

EFCTC Comment on recent paper “Ice core record of persistent short-chain fluorinated alkyl acids: Evidence of the impact from global environmental regulations”.

EFCTC welcomes the detailed and informative paper reporting on “Ice core record of persistent short-chain fluorinated alkyl acids: Evidence of the impact from global environmental regulations¹”. The paper adds to the already extensive body of academic papers and reviews about the environmental effects of Trifluoroacetic acid (TFA), both natural and from HFCs/HFOs, including an extremely detailed environmental risk assessment² and regular reviews of its effects undertaken by the Scientific Assessment Panel³ for the Montreal Protocol. Therefore, the availability of this data is contrary to the claim in the paper about TFA that “*Less attention has been paid by the scientific community to short-chain PFCA⁴s (scPFCAs). Here we will define scPFCAs as PFCAs with carbon chain lengths ≤ 4 , of which there are three compounds: trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), and perfluorobutanoic acid (PFBA).*”

In summary, the paper provides an important understanding of the deposition of TFA at high latitudes and fundamentally supports the current understanding of the environmental effects of TFA.⁵ However, the paper’s focus on the scPFCAs as a group has resulted in some ambiguities or potential misinterpretations. To clarify these ambiguities, it is necessary to take into account these points.

TFA is distinct from other scPFCAs and PFCAs.

TFA occurs naturally: It is well established that TFA is a ubiquitous natural component in rivers, lakes, and other surface water bodies, with over 200 million tonnes in the oceans. More information is provided below.

TFA and its salts present negligible risk to organisms higher on the food chain, including humans.

They do not bioconcentrate in aquatic organisms, and do not biomagnify in the food chain. More information is provided below.

Only some HFOs decompose to TFA in varying yields, but do not decompose to PFPrA or PFBA.

The short atmospheric lifetimes of HFOs and TFA (days) means that TFA from HFOs is lower at high latitudes than the global average. The TFA deposition model for HFO-1234yf from its use in mobile air-

¹ Ice core record of persistent short-chain fluorinated alkyl acids: Evidence of the impact from global environmental regulations; Heidi M. Pickard, Alison S. Criscitiello, Daniel Persaud, Christine Spencer, Derek C. G. Muir, Igor Lehnerr, Martin J. Sharp, Amila O. De Silva, Cora J. Young; Geophysical Research Letters First published: 23 April 2020 <https://doi.org/10.1029/2020GL087535>

² Boutonnet et al 1999 Environmental Risk Assessment of Trifluoroacetic Acid, Human and Ecological Risk Assessment · February 1999, DOI: 10.1080/10807039991289644 <https://www.researchgate.net/publication/254217782>

³ World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 58 SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 2018 Information for Policymakers

⁴ Perfluorinated carboxylic acids

⁵ See EFCTC LEARN ABOUT TFA For a wide range of information about Trifluoroacetic acid/acetate as a breakdown product of some HFCs and some HFOs [here](#).

conditioning referenced in the paper⁶ did not include the effect of Criegee intermediates⁷, which were recently found to react with TFA and act as a gas-phase sink for TFA.

The HFOs have ultra-low Global warming Potentials and have enabled the phase-down of HFCs. Their contribution to global warming is and will continue to be extremely small.

Only some HFCs decompose to TFA in varying yields. However, one HFC may decompose to produce PFPrA although this is uncertain. A detailed environmental impact assessment was carried out for TFA from HFCs in the 1990s.

TFA is distinct from other scPFCAs and PFCAs

TFA occurs naturally: It is well established that TFA is a ubiquitous natural component in rivers, lakes, and other surface water bodies. Amounts deposited in flowing surface water will ultimately accumulate in the oceans and salt lakes where water is lost only by evaporation. The oceans, both coastal and deep-ocean seawater, contain over 200 million tonnes of TFA, having apparently accumulated over many million years from chemical reactions in or around sub-sea volcanic vents. The concentrations in the oceans are higher than the concentrations found in the arctic ice core samples (200 ng l⁻¹ in the oceans⁸; 4.24 - 129 ng l⁻¹ and <0.37 – 148 ng l⁻¹ in the arctic ice core samples).

TFA and its salts present negligible risk to organisms higher on the food chain, including humans.

They do not bioconcentrate in aquatic organisms, and do not biomagnify in the food chain⁹: This is due to the high solubility in water and very small octanol-water partition coefficient. The paper notes only that “The toxicity of TFA to plants is well established (K. Solomon et al., 2016).” Indeed, a summary of this paper and other sources in the 2018 SAP¹⁰ states:

“The effects of TFA on human and ecosystem health resulting from the use of compounds regulated under the Montreal Protocol have been assessed by Solomon et al. (2016). Mammals are insensitive to TFA (Boutonnet et al., 1999), and plants and other animals have a high tolerance to TFA. Solomon et al. (2016) tested a worst-case scenario with upper-limit TFA levels estimated for the future use of HFC-134a, HFO-1234yf, HFC-143a, and HFC-227ea through the year 2050 and selecting the most sensitive biological endpoints for different species. The no-observed-effect-concentrations for aquatic

⁶ Wang, Z., Wang, Y., Li, J., Henne, S., Zhang, B., Hu, J., & Zhang, J. (2018). Impacts of the degradation of 2,3,3,3-tetrafluoropropene into trifluoroacetic acid from its application in automobile air conditioners in China, the United States and Europe. *Environmental Science and Technology*, 52(5), 2819–2826. <https://doi.org/10.1021/acs.est.7b05960>

⁷ Chhantyal-Pun, R., Rotavera, B., McGillen, M. R., Khan, M. A. H., Eskola, A. J., Caravan, R. L., et al. (2018). Criegee Intermediate Reactions with Carboxylic Acids: A Potential Source of Secondary Organic Aerosol in the Atmosphere. *ACS Earth and Space Chemistry*, 2(8), 833–842. <https://doi.org/10.1021/acsearthspacechem.8b00069>

⁸ Solomon, K. R., Velders, G. J. M., Wilson, S. R., Madronich, S., Longstreth, J., Aucamp, P.J., & Bornman, J. F. (2016). Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols. *Journal of Toxicology and Environmental Health, Part B*, 19(7), 289–304. <https://doi.org/10.1080/10937404.2016.1175981>

⁹ UNEP Ozone Secretariat, Ecological Issues on the feasibility of managing HFCs: Focus on TFA Inter-session informal meeting, 12-13 June 2015 - Informal Brief on Ecological Issues on HFCs June 2015

¹⁰ World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 58 SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 2018 Information for Policymakers Chapter 6 page 6.14

organisms considered by Solomon et al. (2016) were in the range 3×10^7 – 2.4×10^9 ng l⁻¹, with an outlier at 1.2×10^5 ng l⁻¹.

Risks for humans, terrestrial vertebrates, plants exposed via soil, and aquatic plants and animals were assessed to be de minimis (Solomon et al., 2016).

Risks for organisms in salt lakes and playas were not assessed because there are no data on the toxicity of TFA for such organisms. It was noted that future increases in TFA levels resulting from ODS replacement (i.e. HFCs and HFOs) degradation in salt lakes will be small compared to the existing burden of other natural salts in such locations (Solomon et al., 2016). The large body of published field measurements, toxicological studies, modelling studies, and environmental assessments point to a clear conclusion: The current and estimated future concentrations of TFA and its salts resulting from degradation of HCFCs, HFCs, and HFOs do not pose any known significant risk to human or ecosystem health (Solomon et al., 2016)."

TFA has the highest solubility in water and lowest octanol water partition coefficient of the PFCAs.

The octanol water partition coefficient (K_{OW}) is a key parameter in studies of the environmental fate of chemical substances. It is the most common way of expressing the lipophilicity of a compound. It has also been shown that K_{OW} is a useful parameter in the prediction of adsorption on soil and sediments and for establishing quantitative structure-activity relationships for a wide range of biological effects. Biological properties such as bioaccumulation and toxicity are largely determined by K_{OW} . It is usually expressed as $\log K_{OW}$, with values typically between -3 (very hydrophilic) and +10 (extremely hydrophobic). The table shows water solubility and $\log K_{OW}$ values for PFCAs. From Table 1, TFA is much more soluble in water than PFOA for example and its K_{OW} is about 2000 times lower.

	PFCAs		Water solubility	Log K_{OW}	Log K_{OW}
			g/l	R-COOH	R-COO ⁻
C ₂	TFA	CF ₃ COOH	Miscible in all proportions	0.2	-4.1
C ₃	PFPrA	CF ₃ CF ₂ COOH	-	0.9	-3.3
C ₄	PFBA	CF ₃ (CF ₂) ₂ COOH	446.7	1.4	-2.8
C ₆	PFHxA	CF ₃ (CF ₂) ₄ COOH	29.5	2.5	-1.8
C ₈	PFOA	CF ₃ (CF ₂) ₆ COOH	9.5	3.5	-0.8

Table 1: Water solubility¹¹ and Log Kow values for PFCAs¹²

Note: KOW is defined as the equilibrium ratio of the compound's concentrations in a two-phase system of n-octanol and water. $KOW = c_{Oequil} / c_{Wequil}$ where c_{Oequil} = concentration of the compound under consideration in n-octanol in the

¹¹ Bhatarai, B., & Gramatica, P. (2011). Prediction of aqueous solubility, vapor pressure and critical micelle concentration for aquatic partitioning of perfluorinated chemicals. *Environmental Science and Technology*, 45(19), 8120–8128. <https://doi.org/10.1021/es101181g> and Kauck, E.A., and A.R. Diesslin. 1951. Some Properties of Perfluorocarboxylic Acids. *Industrial and Engineering Chemical Research* 43(10):2332–2334.

¹² Hidalgo, A., & Mora-Diez, N. (2016). Novel approach for predicting partition coefficients of linear perfluorinated compounds. *Theoretical Chemistry Accounts*, 135(1), 1–11. <https://doi.org/10.1007/s00214-015-1784-6>

equilibrium and c_{Wequil} = concentration of the analyte in water in the equilibrium. As PFCAs are strong acids they will be dissociated in water or be present as salts, so that the conjugate base ($RCOO^-$) log KOW is the most relevant.

ABOUT EFCTC

The European FluoroCarbons Technical Committee is a Cefic Sector Group that monitors legislation related to HFCs (hydrofluorocarbons), and HFOs (hydrofluoro-olefins) in the EU and at global level.

Fluorocarbons are used as feedstock, as refrigerants, as solvents and as blowing agents for insulation plastic foams.

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