

Summary: UNEP EEAP 2022 Assessment Report on Environmental Effects of Stratospheric Ozone Depletion, UV Radiation, and Interactions with Climate Change

Introduction

The United Nations Environmental Programme (UNEP) is responsible for coordinating responses to environmental issues within the UN system. Under the UNEP, the Environmental Effects Assessment Panel (EEAP) assesses the various effects of ozone layer depletion. It consists of members who are scientists working in photobiology and photochemistry, mainly in universities and research institutes.

In 2023 the EEAP produced an Assessment Report titled, Environmental Effects of Stratospheric Ozone Depletion, UV Radiation, and Interactions with Climate Change 2022 Assessment. This report outlines key considerations indicating that TFA should not be classified as a PFAS and should not be subject to regulations related to PFAS.

Below are the four key takeaways to consider from the report.

1. All PFAS Should Not be Grouped Together

UNEP puts forth the point that PFAS should not all be grouped together because of their unique properties and characteristics, and TFA specifically should be excluded for that reason. Because the term PFAS includes thousands of substances, judging them as a group based off persistence is inappropriate as it does not account for differing toxicities, or other characteristics. With additional regard to persistence as the regulatory criterion, UNEP maintains that TFA does not bioaccumulate nor is it toxic at the low to moderate exposures currently measured in the environment, and indicates (page 290) that their "opinion is that persistence should only be considered as a regulatory criterion for substances that are moderately or highly toxic and/or are bioaccumulative in organisms and/or undergo trophic magnification" (i.e., undergo increasing concentration as they move across the nutritional levels in a food chain).

UNEP points out (page 278) that it is well known that perfluorocarboxylic acids (PFCAs) have "key chemical, physical, and biological properties that become quite different with increasing length of the carbon chain". It is therefore inappropriate to compare short-chain (C2) TFA with longer chain PFCAs which have vastly different physicochemical and biological properties. Therefore, TFA should be examined as its own unique chemical as it relates to regulatory action.

- a. A majority of a panel of experts (Anderson, J. K., et.al., 2022) agreed that "all PFAS should not be grouped together, persistence alone is not sufficient for grouping PFAS for the purposes of assessing human health risk, and that the definition of appropriate subgroups can only be defined on a case-by-case manner". In addition, the majority opinion with respect to toxicology was that "it is inappropriate to assume equal toxicity/potency across the diverse class of PFAS." UNEP concludes (page 278) that "This same argument applies to the inclusion of TFA, with a two-carbon chain and a single CF3 group, into a class with longer chain PFAS."
- b. "Trifluoroacetic acid has biological properties that differ significantly from the longer chain polyfluoroalkyl substances (PFAS) and inclusion of TFA in this larger group of chemicals for regulation would be inconsistent with the risk assessment of TFA" (UNEP EEAP 2022 Assessment Report, pg. 25).
- c. "TFA is a perfluorinated acid that has been included in the class of per- and polyfluoroalkyl substances (PFAS). This class of chemicals contains 4730 substances, of which about 256 are in commercial use. Even in the subclass of perfluorinated alkanoic acids, the physical, chemical, and biological properties of these substances differ widely, mostly in relation to length of the alkyl chain. To regulate these substances as a class (as has been suggested) is not scientifically defensible and TFA should be treated as a unique chemical for the purposes of regulation" (UNEP EEAP 2022 Assessment Report, pg. 292).



- d. "An extensive review of the potential effects of TFA in the environment published by the German Environmental Agency did not identify any risks other than the persistence of TFA in the environment, which is a legislative rather than toxicological criterion" (UNEP EEAP 2022 Assessment Report, pg. 290).
- e. "The stability of TFA and its salts indicates a half-life >> 6 months, but our opinion is that persistence should only be considered as a regulatory criterion for substances that are moderately or highly toxic and/or are bioaccumulative in organisms and/or undergo trophic magnification. TFA does not bioaccumulate nor is it toxic at the low to moderate exposures currently measured in the environment or those predicted in the distant future" (UNEP EEAP 202 Assessment 2 Report, pg. 290).

2. TFA Does Not = PFAS Regulation

An analysis of TFA for the purpose of regulation requires an understanding of the physical, chemical, and toxicological data, in addition to a consideration of realistic environmental concentrations. The UNEP believes that TFA should be excluded from the class of PFAS because of its unique properties that would be considered in a focused assessment on it as a unique chemical.

- a. "There is a large uncertainty associated with the magnitude of other sources of TFA (e.g., potential natural sources, fluorinated pesticides, and pharmaceuticals), which do not fall under the purview of the Montreal Protocol" (UNEP EEAP 2022 Assessment Report, pg. 25).
- b. "A sound assessment of the environmental impact of TFA needs to consider the relevant physical, chemical, and toxicological data and realistic environmental concentrations. We are of the opinion that the properties of TFA indicate that it should not be included in this class for the purposes of generic regulatory risk assessment" (UNEP EEAP 2022 Assessment Report, pg. 279).

3. TFA Concentrations are Below the Thresholds of Concern Related to Human Health and the Environment

TFA does not pose a threat to humans or to the environment because the amounts of it in the environment are significantly low, and it has unique qualities that prevent it from bioaccumulating. The UNEP report finds that while TFA has been found in the environment, the levels are so low that they are not likely to pose a significant threat to humans or the environment. Specifically, the amounts of HF and TFA, generated from the degradation of HFOs represent less than a 0.5% contribution to the formation of acid rain in comparison to other sources and is judged to not be of concern.

The UNEP report highlights several properties of TFA that demonstrate the absence of a threat to humans or the environment. For example, TFA is not reactive, so its salts exist in the environment for years. However, since TFA does not react with biomolecules, this example of persistence is not a concern to UNEP. Salts of TFA also do not bioaccumulate in food chains and exemplify low toxicity to animals and plants, demonstrating that they do not present a high risk. Current loads of TFA being released will contribute to existing amounts in the environment, but UNEP's report highlights that the amounts will still be below the threshold of concern for human and environmental health.

- a. "The increases in trifluoroacetic acid concentrations due to replacements of the ozone-depleting substances are not expected to pose significant risk to humans or the environment at the present time" (UNEP EEAP 2022 Assessment Report, pg. 25).
- b. Figure 11 shows HFO-1234yf has an estimated 30 Gg yr⁻¹ (gigagrams per year) of global emissions. (UNEP EEAP 2022 Assessment Report, pg. 26).
- c. "Breakdown products of some fluorinated chemicals include hydrofluoric acid (HF) and TFA, which are strong acids. However, the amounts generated from the oxidation of HFOs represent only a small (< 0.5%) contribution to the formation of acid rain in comparison to other sources



such as sulfur and nitrogen oxides and this is judged to not be of concern" (UNEP EEAP 2022 Assessment Report, pg. 283).

- d. "MIR studies and atmospheric modeling studies of HFO-1234yf, have shown that O₃ production from HFO-1234yf is indistinguishable from that from ethane (also consistent with Table SI 3, Appendix), and that replacing HFC-134a in vehicle air conditioning units with HFO-1234yf across the United States has a negligible impact (< 0.01 %) on the formation of tropospheric ozone. It is clear from the above, that the small increases in tropospheric ozone formation generated from a transition from HFC emissions to emissions of HFOs would not be of concern" (UNEP EEAP 2022 Assessment Report, pg. 291).</p>
- e. "Because of its lack of reactivity, TFA salts are persistent in the environment and estimates of half-life are uncertain but could be in the range of centuries or millennia. This persistence is not a major concern because it does not react with biomolecules. TFA and its salts are easily excreted by animals and do not bioaccumulate in food chains. Salts of TFA have low toxicity to animals and plants and there are very wide margins between current/projected exposures and toxicity values" (UNEP EEAP 2022 Assessment Report, pg. 292).
- f. Replacement of HCFCs and HFCs with HFOs releases "will add to the existing load of TFA in the environment but predicted amounts are well below the threshold for concern with respect to human and environmental health" (UNEP EEAP 2022 Assessment Report, pg. 292).
- g. "The HFOs and HCFOs have shorter lifetimes in the atmosphere and deposition of TFA from these substances is likely to be more localized. This will result in greater concentrations near the locations of release. This is unlikely to present a risk to humans or the environment in these locations but changes in concentration in surface water (or soil) would respond rapidly to releases. Monitoring of the environment for residues of TFA would provide an early warning if trends in concentration indicate rapid increases" (UNEP EEAP 2022 Assessment Report, pg. 293).
- h. "These releases will add to the existing load of TFA in the environment but predicted amounts are well below the threshold for concern with respect to human and environmental health" (UNEP EEAP 2022 Assessment Report pg. 292).

4. TFA is Unlikely to Cause Adverse Effects in Aquatic Organisms

While there is particular concern about TFA in water and how that impacts bodies of water and their organisms, UNEP provides evidence to support that TFA does not have a particularly adverse effect on bodies of water because of its unique properties. TFA has high solubility in water, so it does not bioaccumulate. UNEP therefore resolves that TFA does not threaten terrestrial and aquatic organisms. Further, TFA is also miscible with water, which UNEP points to as another indication that it does not bioaccumulate. Lastly, UNEP provides evidence in Figure 15 to support that because the margin of exposure between the distribution of NOECs and the observed and expected concentrations in the oceans and endorheic basins (i.e., basins having no outflow of water to external bodies of water such as rivers or oceans) is several orders of magnitude, the risk of TFA threatening aquatic life is a de minimis risk.

- a. "TFA has a long environmental lifetime, accumulates in surface and ground waters, and has been found in blood, drinking water, beverages, dust, plants, and agricultural soils. However, it does not interact with biological molecules and, due to its high solubility in water, it does not bioaccumulate. It is unlikely to cause adverse effects in terrestrial and aquatic organisms. Continued monitoring and assessment are nevertheless advised due to uncertainties in the deposition of TFA and its potential effects on marine organisms" (UNEP EEAP 2022 Assessment Report, pg. 5).
- b. "The physical and chemical properties of TFA are well known but key to assessing environmental risk is that it is a strong acid and is completely miscible with water [190]. In the environment, it forms salts with alkali metals, which are also very soluble in water. These properties indicate that



TFA and its salts will not bioaccumulate in organisms other than terrestrial plants and will not biomagnify in food chain" (UNEP EEAP 2022 Assessment Report, pg. 279).

c. "The margin of exposure between the distribution of No Observed Effect Concentrations (NOECs) and the observed and expected concentrations in the oceans and endorheic basins is several orders of magnitude and is indicative of de minimis risk" (UNEP EEAP 2022 Assessment Report, pg. 290).

References

Anderson, J. K., et.al., Grouping of PFAS for human health risk assessment: Findings from an independent panel of experts. Regulatory Toxicology and Pharmacology, 105226 (2022); https://doi.org/10.1016/j.yrtph.2022.105226

2022 Assessment Report, UNEP, March 2023. Environmental Effects of Stratospheric Ozone Depletion, UV Radiation, and Interactions with Climate Change