Deptford facility as a substitute for PFNA since 2010 ([95], [125], [126]). As discussed in the section on the Solvay ClPFPECA cluster, those molecules differ from "C604" in that they contain a (partially) chlorinated section.

3M documentation also indicates a chemical product called "PM-870", for which no CAS numbers are made available, only an "average structure" (indicating yet another potential class of PFAS variants) [127]. It is described as a polymer additive which provides (additional) water and oil repellency to polyolefin and other synthetic resins like polypropylene [128]. A visually inverted depiction of the molecule itself suggests it is based on a C4 sulfonic acid combined with a long hydrocarbon "tail". In other words, it most likely breaks down to PFBS and/or PFBA, assuming no homologues of this sulfonic acid based PFAS specie are present. Notably, PM-870 is described in its product bulletin as not being "associated with ozone depletion" due to the lack of chlorofluorocarbon contents and "not made with, nor does it degrade to, PFOA (perfluorooctanoic acid) or PFOS (perfluorooctane sulfonate)". In other words, PM-870 is perfectly aligned with both the Montreal Protocol and the PFOA Stewardship Program and yet still causes PFAS pollution if in any way released into the environment.

Less complicated PFAS may also be undisclosed: When the author of the paper compared the 3M environmental emissions permit with a list of known byproducts from the 3M Decatur plant, FBSA (a relatively simple molecule) was noted as lacking an emission permit, despite it being a known byproduct and clearly present in environmental samples. The resulting complaint with the environmental regulator lead directly to a closure of the fluorination division until further notice. After this, a virtually identical episode occurred once more with undisclosed ultrashort emissions (TFA and PFPrA). (See previous discussions.) Generally speaking, it would appear these substances have not been monitored historically simply by virtue of not having been mentioned by the company in question (or simply dismissed as a "byproduct") and/or not being included in consent orders.

Detection and identification of unknown PFAS

As noted by Kotthoff and Bücking in 2018, there is a serious problem with what they call "Dark Matter": unknown PFAS and precursors [82]. The list of unregulated and unmonitored (by)products of the fluorination industry mentioned in earlier sections is already quite impressive:

- Ultrashort PFAS: C1-C3 PFSA's and C2-C3 PFCA's.
- Dipoles like DFSA and MMF
- Homologues and isomers
- Partially fluorinated PFAS
- Most fluorinated polyethers, in nearly infinite variations

Unsurprisingly, numerous reports point to the presence of "unknown PFAS" in environmental samples [93], [95], [96], [129]–[133].

As an example, Yeung et al. report that "the percentage contribution of known PFASs to the EOF was around 5−10%" in their study on the bioconcentration of AFFF in Juvenile Rainbow Trout, when applying "Angus Fire" branded product. This list already included 20 common PFAS, corresponding to a "typical" screening which will often include PFCA's and PFSA's in the range C4-C10 and equivalent fluorotelomers. Subsequent research by D'Agostino et al. identified (in total) 12 novel and 10 infrequently reported *PFAS classes* in fluorinated chain lengths from C3 to C15 for a total of 103 compounds [130].

This issue is not only limited to environmental sampling, but occurs in human biomonitoring studies as wel, for example Yeung et al on Chinese blood samples [134]:

> "Analysis of known PFCs and extractable organic fluorine showed that known PFCs (PFOS, PFHxS, PFOSA, PFDoDA, PFUnDA, PFDA, PFNA, PFOA, PFHpA, and PFHxA) could account for >70% of EOF in samples from Beijing, Shenyang, and Guiyang, whereas known PFCs could only account for $\sim$ 30% of EOF in samples from Jintan."

The main method of detection to identify "unknown PFAS" is based on High Resolution Mass Spectrometry (HRMS), using "time of flight" characteristics to identify unknown PFAS molecules [96]. Corresponding to the earlier observation that PFAS production is most likely quite non-specific, the authors show that per- and polyfluorinated compounds often appear as multiple peaks which differ by exactly ± m/z 49.9968 and/or 65.9917, corresponding to a difference of CF2 and CF2O, respectively. In other words, fluorinated mono- and/or polyethers differing by one (or more) carbon number, as to be expected in a non-specific production process. The technique was recently summarised by Strynar [135]:

> “Entrance into the study of novel PFAS discovery requires identification techniques such as HRMS (e.g., QTOF and Orbitrap) instrumentation. This requires practical knowledge of best approaches depending on the purpose of the analyses. The utility of HRMS applications for PFAS discovery is unquestioned and will likely play a significant role in many future environmental and human exposure studies.”

However, for the HRMS technique to work, there needs to already be an idea of what structures to look for. In many of the aforementioned studies, one “official” variant (e.g. GenX) was used to speculate on homologue and analogue structures.

Another potential method employed by Lin Xu et al [132] was to execute a detailed patent search, after which a previously unknown fluorinated benzene ring (sodium p-perfluorous nonenoxybenzenesulfonate/OBS) could be identified near an oil field. Using the Globally Harmonized System (GHS) criteria, the toxicity of OBS was assessed as similar to that of PFOS. OBS appears to not be the only PFAS employed for this purpose, as the Lin Xu et al mention: “In an informal report, which was the only report of this nature, the amount of PFOS released to the sea by Norwegian oil rigs between 1980 and 2005 was assessed to be more than 80 tons.”

Total organofluoride (TOP assay, SOF, AOF)

An obvious question is what the *total of all organofluorides* in fluorinated products and industrial effluent might actually be. Considering the (potential) large amount of “Dark Matter”, a simple sum of all parameters for which there is easy access to analytical standards is most likely a (significant) underestimation.

One approach is to use the “total oxidizable precursor” (TOP) assay [136]. In TOP assay method, samples are (rapidly) oxidised and then analysed for PFCA and PFSA parameters. It could be considered as representing the eventual environmental fate of the sample, as PFCA and PFSA are considered to be the most stable chemical environmental endpoints. However, TOP assay could only be considered fully representative if *all* potential endpoints are analysed. The current “state of the art” already considers C2–C14 perfluoroalkyl carboxylic acids (PFCAs), but perfluoroalkyl sulfonic acids (PFSAs) are still limited to C4–C8 and C10 [116], [137]. This leaves out C1-C3 PFSA’s (TFMS, PFEtS and PFPrS) as well as dipole acids like DFSA, MMF and the like. As discovered/confirmed by Barzen-Hanson and Field, PFEtS and and PFPrS are - for example - present in significant concentrations in AFFF (7-13 mg/L and 120-270 mg/L respectively), as well as in groundwater samples [138].

One remarkable story is that of “soluble organic fluoride” (SOF), a parameter (analytical technique) that was included in the environmental permits of 3M Belgium from at least 2000 to 2020. The method is described [139] as consisting of the combustion of the sample at a temperature of 1000-1100°C, followed by a determination of the resulting HF concentration using an ion-selective electrode. In other words, the HF that would have been required to create the organofluorides in question is recovered. Despite it being included as a legal emission norm for two decades, no governmental SOF monitoring data seems to exist. Nevertheless, it was still monitored by 3M and the concentrations found were used in various permitting discussions.

The earliest found record of such an “SOF” result is associated with the earlier mentioned “amine washing waters” screening from 2003 (fig 9). An incredibly high value of 2700 mg/L was reported, which is 20 times higher than the sum of all individual parameters listed [87]. It should be noted however that the amine washing water samples were taken on different days and the amount of dilution can play a big role here. The reporting limit (possibly the LOQ) on SOF is listed as 2.8 mg/L.

For 2005, 23mg/L SOF is reported in the effluent of the “aerobic filter” and 19 mg/L in the effluent of the active carbon filters [139].

In 2007, in the context of evaluating their effluent filtration system, 3M Belgium executed a direct comparison between SOF and individual PFAS parameters on the same sample of effluent from their water filtration system [139]. 64.2% of the SOF value (36.5 mg/L) can be explained using individual parameters, leaving 35.8% undetermined organofluorides (fig 29). Using the reported maximum daily discharge volume of $1250 m^3/day$, this would result in a maximum daily SOF discharge of 45.6 kg (16.65 metric tons per year).

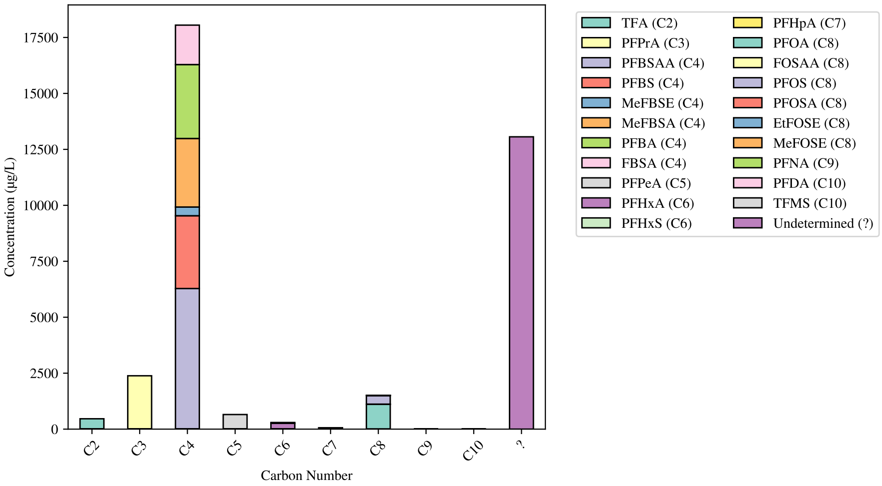


Figure 29: Undetermined SOF components versus individual components in 3M effluent

The emission norm for SOF in the 2008 permit resulting from this evaluation was eventually set at 25 mg/L (maximum 11,4 metric tons per year) [140]. Only PFOS and PFOA, both "historical" products (with "C8" making up only a 5% of the SOF) received an individual emission norm ($30 \mu g/L$ and $220 \mu g/L$ respectively, or about 1% of the SOF emission norm), resulting in a total absence of monitoring data for the dominant C1-C4 fraction in the subsequent years.

In 2011, a reevaluation of the 3M Belgium water filtration system yielded yet more information on this SOF parameter, as a graph was provided (fig 30) [85]. The reporting limit was not mentioned, but might still be around 2.8 mg/L, possibly explaining the 0 values.

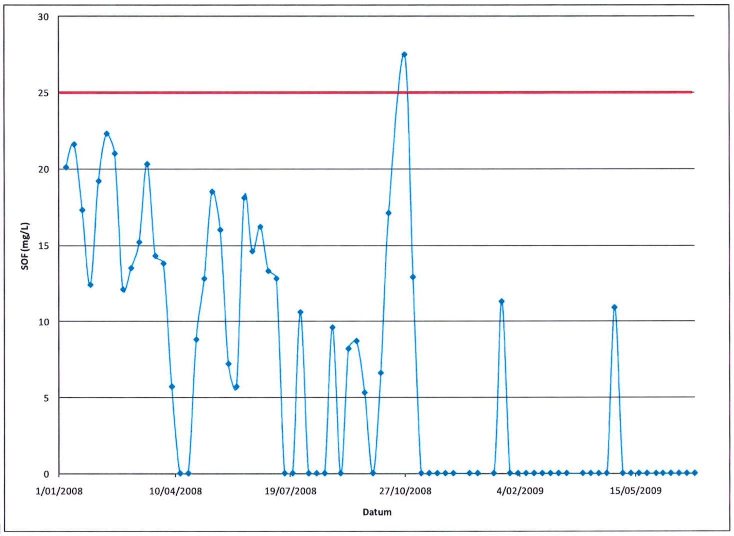


Figure 30: Evolution of SOF concentration in effluent 3M Belgium 2008-2009

The (25 mg/L) SOF emission norm was abandoned during the (re)permitting of 3M Belgium in 2020 [71]. The reason given was that it was not a governmentally certified analysis technique ("WAC"). It was replaced with individual parameters (PFBS, PFHpA, PFHxA, PFOA, PFOS, PFOSA, PFPeA and PFBA or PFCA C4-C8 and PFSA C8) for a total of 8.8 mg/L. After the SOF emission norm was removed from 3M Belgium's permit in 2020, the Flemish Environmental Agency (VMM) requested it would still be monitored bi-weekly by 3M. However, no publicly accessible SOF data was found.

Contrary to the impression that the technique is simply outdated, the SOF method recently featured in a publication on the detection of (total) PFAS in food packaging [141]. It is described as the simplest and most inexpensive analytical technique that is commercially available.

In 3M Belgium's 2023 permit adjustment, the previously requested SOF monitoring was replaced by an AOF measurement "based on DIN EN ISO 9562

2005-02”[9], based on the argumentation that no certified lab standard was available for SOF [88]. An functionally identical technique is described in VITO Belgium’s WAC/IV/B/013 lab standard [142].

In Februari 2019 Consent Order, signed by The Chemours Company FC, one of the requirements was for Chemours to “fund the development by a third party contractor(s) of a sampling and analytical methodology for the measurement of Total Organic Fluorine in its process air emissions and process wastewater. In November 2019 a progress report was published that essentially describes the AOF sampling process.

The SOF and AOF analytical methods differ on two crucial points:

1. Where SOF uses a “solution” of the target sample, the AOF method uses activated carbon wherein the targeted organfluorides are adsorbed for combustion.
2. Where the SOF method requires a combustion temperature of 1000-1100°C, the AOF method requires 950°C (900-1000°C in the ”TOF” parameter resulting from the consent order).

Both differences have a critical impact on the amount of organofluorides that can effectively be detected: Organofluorides that do not adsorb as readily to carbon matrices will be underestimated in the AOF technique. Secondly, as discussed, 950°C is simply too low of a temperature to fully destroy organofluorides, especially the smallest species. Both aspects combine negatively against ultrashort PFAS when the AOF technique is used instead of SOF. It should be noted here that the required temperature for full destruction of CF_4 (1400°C) is also still not attained in the described SOF technique, which means it may still underreport the total organofluoride content.

In fact, the evaluation of the water filtration system included in 3M Belgium’s 2023 permit adjustment confirms exactly this discrepancy [88]. Where in 2007 SOF measurements indicated that 35.8% of organofluorides were not analytically determined even when including ultrashort PFAS like TFA and PFPrA, the 2023 AOF measurements show no such “undetermined” portion. In fact, AOF appears to underreport the total amount of organofluorides present in samples by a factor 1.4-5x (fig 31). Most of this discrepancy can be attributed to PFPrA, which suggest samples with large outliers. The evaluation study mentions that the corresponding lab (SGS) reports that AOF will only capture 10% of TFA, 50% of PFBA (C4) and 100% of PFOS.

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[9] Note that this is actually the ISO standard for “AOX”, a general technique for measuring organically bound halogens. There are other ISO designations for AOF specifically.

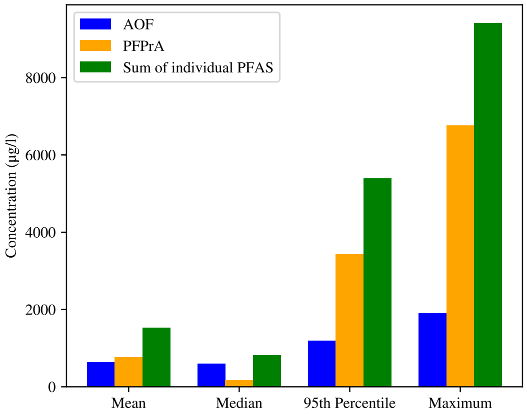

Figure 31: 3M production waters: AOF compared to the sum of PFOS, PFHxA, PFHpA, PFHxS, PFOA, PFPeA, PFBSA, PFBS, MePFBSAA, MePFBSA, PFHxSA, PFPeS, PFHpS, PFOSA, PFPrA, PFPrS, PFBSi, MePFBSE, BPAF, 2333-TFPA, TFA, 2233-TFPA, PFBSE, PFBSAA, PFBA, PFBSEE-DA, PFES, 6:2 FTS, TFMS, HPFO-DA, MePFOSAA, PFNA, EtPFOSAA, 8:2 DiPAP and PFECHS

To determine if SOF is “fit for purpose” for the estimation of total organofluoride content, the expected F-ion concentration was calculated for 158 different PFAS species mentioned in this report (fig 32). The assumption here is that the SOF method will cause a full recovery of all fluorine from the organofluorides. This approach matches the methodology used by EPAS (Eco Process Assessment) in 2007 to determine the amount of “undetermined” organofluoride [139].

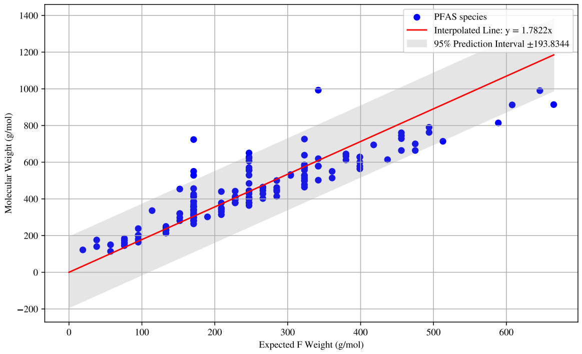

Figure 32: SOF conversion of organofluorides to fluor ions for 158 PFAS

It turns out that, for the vast majority of PFAS species, even a direct estimate of organofluoride content with a conversion factor of around x 1.75 is remarkably accurate for such a simple and cheap method. There is an expected *overestimation* for (proportionally) highly fluorinated species like (unsaturated species) like TFE and HFP, but these are not environmentally stable. Overestimation of 20-25%) will also occur in very long PFAS species like PFODA, PFHxDA, PFTeDA, PFTrDA, PFDoA, PFUdA, PFDA.

Total organofluoride content will be *underestimated* for fluorinated species with large non-fluorinated sections. This is the case for PHSA and PBSA based species, both AFFF related polyethers. Other notable overestimation would occur for MMF (CAS 1514-85-8), the ATLAS monomer (CAS 856220-62-7), the dipolar DFSA (CAS 422-67-3) and 2-Fluoromalonic acid (CAS 473-87-0).

A commonly heard objection to SOF is the idea that *naturally occurring* fluorinated molecules could cause methodological issues. This hypothesis was tested with the extremely short list of naturally occurring fluorinated substances: Fluoroacetic acid, Fluoroacetone, Fluorocitric acid, **ω**-fluorooleic acid (18–fluorooleic acid was used as the representative species), Nucleocidin and 4-Fluorothreonine [143]. Since all of these substances only contain one single fluorine atom, they would be *underestimated* by a factor of 224-1075%. Additionally, none of these substances are associated with plant species in North America or Europe. In other words, they should not be expected to significantly impact the organofluoride assessment of effluent or even surface waters using SOF. Background concentrations for these substances would have to be determined to be sure.

Reporting limits and analytical standardisation

Background: The discussion on SOF and “C4 chemistry” touches on a peculiar pathway through which the environmental presence of organofluorides can become obfuscated, governmentally certified analysis techniques. In Belgium, these are set in the “WAC” compendium by VITO Belgium (the Flemish Institute for Technology & Innovation), a public-private organisation. VITO is also involved in many partnerships with petrochemical organisations like 3M Belgium (e.g. Catalisti, where 3M is also a member and “Vlaanderen Circulair” with petrochemical lobbying group Essenscia). VITO was founded in 1991 and provides services to both government, including certification of lab techniques and proposals for emission norms, as well as the private sector. VITO’s funding in 2020 consisted for 29,6 % (€ 70 million) in governmental grants and assignments, 32% (€ 76 million) in “activation of R&D” and 38% (€ 90 million) in commercial revenue [144].

As previously discussed, the absence of organofluoride parameters (like SOF and ultrashort PFAS) and emission monitoring can at least partially be attributed to their absence in VITO’s list (“WAC compendium”) of certified analytical techniques.

Another issue with “WAC/IV/A/025”, the Flemish (VITO) version of ISO

21675:2019 for the determination of (certain) perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water using LC-MS/MS [145], [146]. Where the LOQ ("Limit Of Quantification") in the ISO standard is set to 0.2 ng/L, the reporting limit in the VITO WAC is set to 10 ng/L for drinking-, ground- and surface-waters and 20 ng/L for effluent. Remarkably, this implies that a drinking- or groundwater norm based on the 2020 EFSA reference dose (4.4 ng/L) is impossible to evaluate based on lab reports following VITO's (obligatory) reporting limits in Flanders.

VITO has also proposed a PFAS groundwater norm for Flanders that is not based on the most current EFSA reference dose (which would be 4.4 ng/L), but based on a generic WHO norm (100 ng/L). This was preceded by a proposal for a groundwater sanitation norm of 120 ng/L in 2020, which was based on the (completely outdated) 2016 EPA reference doses for PFOS and PFOA [147]. By contrast, the Netherlands authorities have simply adopted the ISO analytical technique (implemented as NEN-ISO 21675:2019). Research by the Dutch RIVM shows that the sum PFAS concentration of the four "reference parameters" from the EFSA reference dose in Dutch drinking water gained from surface water ranged from 0 to 36 ng/L with an average of 6,7 ng/L and from 0-12 ng/L with an average of 0.8 ng/L in drinking water gained from groundwater [148]. As reported by the RIVM, 53% of all samples from surface water derived drinking water and 10% of all samples from groundwater are above the EFSA 2020 derived drinking water threshold of 4.4 ng/L. The report in question clearly demonstrate that the Flemish (VITO) reporting limit of 10 ng/L for individual PFAS would simply make most of these transgressions disappear.

Toxicity revisited

A limited literature review was made for all PFCA and PFSA molecules below C4 (TFA, PFPrA, TFMS, PFEtS and PFPrS). PubMed was search with a combination of 'Toxicity' AND 'substance'. Where alternative names were known (e.g. PFPrA used to be referred to as 'PPF acid'), those were searched as well.

Modes of action/tissue preference

One of the main pretexts under which shorter (monoether) PFAS are dismissed as "no reason for concern" is the idea that they bio-accumulate (significantly) less. However, a Spanish study on (human) tissue samples showed that this assumption may very well be incorrect [149]. As shown in fig 33, C4 PFCA (PFBA) is far more prevalent in the kidneys and the lungs than longer chain PFAS. The brain appears as "host" to PFHxA (C6). The concentrations found for PFBA/C4 (263 and 807 ng/g in kidney and lung, respectively) were much higher than those of PFHxS (68.3 and 141 ng/g in liver and brain, respectively) or PFOA (C8) (20.9 ng/g in bone). It should be noted that this goes directly against the bio-accumulation argument so often made in PFAS evaluation. Even when adjusted using the "PFOA Equivalent" (PEQ) scale developed by Bil et al [150], the mean concentration of PFBA in lungs comes out as 2x as problematic as PFOA in bone. (It should be noted though that the PEQ methodology is not typically meant for assessing the relative toxicity of concentrations in the human body. Rather, it is meant to be used to evaluate exposure.)

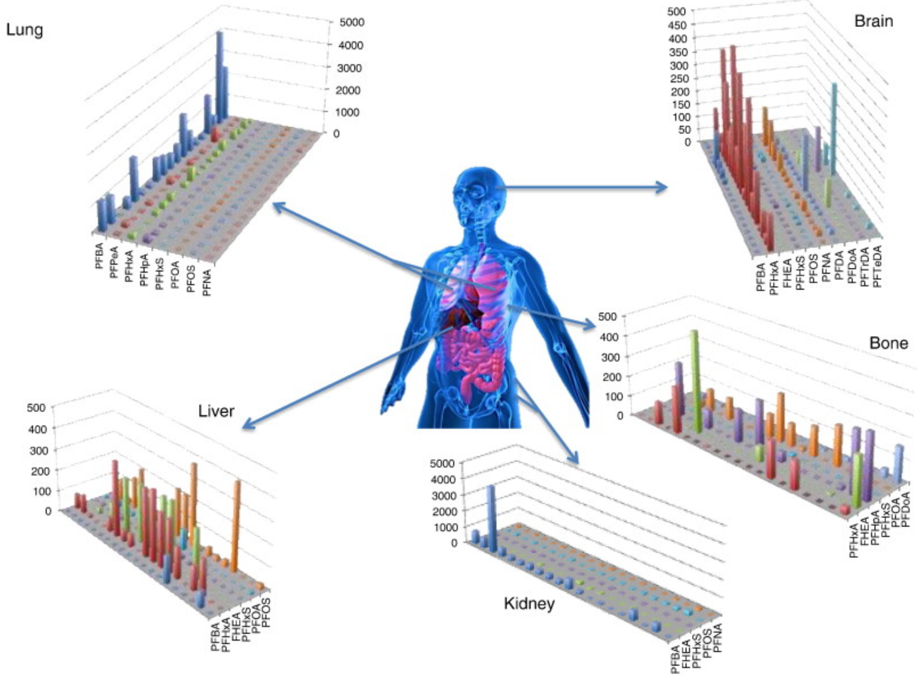

Figure 33: Concentrations of various PFASs (in ng/g) in 5 human tissues from 20 residents of Tarragona (Catalonia, Spain)

Worryingly, even though older people did tend to show higher concentrations of PFAS, as expected from long-term exposure to a bio-accumulative substance, some young subjects (18–39 years) also showed relatively high levels of PFASs. It should be noted that the Perez et al study (unfortunately) did not consider C2-C3 PFAS, which should be cause for significant concern due to the environmental correlation between PFBA production, PFPrA and TFA.

TFA (trifluoroacetic acid)

Due to the worrying elements found in the “Bending Science” chapter, it is deemed imprudent to take all publications related to TFA at face value. This includes papers authored by employees of industrial fluorination companies ([152]) or researchers connected one of the two suspected covert lobbying groups ([58]).

> “Based on the relative insensitivity of aquatic organisms to TFA, predicted concentrations of TFA in terminal water bodies are not

> expected to impair aquatic systems, even considering potential emissions over extended periods.” - Russel (2012) [152]

> “As an acid or as a salt TFA is low to moderately toxic to a range of organisms. Based on current projections of future use of HCFCs and HFCs, the amount of TFA formed in the troposphere from substances regulated under the MP is too small to be a risk to the health of humans and environment.” - Keith R. Solomon (2016) [58]

A 2009 publication of the effect of TFA on the plant species phaseolus vulgaris (common bean) and zea mays (corn) reports a distinctly negative effect on root and plant growth [153]:

> “In general Z. mays was affected more severely than P. vulgaris showing a large TFA-induced decrease in both apparent carboxylation efficiency and in vitro Rubisco activity.”

A 2009 article on potential reproductive toxicology of TFA concluded that there is a lack of information on the toxicity of TFA.

One paper from 2016 mentions a case of dermal exposure to industrial quantities of TFA, resulting in burn wounds.

One toxicity assessment on the rotifer Brachionus calyciflorus (a type of plankton). From the abstract:

> “The results indicated that the 24-h median lethal concentration (LC50)valuesoftrifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), perfluorobutanoic acid (PFBA), perfluopentanoic acid (PFPeA), and perfluorohexanoic acid (PFHxA) towards B. calyciflorus were 70, 80, 110, 130 and 140 mg L^{-1}, respectively. *The acute effects of PFCAs decreased with the increase of carbon chain length.*”

This observation of course runs entirely counter to the generalized idea that shorter carbon chain lengths would automatically imply lower toxicological risks. Acute effects to a freshwater invertebrate appear to increase with decreasing PFCA chain length.

Most interestingly, is a recent (2023) article titled “Mammalian toxicity of trifluoroacetate and assessment of human health risks due to environmental exposures”. In it, the AFEAS associated authors (Wolfgang Dekant and Raphael Dekant) claim that based on recent levels of TFA in water and diet, MoEs for human exposures to TFA are well above 100 and do not indicate health risks.

Meanwhile, some efforts have been made to determine the toxicity of TFA. In 2020, the German UBA arrived at a total daily intake of 18 $\mu g/kgbw/day$ [154], based on an estimated NOAEL of 1,8 $mg/kgbw/day$ due to liver damage detected in a 52-week drinking water study using rodents (2019). Based on the similarity in dose-response curves, RIVM recently assigned an RPF (relative potency factory) of 0.002 to TFA [30]. Using the EFSA reference dose of 0.65

ng/kg bw/day for the sum of all PFAS, this implies a maximum daily intake of 325 ng/kg bw/day (55x lower than the UBA estimate) or a drinking water norm of 2200 ng/L *in the absence of all other PFAS.*

PFPrA, TFMS, PFEtS, PFPrS

One article was found on the toxicity of TFMS, which concluded that TFMS disturbed the liver lipid metabolism (in mice) possibly via altering the gut microbiota. It should be remarked that hepatoxic effects of PFOA on the (human) liver were part of the initial discoveries within DuPont and are commonly used to determine the (relative) toxicity of specific PFAS and their precursors ([157]). (See also the section on Lipinski's Rule of Five.)

No articles were found on the toxicity of PFPrA. This remarkable knowledge gap is confirmed by 3M, who mentioned this in their permit change request for the emission of ultrashort PFAS, where they resort to using a "read-across" method for estimating the toxicity of PFPrA due to the lack of available studies. This gap is quite surprising as PFPrA is one of the most ubiquitous PFAS on earth.

No articles were found on the toxicity of PFEtS.

No articles were found on the toxicity of PFPrS.

Hazard classification and Lipinski's "Rule of Five"

A common argument when discussing the potential toxicological harm of PFAS, is the assumption that shorter PFAS are overall less harmful because they tend to bioaccumulate less due to their relatively smaller size. This is often used in environmental assessments, where BCF is often used as the primary discriminator when deciding on PFAS monitoring and/or regulation when there is no known information on the toxicity of a substance. For example, 3M uses a (Flemish) regulatory rule wherein a "biota assessment" is not necessary for substances that have a BMF (bio magnification factor) < 1 and a BCF/BAF (bio concentration/accumulation factor) < 100.

Additionally, in the UN "Globally Harmonized System of classification and labelling of chemicals" (GHS) both health and environmental hazards are only based on *known* toxicity and/or carcinogenicity [158]. There is a clear disconnect here with the vast amount of PFAS variants for which no such data is available, making them "harmless until proven otherwise" despite the repeated rejection of this premise for many PFAS substances over the years.

The threshold used based on a BMF/BCF approach may also break down if there is *continuous* exposure to non-neglible concentrations, for instance through drinking water, which may result in similar bloodserum concentrations as seen for longer PFAS. Unfortunately, shorter PFAS also tend to be more mobile, resulting in a significantly easier pathways into drinking water and derivative products like beer. Some research also suggests that the length of the carbon chain merely modifies the *mode of action*, in other words, the toxicity profile may simply shift to new (eco)toxicogical problems.

Halothane, HCFC-123 and HCFC-124 (fig 34) also hint at the notion that size might not always matter in regards to halogenated chemicals: Halothane-induced hepatitis is the reason it was soon replaced by different anesthetics (in countries that could afford it). The exact mechanism of halothane-induced hepatotoxicity is unknown, but there is strong evidence that it is related to the immune system. It is also worth noting that halothane readily crosses the placenta and its oxidative metabolite, TFA, accumulates in embryonic and fetal tissues and amniotic fluid in mice and rats [159]. Very similar liver toxicity was found for HCFC-123 and HCFC-124 [156]. Disorders of the liver lipid metabolism were also detected for TFMS [160]. No information could be found on two "missing" C2 variants: 2,2-dibromo-1,1,1-trifluoroethane and 2-bromo-1,1,1,2-tetrafluoroethane (also known as the anesthetic Teflurane).

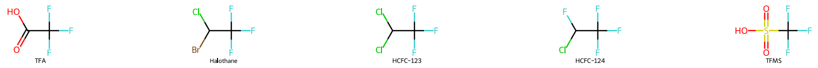

Figure 34: TFA compared with hepatoxic substances

Similar hepatotoxicity has also been detected for halogenated polyether anesthetics: desflurane, isoflurane and sevoflurane [161].

It may be relevant to revisit the way these substances are evaluated, especially the "presumption of innocence" from the GHS framework, by making an early (theoretical) assessment of the oral bioavailability of organofluorides, which is possible even when there is no toxicological study available at all.

A commonly used discriminator in pharmacological research is "Lipinski's Rule of Five", which is a guideline for predicting the *oral bioavailability of a compound*. Lipinski states that a molecule is likely to be absorbed and become bioactive in the human body if it meets the following criteria:

- No more than 5 hydrogen bond donors (OH and NH groups).
- No more than 10 hydrogen bond acceptors (N and O atoms).
- A molecular mass less than 500 daltons.
- A calculated octanol-water partition coefficient (Log P) not greater than 5.

When applied to PFCA's and PFSA's, all variants up to C9/C10 conform to Lipinski's "Rule of Five"[10]. For several of these molecules, research has shown that they are indeed bioactive (toxic). Lipinski's rule would suggest it is entirely

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[10] The criteria were normalised to fit a radar plot by dividing each criterium witt its threshold. The "Lipinski" module from RDKit.Chem was used in calculating the various parameters. Note that the H-bond acceptors and donors calculated with this method do not necessarily match those on e.g. PubChem.

wrong to dismiss the potential danger of ultrashort PFAS without extensive research.

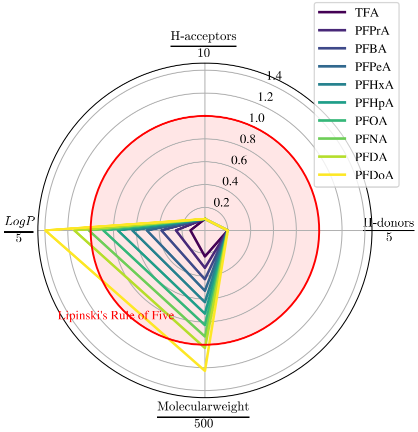

Figure 35: Lipinski criteria applied to PFCA's

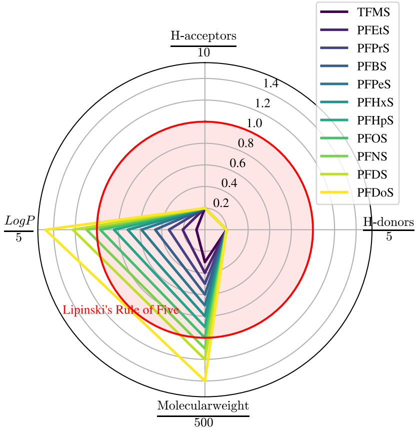

Figure 36: Lipinski criteria applied to PFSA's

This method was also applied to the substances in both polyether clusters found in the Cape Fear River. All of the identified molecules fit "within" Lipinski's rule, again suggesting they may very well be bioactive and absorbable (fig 37 and 38).

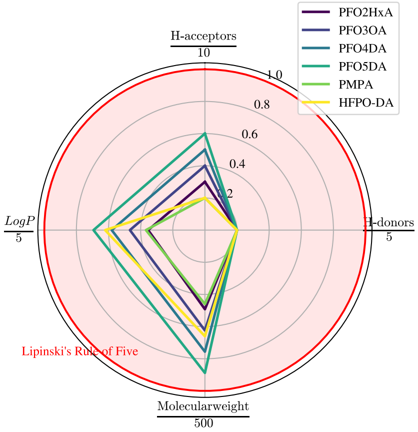

Figure 37: Lipinski criteria - Polyether PFCA's

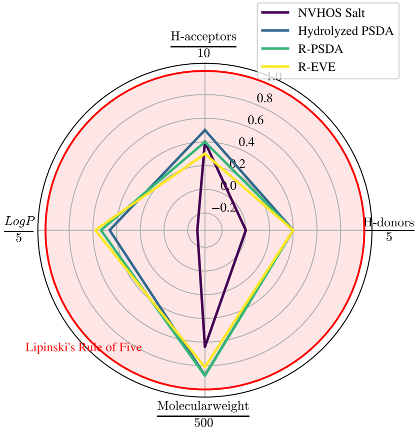

Figure 38: Lipinski criteria - Polyether PFSA's

The Lipinski evaluation can also be applied to the EMSD related molecules and the set of AFFF[11] related molecules as reported by 3M (fig 39 and 40).

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[11] Fire Fighthing Foams. These molecules were listed as the ingredients of "3M Fluorocarbon Analytical Standard #1 for quantitative analysis of PFAS related to historical AFFF".

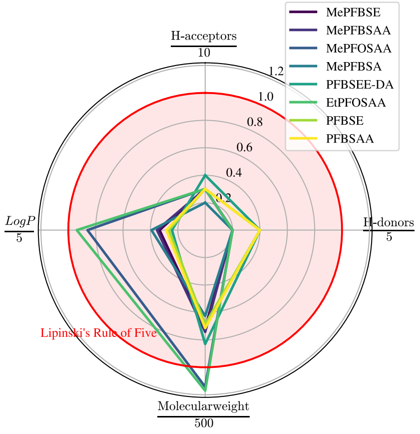

Figure 39: Lipinski criteria - EMSD related

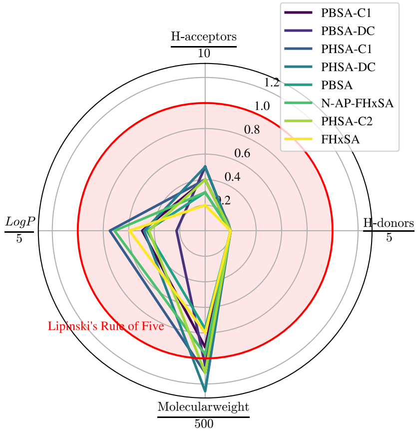

Figure 40: Lipinski criteria - AFFF related

The “ClPFPECA-cluster” found near Solvay, New Jersey, only shows marginally better Lipinski characteristics (fig 41).

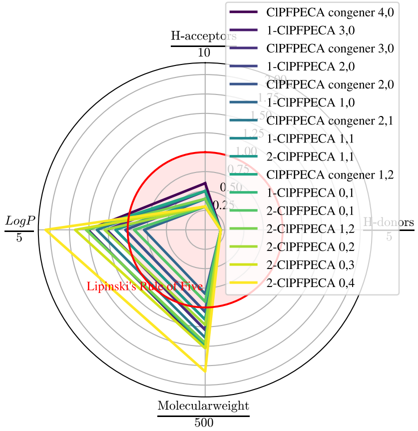

Figure 41: Lipinski criteria - ClPFPECA related

Cramer classification

Another common way to evaluate substances for which little to no toxicological data is available, is to use the Cramer method for the estimation of toxic hazard, using a decision tree approach [162]. This classification is used, amongst others, in the EFSA Guidance on the use of the Threshold of Toxicological Concern approach in food safety assessment [163].

All PFAS under discussion in this paper have a "High (Class III)" Cramer classification, due to the following rules in the Cramer decision tree[12]:

1. Is it a normal constituent of the body? No.
2. Does it contain functional groups associated with enhanced toxicity? No.
3. Does it contain elements other than C, H, O, N, divalent S? Yes.
4. Do the elements not listed in question 3 occurs only as a Na, K, Ca, Mg, N salt, sulfamate, sulfonate, sulfate, hydrochloride? No.

The description of Cramer's Class III is as follows:

> "Class III substances are those that permit no strong initial presumptions of safety, or that may even suggest significant toxicity. They thus deserve the highest priority for investigation. Particularly when per capita intake is high or a significant subsection of the population has a high intake, *the implied hazard would then require the most extensive evidence for safety-in use.*" [162]

Based on 613 organic chemicals, Munro et al. derived a proposal for human exposure levels (TTC values) [164], [165] of 1800, 540 and 90 $\mu g/person/day$

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[12] The ToxTree application was used to verify this classification for the 162 PFAS substances that are mentioned in this paper.

for Cramer class I, II and III, respectively in 1996. In 2019 the EFSA Scientific Committee [163] converted this assessment to 30, 9.0 and 1.5 $\mu g/kgbw/day$ for Cramer Classes I, II and III, respectively, using a body weight of 60kg.

In other words, a default reference dose of 1.5 $\mu g/kgbw/day$ would automatically be suggested for all PFAS for which no toxicological data is available. Notably, a very recent study by Lea et al. (all ToxStrategies researchers) derived a human exposure level based on Munro's methodology for a "PFAS-enriched data set" of 1.3 $\mu g/kgbw/day$ [78]. The study was funded by The Chemours Company FC, LLC.

This value contrasts sharply with the tolerable daily intake of 0.63 $ng/kgbw/day$ (0.00063 $\mu g/kgbw/day$) for the sum of four other PFASs: PFOA, PFNA, PFHxS and PFOS derived by the EFSA CONTAM panel in 2020 [166]. The difference between the two dosages (a factor 2000x) can be attributed almost exclusively to the methodology used by ToxStrategies, wherein only PFAS for which a rodent based study was available was included for evaluation. This is similar to the enormous difference between the 2023 RIVM drinking water assessment of TFA and the reference dose calculated by UBA in 2020, which was also solely based on rodent studies [30], [154]. This methodology might also explain why PFOS or PFBS are not included in PFAS-set selected by ToxStrategies. By contrast, the dominant toxicological pathway for PFAS is immunological [167], predominantly derived from epidemological studies, which *are* included in the EFSA consideration. It is therefore reasonable to assume that a threshold value of 1.5 $\mu g/kgbw/day$ would be a serious underestimation of the chronic toxicity of many PFAS, by several orders of magnitude.

Converted to a drinking water (assuming a dietary contribution of 20% and a consumption of 2 liters), a "Cramer Class III" threshold concentration based on the original Munro et al. thresholds would be 10500 ng/L, whereas a drinking water norm based on the current EFSA reference dose and a Relative Potency Factor of 0.002 as determined by RIVM, resulted in a concentration of 2200 ng/L for the evaluation of drinking water [30].

PFAS mixtures

An interesting artefact in the context of this paper is the recently published report titled "Evaluation of Approaches for Assessing PFAS Mixtures" by ToxStrategies [168], which was included in the environmental permit request for the emissions of ultrashort PFAS by 3M in June 2023. In it, the author(s)[13] suggest that the findings from an independent panel of experts on the grouping of PFAS for human health risk assessment can be interpreted such that a weighted risk assessment like RIVM's RPF approach is not supported[169]. In short, the

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[13] Even though no authors are listed in the report itself, the meta-data of the PDF suggests that Lee Ann Racz, employee of ToxStrategies, appears to have at least co-authored the report. As mentioned earlier, the true beneficiary of the report can not even be discerned, as it was "prepared for" Hogan Lovells, LLP, a law firm that regularly represents different large fluorination companies.

ToxStrategies report would suggest that the RPF approach used by RIVM is not scientifically sound. However, this is already contradicted in the abstract of the actual paper by Anderson et al.: "A tiered approach combining multiple lines of evidence was presented as a possible viable means for addressing PFAS that lack analytical and/or toxicological studies." While Anderson et al. do caution that this approach should only be used for screening purposes, a valuable nuance, it should be noted that ToxStrategies is simply misrepresenting the results of the paper in question. This is followed by a remarkably sustained attack on the RPF approach by RIVM, while simultaneously favouring a case by case risk evaluation approach for PFAS and not assuming additive effects at all. Instead, ToxStrategies suggests an approach based on the "sums of specific PFAS compound concentrations".

It is not difficult to see that the counter-suggestion by ToxStrategies, evaluating PFAS compounds on a case by case basis and simply adding their toxicological thresholds without assuming dose additivity, would result in a completely unworkable regulatory environment. Many compounds most likely never be fully assessed within any reasonable timeline. Due to the enormous variety of species that can be produced by the industry, for instance through partial fluorination, variation in moiety and especially (poly)esterification, the combined dosage would also be open to arbitrary increases without any regulatory implications.

ToxStrategies also takes aim at the "read-across" methodology in which the toxicity of PFAS is estimated by interpolating the known toxicity of "nearby" compounds. There is an irony at play here, as this ToxStrategies report was used in a permit request for the emission of PFPrA by 3M Belgium, for which no toxicological studies are available. Consequently, 3M has to resort to precisely such a "read-across" method to make its environmental assessment [89]. Clearly, real life scenarios simply require a read-across or similar assessment for substance without detailed toxicological profiles.

To complete the picture, the "Evaluation of Approaches for Assessing PFAS Mixtures" paper also includes a discussion on "Mixtures with Short- and Ultrashort-Chain PFAS". In it, ToxStrategies suggests that ultrashort PFAS like TFA and PFPrA should simply not be grouped with other perfluoroalkyl carboxylates and perfluoroalkyl sulfonates at al, based on an opinion by Colnot and Dekant that was financed by 3M [26].

"Evaluation of Approaches for Assessing PFAS Mixtures" by ToxStrategies can be categorised as a prime example of purposefully "manufacturing uncertainty" in a scientific field, described in chapter "The Art of Turning Reliable Research into Junk" by McGarity and Wagner [6]:

> "The attacks, in other words, are offered not in the spirit of advancing collaborative scientific dialogue, but in the hope of throwing the research into doubt and, if possible, discrediting it."

Discussion

An incredibly problematic picture emerges from the results our research into potential "science bending" originating from the fluorination industry. Numerous examples were found where significant aspects of the fluorination process and the environmental fate of organofluorides appear obfuscated by a coordinated effort of the leading industrial producers. This would be considered to be a wild claim under regular circumstances, were it not that this make it the third scandal of this type involving the halogenation industry, preceded by a similar episode involving CFC gases and the resulting hole in the ozone layer and of course the "Dark Waters" lawsuits two decades later.

Note that it is impossible to know the true intention of researchers involved. It is also enormously difficult to retrospectively prove any direct scientific fraud, in the form of manipulated or suppressed data in this area. However, what can be shown is that large financial incentives were created with a singular stated goal: To prove that PFC replacements for CFC gases are "environmentally acceptable". Additionally, several key researchers in this domain have shown up in other lobbying scandals: The Monsanto Papers, Chromium VI (the "Erin Brockovich" story), the regulation of magnanese and aspartane (artificial sweetener) and the "Endocrine Disruptors" group of scientists acting as lobbyists.

> Observation 1: The Montreal Protocol gave rise to a decades long science bending campaign that continues to this day and negatively affects our understanding of the environment fate of fluorinated substances. Especially the anthropological sources of TFA (and other ultrashort) PFAS in the environment appear to have been actively obfuscated.

Without directly proving the unreliability of the research in question, this observation does throw a large shadow of doubt over decades of publications. When looking at foundational publications especially those concerning TFA are troubling, as there is very little to no independent research to be found. Toxicological knowledge about very common environmental pollutants like TFMS, PFPrA, PFEtS and PFPrS is (almost) entirely missing and all these ultrashort PFAS are regularly excluded from environmental monitoring and permitting. While the potential bio-accumulation of substances is certainly an important factor in evaluating the potential harm of specific PFAS substances, it seems like this has become the overwhelmingly dominant regulatory discriminant. Ultrashort PFAS may not have the same accumulation factors, but their (much) higher mobility, bioavailability and often higher environmental concentrations should be enough for a thorough and fully independent reevaluation in the light of such a contestable body of evidence. For other ultrashort PFAS, such as PFPrA, PFEtS and PFPrS, for which no toxicological research is available, it is important to keep in mind that all of them have a Class III Cramer classification, "requiring the most extensive evidence for safety-in use" and fall easily within Lipinski's assessment of bioavailability.

> Observation 2: The toxicology of ultrashort PFAS may be significantly underestimated and/or dismissed on dubious grounds.

It would also appear that the industry has deliberately pivoted from “C8” like surfactants to complex fluorinated polyethers that pose significant analytical challenges. The production process appears to be far more non-specific than often though and various “styles” of polyethers appear to have been developed, making the variability of such products extremely large. Coupled with lacking analytical standards, this makes such compounds near invisible for commonly used analytical techniques. Determining the toxicity of each individual variant, especially when environmental degradation is involved, would appear to be impossible within any relevant timeframe.

> Observation 3: Fluorinated polyethers (used as modern surfactants) may have been developed/selected at least partly based on how difficult they would be to discover and/or analyse. They are designed to dodge regulation (the Montreal Protocol and the PFOA stewardship program) more than they are evaluated for environmental impact.

In general, numerous examples were found of significant “details” about the fluorination processes themselves that appear to have been obfuscated or simply left out of consideration. It has been shown that such “details” can often lead to as yet undisclosed emissions and unregulated/unmonitored compounds.

One of the noticeable aspects of environmental PFAS pollution, if both production and degradation/incineration processes are taken into consideration, is the fact that in virtually all cases there appears to be a static distribution of co-traveling PFAS compounds. In other words, if the production and/or degradation process is well known, it might be possible to (approximately) predict the entire distribution of PFAS variations. More profoundly, the case can be made that exposure to such “clusters of co-traveling PFAS” is much more common than exposure to a single molecule. This would imply that knowing the toxicity of such congener mixtures should be considered to be more environmentally and regulatory relevant than the toxicity of every single compound/variant. There may even be ways to reduce the enormous variety of compounds to a few distinct and dominant sets of congeners with predictable distributions.

> Observation 4: PFAS production, incineration and degradation processes could be predictive of specific distributions of congeners that are more relevant to additive toxicity and environmental regulation than individual compounds.

A critical element in PFAS monitoring and regulation is of course knowing what the total amount of organofluorides in products, emissions and the environment. Surprisingly, this is still begin evaluated, even though a commercially available and simple technique (SOF) that is perfectly “fit for purpose” and has been used for decades by 3M. The “total organofluoride” technique that is currently being put forward by 3M and Chemours (AOF) will *significantly* underestimate the true organofluoride concentrations present, making it not fit for purpose for controlling the total toxicological burden of PFAS.

> Observation 5: Analytical methods used to determine and evaluate "total organic fluoride" are deliberately contested, selected or adapted to make regulatory assessments more difficult.

Taken together, the potential existence of predictable "base distributions" of PFAS concentrations, especially in predictable industrial effluent and PFAS-based products, combined with the RPF methodology proposed by RIVM, might create a pathway towards an rough assessment of toxicity based on total organofluoride concentrations (TOF) alone. This would allow for a far more cost-efficiënt regulatory monitoring. Obviously this approach would not be appropriate for general environmental assessments due to the intermixing of different sources of fluor containing substances.

> Observation 6: A better understanding of the production and degradation distributions of PFAS could allow for far more effective regulatory assessments and monitoring, such industrial methods and even product compositions are however actively obscured by the fluorination industry.

In conclusion, the results found while researching potential 'Science Bending' by the fluorination industry are deeply concerning. Not only was a pattern of deceptive behaviour identified, it appears that the techniques used have only gotten more sophisticated, even involving the manipulation of (the certification of) analytical techniques. The negative impact on environmental regulation is undeniable.

The Dark PFAS Hypothesis

> Large multi-nationals like DuPont/Chemours, 3M, Solvay, Honeywell and others have conducted a coordinated campaign of deliberate science bending and regulatory capture to safeguard their fluorination businesses starting at the ratification of The Montreal Protocol and continuing to this day. In service of the introduction of HFK's as replacement products for CFK's, the source and toxicological relevance of environmental TFA (and other ultrashort PFAS) was deliberately obfuscated. Replacement products resulting from the PFOA stewardship program may have been designed specifically to dodge analytical detection by targeting ultrashort molecules as primary degradation products. Access to proper analytical techniques, standards and critical production information, which could all contribute to a full understanding of the environmental impact of PFAS, was and is actively and continually stymied.

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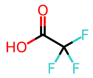
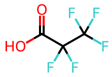
Appendix A: monoether PFAs



TFA



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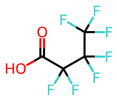

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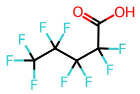

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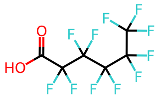
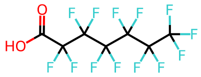
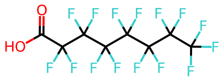


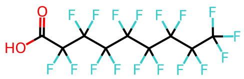
PFHxA



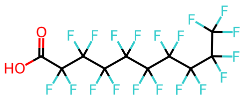
PFHpA



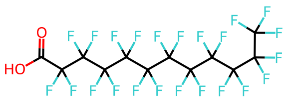
PFOA



PFNA



PFDA



PFDoA

Figure 42: PFCA's: perflourinated monoether carboxylic acids

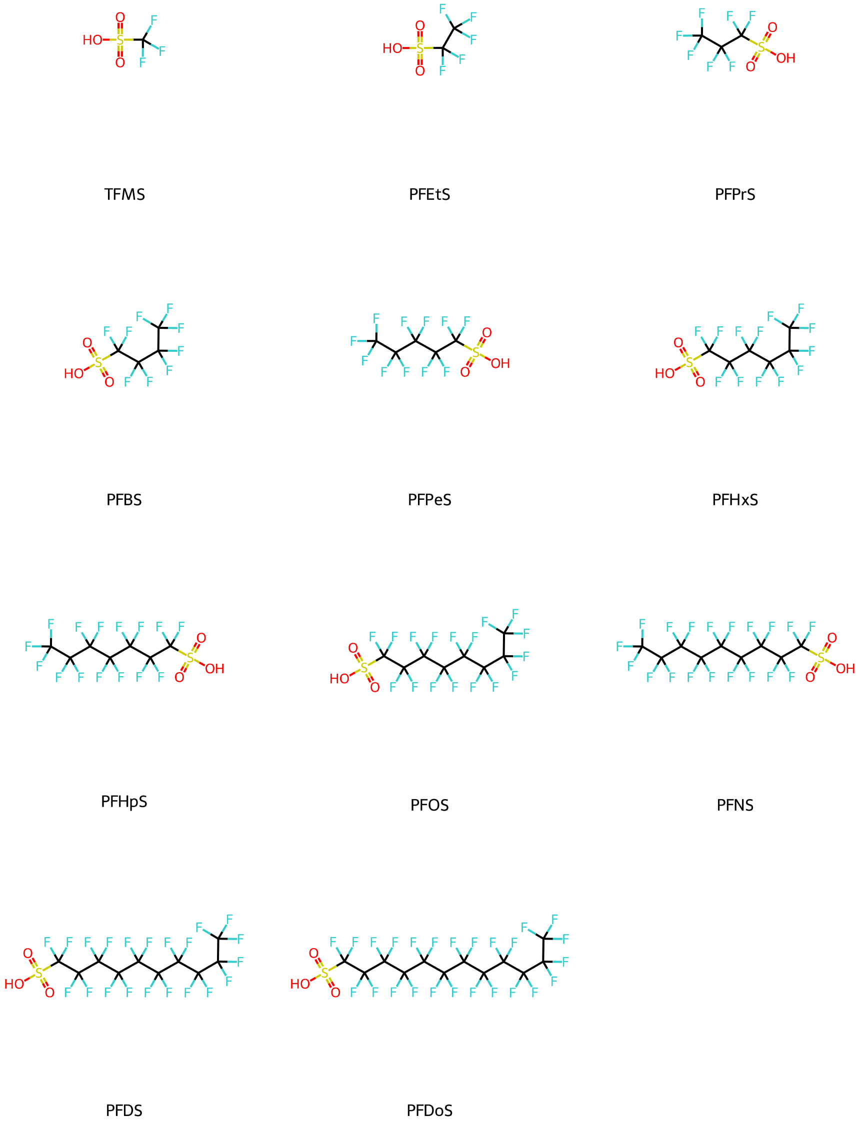


Figure 43: PFSA's: perflourinated monoether carboxylic acids

Appendix B: Research funding

Henry J. Trochimowicz, Hartmut Frank, Armin Jordan, Armin Klein, Melvin W. Anders, Wolfgang Dekant, George M. Rusch

- “Industrial research on alternative fluorocarbons” - *Henry J. Trochimowicz* (1993)
- “AFEAS Workshop on the Environmental Fate of Trifluoroacetic Acid” - *Hartmut Frank* (1994) , Funding: **AFEAS**
- “Trace analysis of airborne haloacetates” - *Hartmut Frank, Armin Klein, ...* (1995) , Funding: **State of Baden-Wurtternberg**
- “Toxicology of chlorofluorocarbon replacements.” - *Wolfgang Dekant* (1996)
- “Correspondence: Environmental Trifluoroacetate” - *Hartmut Frank, Armin Klein, ...* (1996)
- “Correspondence re: Epidemic of liver disease caused by hydrofluorocarbons used as ozone-sparing substitures of chlorofluorocarbons” - *George M. Rusch, Wolfgang Dekant, Melvin W. Anders* (1997)
- “Environmental Risk Assessment of Trifluoroacetic Acid” - *George M. Rusch, ...* (1999)
- “Environmental Risk Assessment of Trifluoroacetic Acid” - *George M. Rusch, ...* (1999)
- “Correspondence - New Directons: Exchange of comments on the origins and occurrence of trichloroacetic acid” - *Armin Jordan, Hartmut Frank, ...* (1999)
- “Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs” - *Armin Jordan, Hartmut Frank* (1999) , Funding: **AFEAS**
- “Natural fluorinated organics in fluorite and rocks” - *Armin Jordan, ...* (2000) , Funding: **Max-Planck-Society**
- “Volcanogenic Halocarbons” - *Armin Jordan, ...* (2000) , Funding: **EU-Japan Centre for industrial cooperation**
- “Haloacetates in Fog and Rain” - *Hartmut Frank, ...* (2001) , Funding: **German Federal Ministry**
- “Biotransformation of 1,1,1,3,3-Pentafluoropropane (HFC-245fa)” - *George M. Rusch, Melvin W. Anders, Wolfgang Dekant, ...* (2002) , Funding: **Honeywell**
- “Trifluoroacetylated adducts in spermatozoa, testes, liver and plasma and CYP2E1 induction in rats after subchronic inhalatory exposure to halothane” - *Wolfgang Dekant, ...* (2003) , Funding: **European Community**
- “Risks and Benefits of Fluorinated Greenhouse Gases in Techniques and Products under Special Consideration of the Properties Intrinsic to the Substance” - *Armin Jordan, ...* (2004) , Funding: **Umweltbundesamt**
- “Exposure of an Adult Population to Perfluorinated Substances Using Duplicate Diet Portions and Biomonitoring Data” - *Wolfgang Dekant, ...*

(2007) , Funding: **State of Bavaria**

- "Biotransformation of 2,3,3,3-tetrafluoropropene (HFO-1234yf)" - *George M. Rusch, Wolfgang Dekant, …* (2008) , Funding: **Honeywell**
- "Biotransformation of trans-1,1,1,3-tetrafluoropropene (HFO-1234ze)" - *George M. Rusch, Wolfgang Dekant, …* (2009) , Funding: **Honeywell**
- "Experimental Exposure to 1,1,1,3,3-Pentafluoropropane (HFC-245fa): Uptake and Disposition in Humans" - *Wolfgang Dekant, …* (2010)
- "Biotransformation of 2,3,3,3-tetrafluoropropene (HFO-1234yf) in rabbits" - *George M. Rusch, Wolfgang Dekant, …* (2010) , Funding: **Honeywell**
- "Uptake and disposition of 1,1-difluoroethane (HFC-152a) in humans" - *Wolfgang Dekant, …* (2012)
- "Biotransformation of 2,3,3,3-tetrafluoropropene (HFO-1234yf) in male, pregnant and non-pregnant female rabbits after single high dose inhalation exposure" - *George M. Rusch, Wolfgang Dekant, …* (2012) , Funding: **Honeywell**
- "Endocrine effects of chemicals: Aspects of hazard identification and human health risk assessment" - *Wolfgang Dekant, …* (2013)
- "Biotransformation of trans-1-chloro-3,3,3-trifluoropropene (trans-HCFO-1233zd)" - *George M. Rusch, Wolfgang Dekant, …* (2013) , Funding: **Honeywell**
- "The development of environmentally acceptable fluorocarbons" - *George M. Rusch* (2018) , Funding: **AFCTC**
- "Commentary: cumulative risk assessment of perfluoroalkyl carboxylic acids and perfluoralkyl sulfonic acids: what is the scientific support for deriving tolerable exposures by assembling 27 PFAS into 1 common assessment group?" - *Wolfgang Dekant, …* (2022) , Funding: **3M**

Keith R. Solomon, Brian F. Scott, Mark L. Hanson, D. C. G. Muir

- "Detection of Chlorodifluoroacetic Acid in Precipitation: A Possible Product of Fluorocarbon Degradation" - *Mark L. Hanson, Keith R. Solomon, Brian F. Scott, …* (2000) , Funding: **NSERC "Strategic Program"**
- "Haloacetic Acids in Canadian Lake Waters and Precipitation" - *Brian F. Scott, …* (2000)
- "Trifluoroacetic acid in ancient freshwater" - *Brian F. Scott, …* (2001)
- "Trichloroacetic acid (TCA) and trifluoroacetic acid (TFA) mixture toxicity to the macrophytes Myriophyllum spicatum and Myriophyllum sibiricum in aquatic microcosms" - *Mark L. Hanson, Keith R. Solomon, …* (2002) , Funding: **NSERC, CNTC**
- "Distribution of Haloacetic Acids in the Water Columns of the Laurentian Great Lakes and Lake Malawi" - *Brian F. Scott, …* (2002)
- "Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mykiss)" - *Keith R. Solomon, …* (2003) , Funding: **HCEC (Toxic Substances Research Initiative), CNTC**
- "Haloacetic acids in the aquatic environment. Part II: ecological risk as-

sessment" - *Mark L. Hanson, Keith R. Solomon* (2004)

- "Haloacetic acids in the aquatic environment. Part I: macrophyte toxicity" - *Mark L. Hanson, Keith R. Solomon* (2004) , Funding: **NSERC, CNTC**
- "Comparison of Haloacetic Acids in the Environment of the Northern and Southern Hemispheres" - *Brian F. Scott, D. C. G. Muir, …* (2005) , Funding: **Euro-CHlor (Cefic)**
- "Poly and Perfluorinated Carboxylates in North American Precipitation" - *Brian F. Scott, …* (2006)
- "Effects of Atrazine in Fish, Amphibians, and Reptiles: An Analysis Based on Quantitative Weight of Evidence" - *Keith R. Solomon, …* (2014)
- "Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols" - *Keith R. Solomon, …* (2016)