Comments on

Annex XV RESTRICTION REPORT

PROPOSAL FOR A RESTRICTION

SUBSTANCE NAME(S): Per- and polyfluoroalkyl substances (PFASs)

Submitted by Individual Mr. Luke Lu from China

Submitted on August 14, 2023

1. The term "PFASs" is not clear and easy to confuse with other PFASs defined by other countries, institutions and scientists.

Per- and polyfluoroalkyl substances (PFASs) has been used and defined by many scientists and organizations.

In an article published by Emily Hammel, Thomas F. Webster, Rich Gurney, and Wendy Heiger-Berneys (Implications of PFAS definitions using fluorinated pharmaceuticals, iScience, 25, 104020, April 15, 2022, https://doi.org/10.1016/j.isci.2022.104020), nine PFASs definitions were listed in Table 1 therein and 360 organofluorine pharmaceuticals between 1954 and 2021 screed against the nine PFASs definitions, the result was shown in Table 3 therein. For the same group of pharmaceutical substances, the nine PFASs definitions cover a different members of the pharmaceuticals, in a range from 4 to 360, i.e., 1.1% to 100%.

With the fact as shown, I suggest that the dossier submitter create a novel term to name the substances that they plan to restrict in EU in order to avoid any confusion with these existed definitions in the future.

As another choice, I suggest that the dossier submitter list all the specific substances in their names and CAS numbers out so that a precision control can be enforced without any confusion caused by using a general and inexact definition. If so, the requirement on the clearness of the definition may be lowered, namely no further explanation needs.

2. CAS NUMBER(S) should not be missed or omitted, and the dossier submitter should provide them in the proposal in a future version for a better enforcement of this Proposal of a Restriction if it will be approved.

This proposal for a restriction in the current version did not provide the CAS numbers for the said substances.

This proposal for a restriction can only be enforced by limiting the manufacturing activities and using activities in EU, as well as by limiting the importing activities from other countries and areas out of EU into EU. CAS numbering system has been widely accepted and used globally. Providing CAS NUMBER(S) will let foreign companies and individuals clearly know what substances can enter the territory of EU.

3. Whether have all PFASs as defined by the Proposal for a Restriction the said very high persistence? The answer is “NOT ALL”.

Based on my understanding and guess of the meaning of the PFASs definition as provided by this proposal for a restriction, persistence plays a key role to establish this proposal of a restriction.

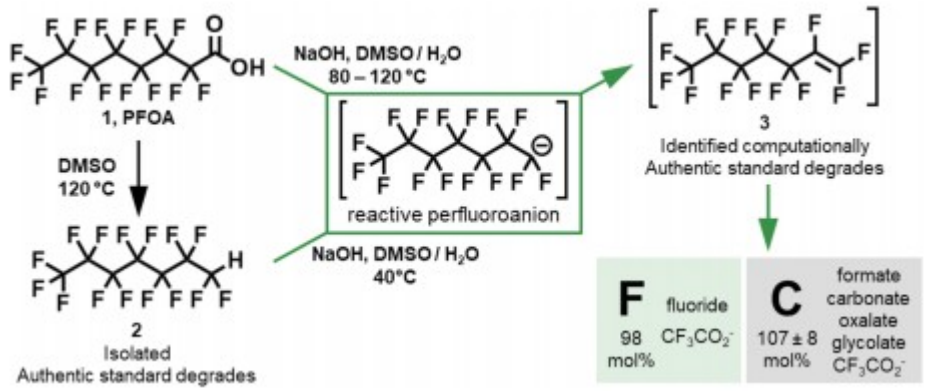
The article entitled “Low-temperature mineralization of perfluorocarboxylic acids” (published in Science, 377 (6608), DOI:10.1126/Science.abm8868, view this article online https://www.science.org/doi/10.1126/science.abm8868), shows that perfluorooctanoic acid (PFOA) can be degraded in the presence of NaOH in a mixture of water and dimethyl sulfoxide (DMSO) at mild temperatures (80 to 120 ℃) and ambient pressure. This demonstrates that PFAS can be degraded and the said persistence does not exist or can be overcome by technology innovation. Under these conditions, perfluorooctanoic acid (PFOA, **1**) is completely degraded with > 90% defluorination and minimal formation of fluorocarbon by-products. In a solution of DMSO and H_2O (8:1 v/v) at 120℃, PFOA dicarboxylates to form perfluo-1H-heptane **2**, which phase separates from solution as an oil. Please see Fig. 1. Overview of degradation pathways identified in this study.

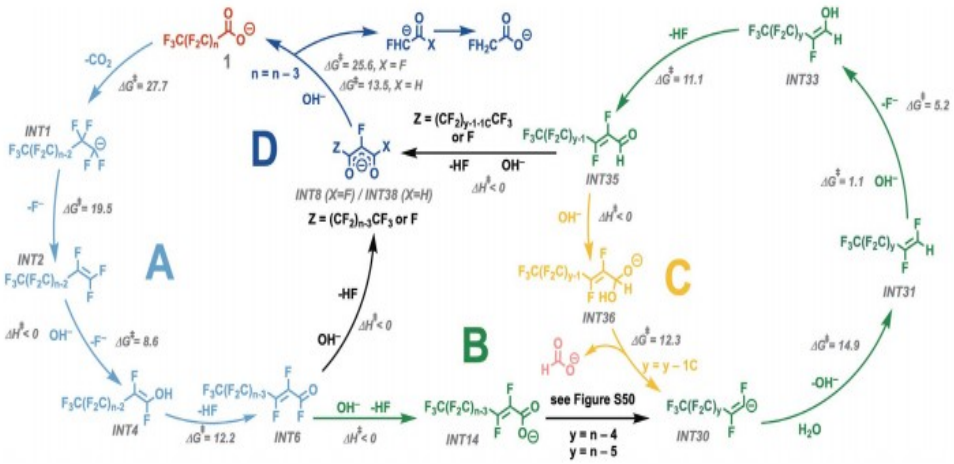
The research work of Brittany and et al shows perfluoroalkyl carboxylic acids (PFCAs) could be mineralized through a sodium hydroxide-mediated defluorination pathway. PFCA decarboxylation in polar aprotic solvents produced reactive perfluoroalkyl ion intermediates that

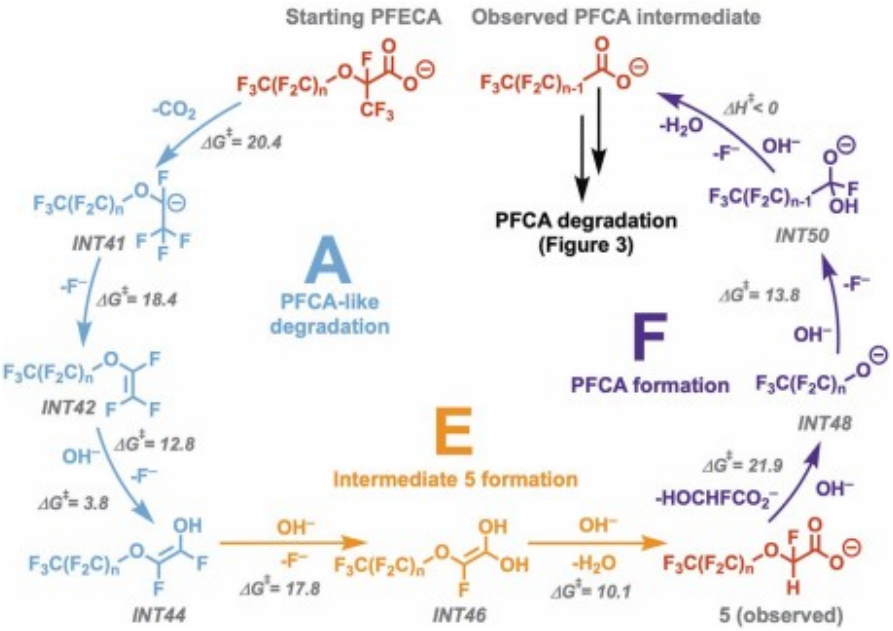
degraded to fluoride ions (70 to ~100%) within 24 hours. The carbon-containing intermediates and products were inconsistent with oft-proposed one-carbon-chain shortening mechanisms. Degradation was also observed for branched perfluoroalkyl ether carboxylic acids and might be extended to degrade other PFAS classes as methods to activate their polar headgroups are identified.

Therefore, at least, the class, PFCA, among the said PFAS, are degradable. **So, this proposal for a restriction was not based on a complete investigation of scientific facts.**

The following is a copy of Fig. 1, Fig. 3, and Fig. 4 of this Brittany's article.







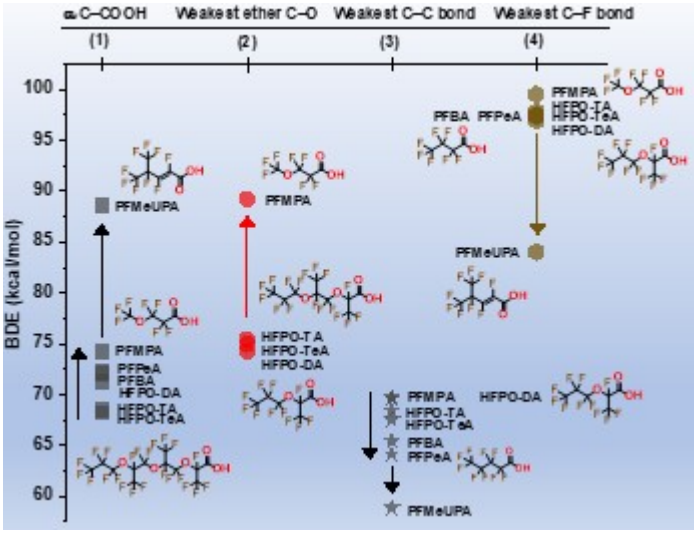
4. **Some PFASs have the property of thermal decomposition. Please exclude them from this Proposal for a Restriction.**

This proposal for a restriction is based on the high persistence of the said substances.

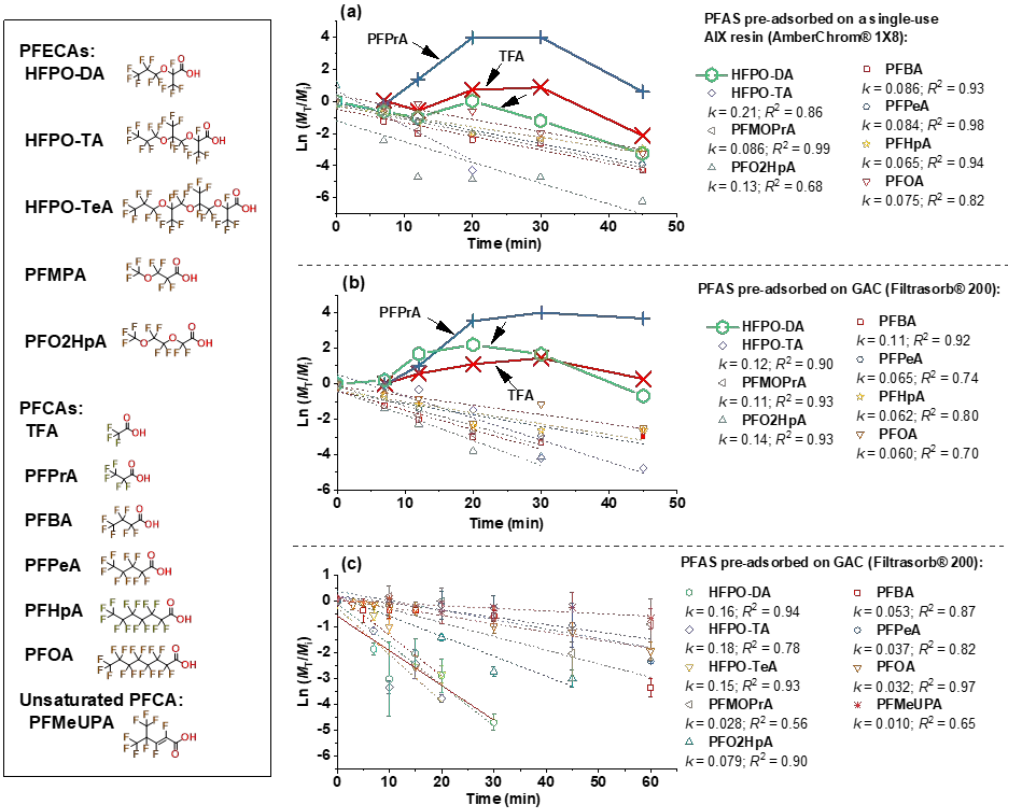
However, as I know, a recently-published article (Ali Alinezhad and et al, Mechanistic Investigations of Thermal Decomposition of Perfluoroalkyl Ether Carboxylic Acids and Short-Chain Perfluoroalkyl Carboxylic Acids, Environmental Science & Technology, 2023, 27, 8796-8807, https://doi.org/10.1021/acs.est.3c00294) says that perfluoroalkyl ether carboxylic acids (PFECAs) and short-chain perfluoroalkyl carboxylic acids (PFCAs) can be degraded by thermal decomposition.

The following is a copy of the figures in the article written by Ali Alinezhad and et al.

1). The Figure of the Abstract

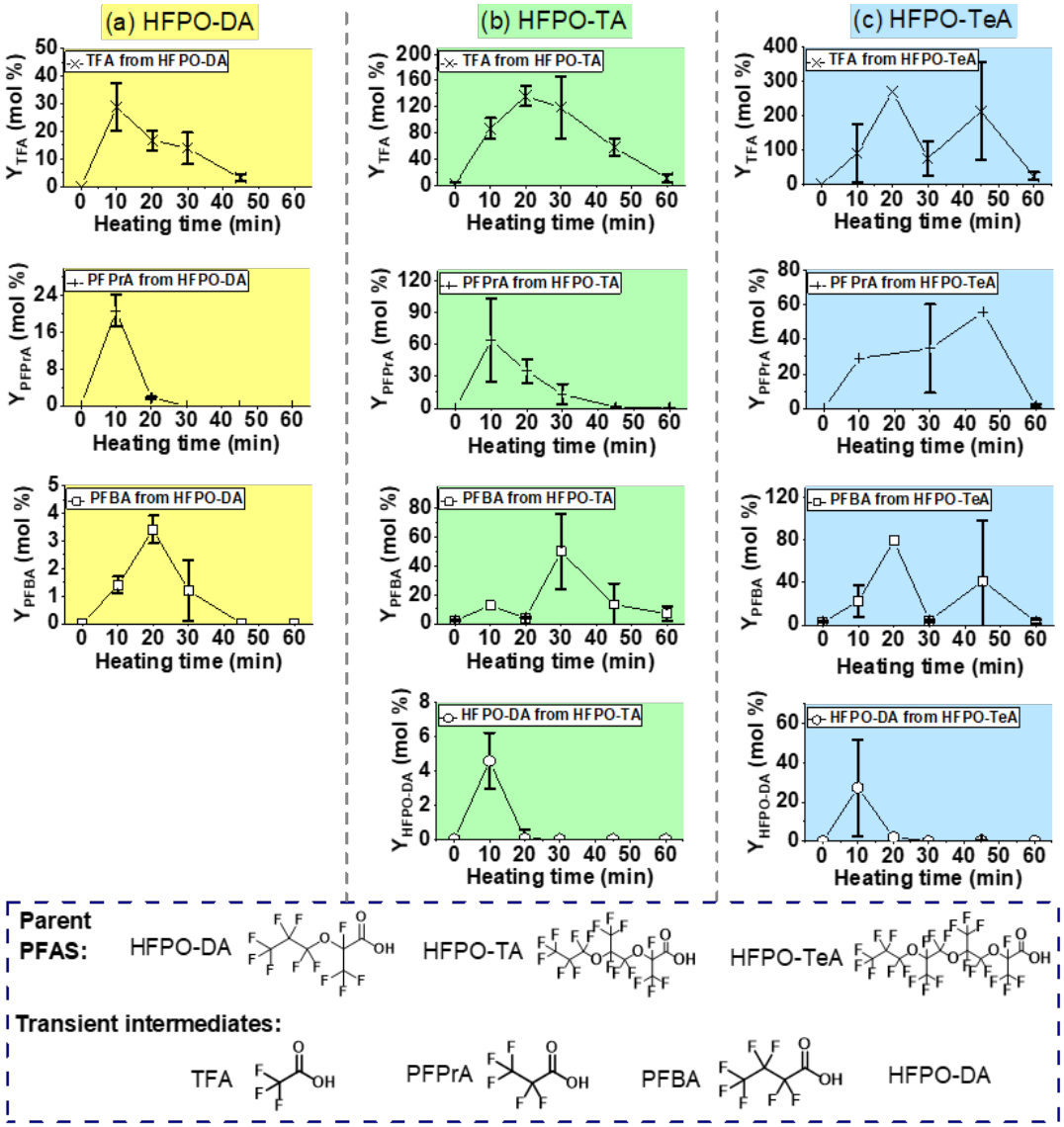


2). Thermal degradation of PFECAs and PFCAs on adsorbents at 200°C for up to 60 min in N_2.

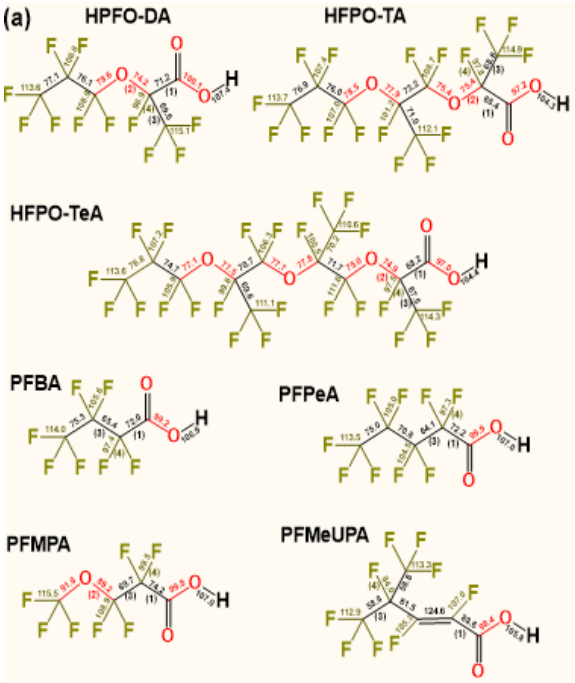


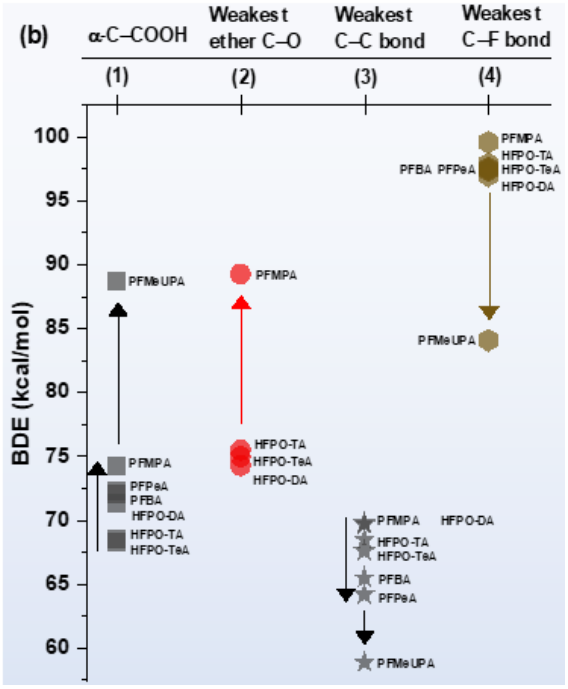
The generation and subsequent degradation of TFA, PFPrA and HFPO-DA during the thermal treatment are illustrated by arrows.

3). Yield of intermediates from a single PFECA preadsorbed on GAC after heating at 200°C for a different durations.

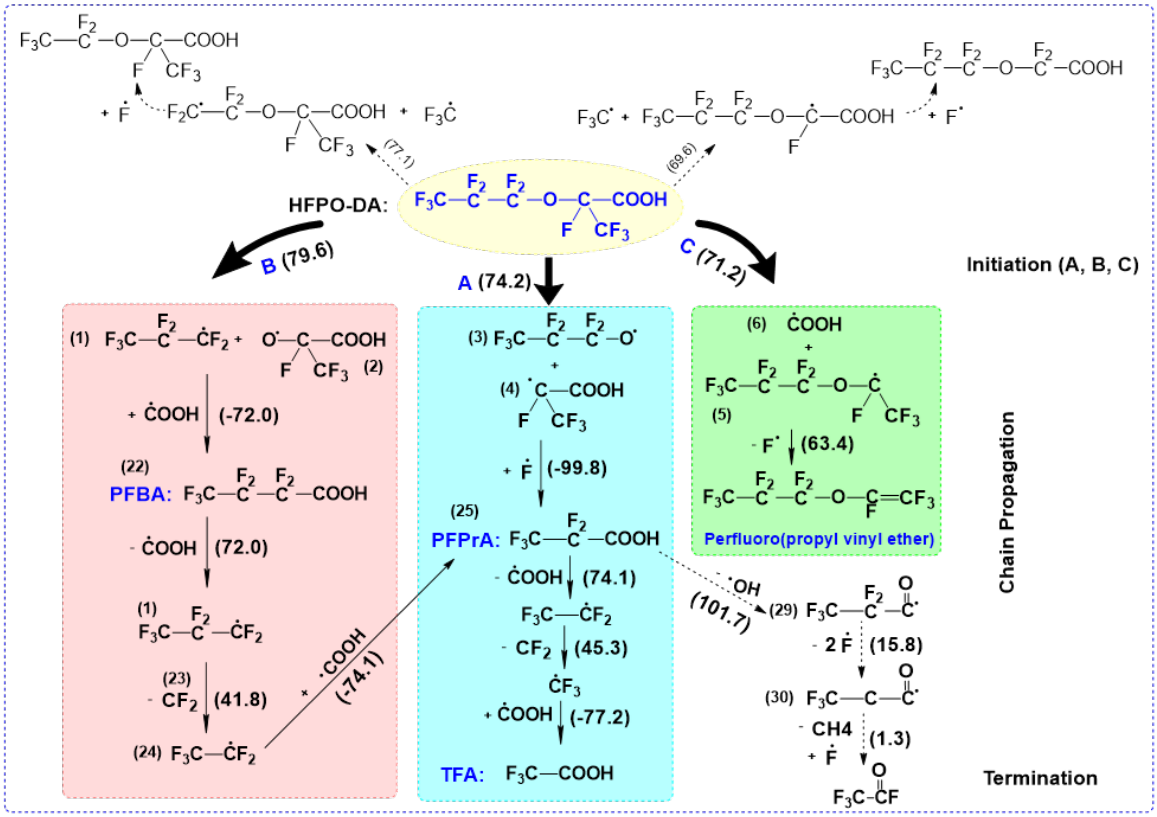


4). BDEs of PFAS calculated at the M06-2X/Def2-TZVP level of theory using high-performance computing resources.

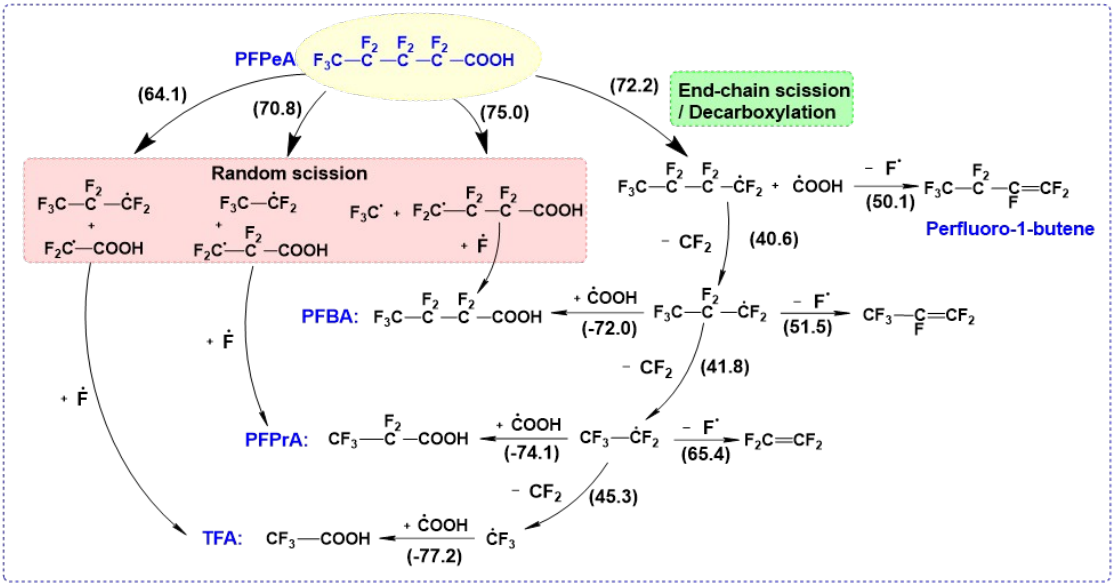




5). Proposed thermal decomposition pathways of HFPO-DA



6).Proposed thermal decomposition pathways (i.e., random-chain scission and end-chain scission) of PFPeA. PFBA, PFPrA, TFA and perfluoro-1-butene are detected as thermal decomposition products of PFPeA.



Based on the scientific facts recently-published, there are some substances in the scope of PFASs as defined by the dossier submitter, which do not have the property of persistence, and are not PFAS substances in fact. From this view, the Proposal of a Restriction should discuss the risk of the substances one by one. It is unsuitable to discuss them group by group. This is not based on scientific findings and makes the Proposal of a Restriction not meet the clearness requirement as a regulation. If the Proposal of a Restriction would be passed, it will limit the development of society and economy of EU.

5. **The scope of this Proposal of a Restriction is not clear**.

According to the text of this Proposal of a Restriction, the substances as defined therein is PFAS. In the second paragraph entitled “Introduction of Summary” of Page 1, the expression “thousands” is used to described the number of the substances covered by this Proposal. But on February

7, 2023, during the Media Briefing at Brussels, the number was said as “Roughly 10 000 PFASs”. Then, on 5 April 2023, during the webinar: Consultation on restriction proposal for per- and polyfluoroalkyl substances (PFAS), the number was said as “>10 000 PFASs”. These facts show that it is unclear how many substances are covered by this Proposal of a Restriction. The dossier submitter needs to make more efforts to make the scope clear.

6. This Proposal of a Restriction took the PFAS definition provided by OECD 2021, but omitted a key piece of information that OECD 2021 stressed “which does not inform whether a compound is harmful or not” in Paragraph 3 of Page 8. And the boundary between PFAS and non-PFAS is not clear.

In the document entitled “Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance”, it says “The rationals behind the revision is to have a general PFAS definition that is coherent and consistent across compounds **from the chemical structure point of view** and is easily implementable from distinguishing between PFASs and non-PFASs, also by non-experts”. Therefore, it defines the group of substances by its molecular trait. Further, in Figure 5 and Figure 6, it gives examples to illustrate which substance is a PFAS or not a PFAS. However, it did not indicate whether the non-PFAS example list is exhaustive or not. For a specific substance,

it is unclear whether the substance should be a PFAS or a non-PFAS. In Page 20 of this Proposal of Restriction, it does not provide a clear boundary between PFAS and non-PFAS.

Because the document entitled “Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance” stressed that it does not inform whether a compound is harmful or not, the Proposal of Restriction needs firstly to provide a reason and solid evidence to regard these substances as a risk to environment and human health. Otherwise, there is lack of basis for the restriction.

7. **The definition of OECD 2021 is one based on molecular structure alone, and does not relate any risks to these substances under the definition**.

Please refer to Page7, Executive Summary of the document named as “OECD (2021), Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, OECD Series on Risk Management, No. 61, OECD Publishing, Paris”. It says “this report highlights… (3) a systematic approach to characterization of PFASs based on molecular structural traits to assist stakeholders, including non-experts, in making their own categorization based on their needs (Chapter 4)….”.

Also, please refer to Page C of the article entitled “A New OECD

Definition for Per- and Polyfluoroalkyl Substances" written by Zhanyun Wang et al, https://doi.org/10.1021/acs.est.1c06896. In the section "PRACTICAL GUIDANCE ON HOW TO USE THE PFAS TERMINOLOGY", it says that the report highlights the need to distinguish between the general definition and user-specific working scopes of PFASs. The general definition is based on molecular structure alone and serves as a starting and reference point to guide individual users to have a comprehensive understanding of the scale and diversity of chemicals in the PFAS universe."

Therefore, **OECD (2021) definition is only based on molecular structure, did not relate the substances with risks**.

Now, the Proposal of a Restriction takes the definition of PFASs to manage the risks to environment and human being.

However, the Proposal of a Restriction did not prove what risks are related to the PFAS grouped together only based on the molecular structure. Therefore, this Proposal of a Restriction needs to provide solid information on why these substances should be managed based on what risks.

8.The Proposal of a Restriction studied 14 use sectors and/or uses, which is far less than the broad uses of these substances.

I provide a copy of the paper written by Juliane GlÜge and et al (An overview of the uses of per- and polyfluoroalkyl substances (PFAS),

Environmental Science Processes & Impacts, 2020, 22. 2345-2373, DOI:10.1039/d0em00291g). This paper studied more than 200 use categories and subcategories for more than 1400 individual PFAS. I hope the Dossier Submitter to make more efforts to investigate the uses and the individual compounds under the said PFAS definition. Better understanding an issue will lead to a better solution.

9. The Proposal of a Restriction did not give a clear requirement on how to meet a derogation basis and how to apply a derogation from it.

The essential-use concept is a key thing when giving a derogation for a specific use. But, the Proposal of a Restriction did not give a clear requirement on it.

Now, I provide a copy the article “Juliane Glüge, Rachel London, Ian T. Cousins, Jamie DeWitt, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Mark Miller, Carla A. Ng, Sharyle Patton, Xenia Trier, Zhanyun Wang, and Martin Scheringer, Information Requirements under the Essential-Use Concept: PFAS Case Studies, Environ. Sci. Technol. 2022, 56, 6232-6242”. Please refer to this article to make the Proposal of a Restriction more complete.

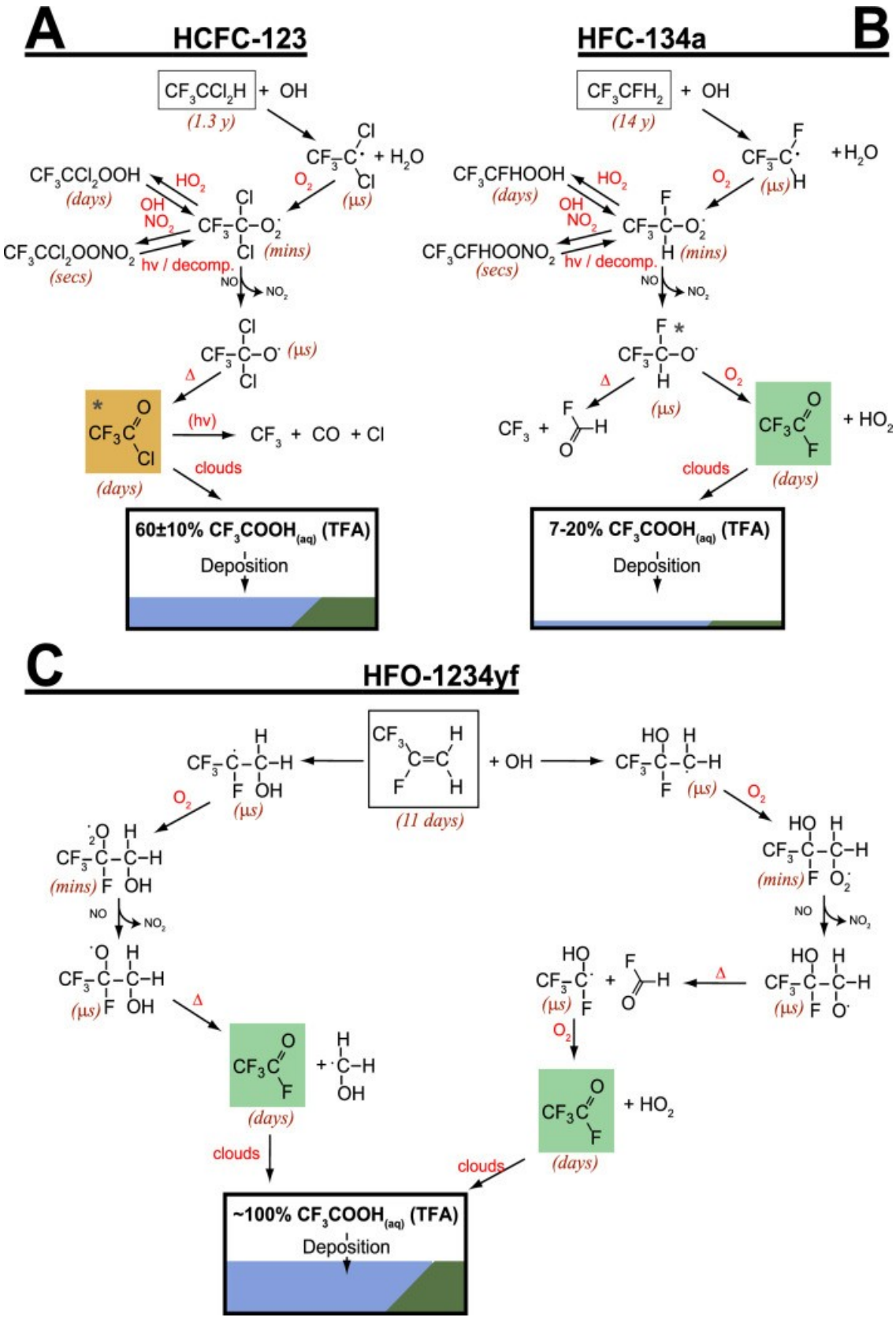
10. This Proposal of a Restriction should not cover the F-gas used as refrigerants.

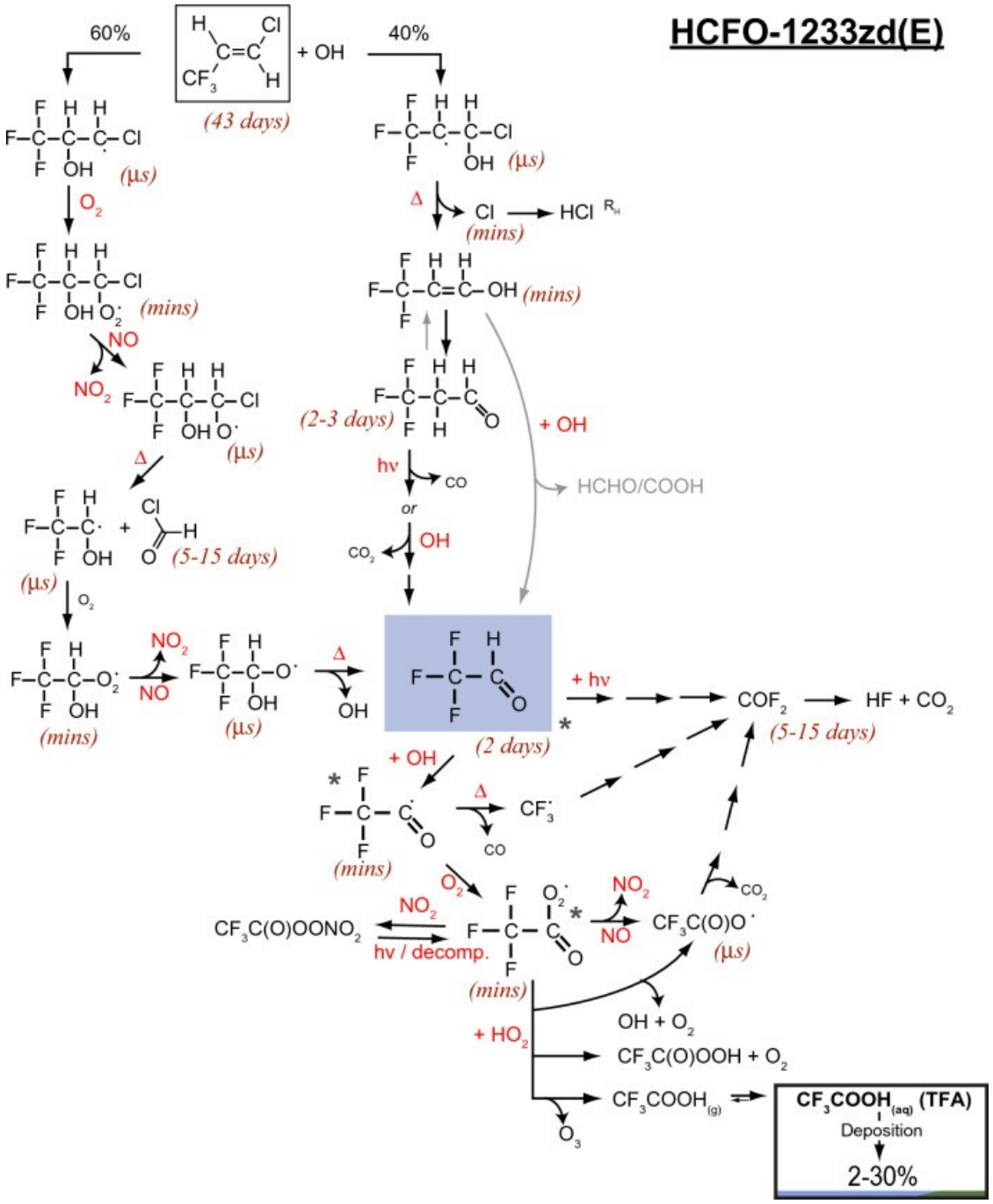
The fluorinated gases (i.e., F-gas) are used as refrigerants. These substances fall under the purview of the Montreal Protocol and its

Amendments.

Trifluoroacetic acid (TFA) is the terminal breakdown product of many F-gas.

Here is a copy of Fig. 10 and Fig. 11 of the article (S. Madronich and et al, Changes in tropospheric air quality related to the protection of stratospheric ozone in a changing climate, Photochemical & Photobiological Sciences, published online 13 June 2023, https://doi.org/10.1007/s43630-023-00369-6).


A
HCFC-123
B
HFC-134a
C
HFO-1234yf
(1.3 y)
(14 y)
(11 days)
(days)
(secs)
(mins)
(μs)
hv / decomp.
(hv)
clouds
Deposition
60±10% CF3COOH(aq) (TFA)
7-20% CF3COOH(aq) (TFA)
~100% CF3COOH(aq) (TFA)



These two figures show the atmospheric degradation pathways of said F-gases, i.e. HCFC-123, HFC-134a, HFO-1234yf and HCFO-1233zd(E). There are TFA formed.

The following information is from Table 3:

Table 3

Projected global yields of TFA from HFC-134a and HFO-1234yf and total deposition between 2020 and 2100

	HFC-134a	HFO-1234yf	Sum
Annual formation of TFA (a. e., acid equivalents)			
2020	0.01–0.03 Tg year^{-1}	0.03–0.03 Tg year^{-1}	0.04–0.06 Tg year^{-1}
2050	0.02–0.05 Tg year^{-1}	0.34–0.49 Tg year^{-1}	0.36–0.54 Tg year^{-1}
2100	0.01–0.02 Tg year^{-1}	0.63–1.03 Tg year^{-1}	0.64–1.05 Tg year^{-1}
Sums of deposited TFA (a. e.)			
2020–2050	0.5–1.5 Tg	5.3–6.6 Tg	5.8–8.1 Tg
2020–2100	1.0–2.9 Tg	30.5–49.0 Tg	31.5–51.9 Tg
		2050	244–246 ng L^{-1}
Concentration of TFA as the sodium salt in the oceans in			
		2100	266–284 ng L^{-1}

These data are taken from Table 7.3 of the 2022 report of the Science Assessment Panel [212] and currently are best estimates for the two listed refrigerants. Releases of other potential sources of TFA (see Fig. 12) have not been included but are expected to be much smaller. Estimated future concentration in the oceans is based on the nominal value of 200 ng a.e. L^{-1} in 2020 and a total volume of 1.36×10^9 km^{-3}. For comparison to toxicity values, concentrations have been converted to sodium salt

This article says that trifluoroacetic acid (TFA) has no obvious pathway of degradation and might accumulate in some water bodies, bu is unlikely to cause adverse effects out to 2100 (please see the last two lines of the Abstract of this article).

References:

1. Emily Hammel, Thomas F. Webster, Rich Gurney, and Wendy Heiger-Berneys (Implications of PFAS definitions using fluorinated pharmaceuticals, iScience, 25, 104020, April 15, 2022, https://doi.org/10.1016/j.isci.2022.104020).

2. Brittany Trang, Yuli Li, Xiao-Song Xue, Mohamed Ateia K.N. Houk, William R. Dichtel, Low-temperature mineralization of perfluorocarboxylic acids" (published in Science, 377 (6608), DOI:10.1126/Science.abm8868, view this article online https://www.science.org/doi/10.1126/science.abm8868).

3.Ali Alinezhad and et al, Mechanistic Investigations of Thermal Decomposition of Perfluoroalkyl Ether Carboxylic Acids and Short-Chain Perfluoroalkyl Carboxylic Acids, Environmental Science & Technology, 2023, 27, 8796-8807, https://doi.org/10.1021/acs.est.3c00294).

4.OECD (2021), Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, OECD Series on Risk Management, No. 61, OECD Publishing, Paris.

5. Zhanyun Wang et al, A New OECD Definition for Per- and Polyfluoroalkyl Substances, https://doi.org/10.1021/acs.est.1c06896.

6. Juliane GlÜge and et al, An overview of the uses of per- and

polyfluoroalkyl substances (PFAS), Environmental Science Processes & Impacts, 2020, 22. 2345-2373, DOI:10.1039/d0em00291g.

7.Juliane Glüge, Rachel London, Ian T. Cousins, Jamie DeWitt, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Mark Miller, Carla A. Ng, Sharyle Patton, Xenia Trier, Zhanyun Wang, and Martin Scheringer, Information Requirements under the Essential-Use Concept: PFAS Case Studies, Environ. Sci. Technol. 2022, 56, 6232-6242.

8. S. Madronich and et al, Changes in tropospheric air quality related to the protection of stratospheric ozone in a changing climate, Photochemical & Photobiological Sciences, published online 13 June 2023, https://doi.org/10.1007/s43630-023-00369-6).