CORPUS PUBLISHERS

Environmental Sciences and Ecology: Current Research (ESECR)

ISSN: 2833-0811

Volume 6 Issue 2, 2025

Article Information

Received date : November 23, 2025

Published date: December 03, 2025

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DOI: 10.54026/ESECR/10117

Research Article

The Environmental Fate of Fluorinated Refrigerant R-1234ze(E): Degradation to TFA Poses No Threat to Living Organisms

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Abstract

There is currently significant public alarm about presence of PFAS in the environment because these chemical species are persistent and some have been shown to be deleterious to the health of living organisms. This concern has been extended to some fluorinated refrigerants, including R-1234ze(E), because some of these can partially degrade in the atmosphere to Trifluoroacetic acid (TFA), which some agencies classify as a PFAS. However, a review of authoritative independent opinion reveals that TFA at concentrations that are currently present in the environment, or are likely to pertain for the remainder of this century, do not, and will not, reach levels which pose a threat to within several orders of magnitude. The reason that TFA is toxicologically benign is that, unlike its longer chain Perfluoro carboxylic acid cousins, it does not readily adsorb to surfaces and thus is readily excreted from organisms. It is vital to understand that there are many thousands of species which can be classified as PFAS and, although some indeed pose a threat to environmental health, some do not; TFA does not.

Introduction

Hydrofluoroolefins (HFOs) Hydrofluorocarbons (HFCs) have been routinely used as refrigerants since the 1987 “Montreal Protocol on Substances That Deplete the Ozone Layer” began the process of phasing out the use of various problematical compounds, including Chlorofluorocarbons (CFCs). These fluorinated compounds are sometimes known as ‘F-gases’ and some exhibit low global warming potential (GWP) in addition to low Ozone Depletion Potential (ODP). One such HFO, R-1234ze(E) (trans-1,3,3,3-Tetrafluoropropene), whose excellent properties as a refrigerant were reviewed by Mota-Babiloni et al. [1], exhibits a very low GWP of 7, for instance [2]. Over the past decade there has been increasing public alarm, and subsequent regulatory action, about the presence of Per- and polyfluoroalkyl substances (PFAS) in the environment. Some of this alarm is justified, and some is not. There are many thousands of chemical species which one agency or another classifies as a PFAS, each with their unique set of chemical and physical properties. Some pose a threat to environmental health but some do not. Most PFAS are very persistent in the environment (although they are not, in fact, ‘forever chemicals’ because they degrade, albeit very slowly, down gradients of Gibbs free energy), and this appears to be the primary reason for concern. However, it is not apparent that all PFAS are, in fact, toxic [3].

The alarm surrounding PFAS in the environment is having an impact on the fluorinated refrigerant business, and especially the commercial use of the refrigerant R-1234ze(E) because this refrigerant degrades, partially, in the atmosphere to Trifluoroacetic acid (TFA), and some agencies consider TFA to be PFAS, but the United States Environmental Protection Agency does not, and has described TFA as a “well-studied non-PFAS” [4]. Whether or not one agency or another considers TFA to be PFAS or not is practically immaterial because concern about TFA’s presence should be dictated by its individual toxicology rather than by a definition. But it is the very association of TFA as PFAS which appears to be driving the alarm and calls for regulation and even proscription of fluorinated refrigerants, including R-1234ze(E). Herein, mechanisms for the environmental degradation of R-1234ze(E) are considered, along with information about the toxicology of TFA, to explore whether such alarm is justified.

Degradation to R-1234ze(E) in the Atmosphere

Refrigerant R-1234ze(E) has complex degradation pathways in the atmosphere which have been recently described in a German Environment Agency report [5]. A grossly-simplified version of these pathways is shown in Fig. 1. R-1234ze(E) degrades to Hydrogen fluoride, Carbon dioxide, Formic acid and Trifluoroacetic acid (TFA). It is the latter degradation product that has recently been the subject of public concern on the basis that it is classified by some agencies as PFAS. There is no such alarm about the former three degradation products because it has not been suggested that these are problematical at quantities caused by environmental degradation of R-1234ze(E).

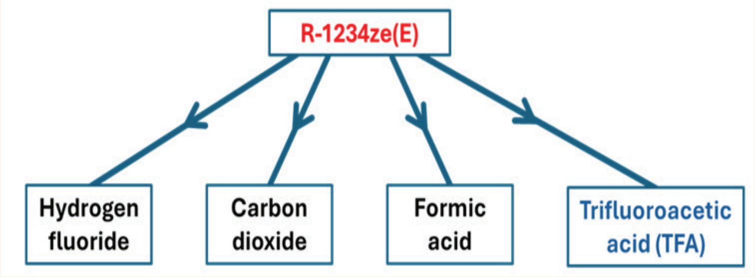

Figure 1: The degradation of R-1234ze(E) in the atmosphere, simplified from Behringer et al. [5].

How to cite this article : Stevenson P (2025) The Environmental Fate of Fluorinated Refrigerant R-1234ze(E): Degredation to TFA Poses No Threat to Living Organisms. Environ Sci Ecol: Curr Res 6: 10117

TFA is not Eco-Toxic at Relevant Concentrations

The scientific opinion that TFA is not toxic at environmentally relevant concentrations is overwhelming. In a review of the environmental impact of TFA, Hanson et al. [6] stated: "Current and predicted concentrations (to the year 2100) of TFA in the oceans are orders of magnitude lower than the thresholds of toxicity, and the risk to environmental health have been assessed to be de minimis." Specifically, on the eco-toxicity of TFA, Garavagno et al. [7] stated that: "The toxicity of TFA appears to be low, but further studies of a much wider range of animal and plant types are required." There can be no more-independent opinion on the matter than the UN Environment Programme's 2022 Assessment Report [8] on the Montreal Protocol of Substances that Deplete the Ozone Layer which states that: "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."

In a 2024 peer-reviewed assessment of the Montreal Protocol, Madronich et al. [9] said about TFA: "There is no change to the conclusion in the 2022 Quadrennial Risk Assessment of the de minimis risk to the environment with margins of exposure of four orders of magnitude for TFA salts in oceans and in terminal endorheic basins expected for gases related to the Montral Protocol up to 2100. Margins of exposure for organisms in flowing water are much greater, indicating de minimis risk." Further, there has been a more recent opinion from the 2025 "Thirty-Seventh Meeting of the Parties to the Montreal Protocol", MOP 37 [10], specifically their 'Technology and Economic Assessment Panel' who stated in their interim reporting: "The PBT [persistent, bio accumulative toxins] properties of PFOA/PFOS are improperly extended to other chemicals including MP-CS&A [Montreal Protocol controlled substances/alternatives]. MP-CS&A are not persistent, bioaccumulate toxins. Some MP-CS&A degrade to a variable degree to trifluoroacetic acid (TFA) salts. TFA is persistent in surface waters; increasing concentrations are currently projected to remain below toxicity concern levels".

The implications of the opinion of MOP 37 upon the use of F-gas refrigerants (including R-1234ze(E)) are clear:

a. Fluorinated refrigerants do not exhibit the PBT properties of PFAS species that are currently of concern, including PFOA and PFOS, and ascribing these properties to fluorinated refrigerant is 'improper'.
b. Some fluorinated refrigerants do indeed, partially, degrade to TFA in the atmosphere and TFA (and its salts) are persistent in the environment, but the concentration of these species will remain below levels of concern with respect to toxicity.

MOP 37 goes on to caution that the improper translation of PFAS regulations to MP-CS&As (which includes F-gases) might delay legitimate commercial investment, narrow the availability of alternatives (which includes refrigeration) and slow down the uptake of lower GWP alternatives. It is clear that the overwhelming independent scientific consensus is that TFA does not pose a threat to environmental health.

When assessing the potential toxicity of a chemical species it is usual to consult 'Safety Data Sheets' (SDSs). TFA is a strong acid, and it is indeed dangerous at high concentrations, but it is the concentration of TFA at environmentally relevant concentrations that is pertinent herein. There is an analogy: The non-fluorinated cousin of TFA is acetic acid, which is indeed hazardous in its glacial form, but culinary use of acetic acid as vinegar poses no threat, of course. Thus, it is relevant to consult the eco-toxicity data in SDSs, because this reveals the concentrations of a substance that pose a threat to living organisms. The SDSs of the two chemical companies Roth [11] and Sigma Aldrich [12] are consulted for the present purpose. In both SDSs, the eco-toxicity of TFA to non-plant organisms is reported as being so low that it cannot be measured in the laboratory. In both SDSs, a finite eco-toxicity to algae is reported; the 72-hour EC50 is 237.1 mg/l which far exceeds concentrations that are environmentally relevant. For instance, the very highest concentration of TFA in surface water reported by the German Environment Agency is 11 µg/l at a site north of Leipzig [13], which is a factor of 22,000 lower than that toxic to algae.

There is a fundamental scientific reason that TFA does not pose a threat to living organisms at environmentally relevant concentrations:

i. TFA is a very stable molecule that does not biologically interact with anything else in organisms, and
ii. TFA is particularly non-adsorptive, meaning that it does not 'stick' to surfaces in organisms, and thus is readily excreted (as urine in the case of mammals).

TFA is a member of the sub-class of PFAS called perfluoroalkyl carboxylic acids (PFCA), and is the shortest-chain (i.e. simplest) member of this class. A consequence of its low-molecular weight is that is does not readily adsorb to surfaces in organisms, whereas its longer-chain cousins do adsorb. For instance, Perfluorooctanoic acid (PFOA), which is a 'headline' PFAS in the public debate and is a member of the sub-class PFCA, is much more adsorptive than TFA and therefore presents a genuine threat to environmental health. The tendency of chemical species to adsorb to surfaces is described using an 'adsorption coefficient'; a high value indicates a strong tendency to adsorb, and vice versa. Figure 2 shows the adsorption coefficient of various PFCA to, for the sake of argument, the water-air interface [14]. Please note the logarithmic scale. It is seen that as the chain-length (expressed as the number of carbons in the molecule) increases, the adsorption coefficient significantly increases. There is no data for the adsorption coefficient of TFA precisely because it is so non-adsorptive that the coefficient is not measurable in the laboratory. It is this lack of absorptivity which is the fundamental reason in science that TFA is not eco-toxic.

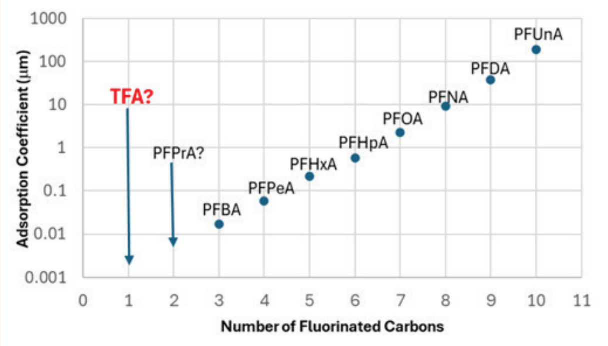

Figure 2: The adsorption coefficient of PFCA to the water-air interface as a function of the number of fluorinated carbons in the molecule [14]. TFA is so non-adsorptive that the adsorption coefficient cannot be measured.

Contribution of R-1234ze(E) to Environmental Inventory of TFA

TFA is not eco-toxic at environmentally relevant concentrations, but it is a persistent chemical species which does not readily mineralise (i.e. the fluorine does not tend to manifest as fluoride salts or Hydrogen fluoride) in the environment. Thus, there is an inevitable build-up of TFA in the environment due to the fugitive emissions of R-1234ze(E), and it is legitimate to pose the question whether this is likely to be significant compared to current background concentrations, despite the fact that TFA poses no threat to environmental health. It has been shown by Qing et al. [15] that the rate constants of TFA production are low compared to other produced species in Figure 1 and so yields of TFA are estimated to be very low at between zero to 2%. This means that a maximum of only 2% of the fluorine which is present in R-1234ze(E) manifests as environmental TFA. The estimated contribution of the use of R-1234ze(E), along with other F-gas refrigerants, to European rainwater through to 2050 has been estimated by Behringer et al. [5] to be <0.01 µg/l, which is very low compared to background concentrations. The average TFA concentration in precipitation in Germany during 2018 was 0.335 µg/l and the German Environment Agency's health guidance TFA concentration for drinking water is 60 µg/l [16]. It is seen that the contribution due to R-1234ze(E) to environmental TFA is vanishingly small in the context of this guidance concentration for drinking water.

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The Possibility of Production of the Potent Greenhouse Gas CHF_3

Very recently, it has been suggested in the academic community that another degradation product of R-1234ze(E), not appearing in the above reaction pathway (given in simplified form in Figure 1), is Trifluoromethane (also known as Fluoroform or CHF_3). This is a very potent gas with global warming potential (GWP) of 14,800. Clearly, the production of CHF_3 in the atmosphere is undesirable. The production of CHF_3 from Trifluoro acetaldehyde, which is an implicit intermediate species in figure 1, was suggested by Pérez-Peña et al. [17] via computer simulations, but has since been shown by Andersen et al. [18] to be produced in minute quantities under very tightly-controlled laboratory conditions. It is thus a legitimate, and important, question to ask whether CHF_3 is produced in the atmosphere as a result of discharge of R-1234ze(E). Relevant study into this question is in its infancy, but the preliminary answer is 'no', because no such degradation to CHF_3 has been demonstrated under any experimental conditions representative of the troposphere [19].

Conclusion

There is no compelling evidence for natural production of TFA [20], and so the TFA which is present in the environment, the concentrations of which appear to me monotonically growing, are likely to be entirely anthropogenic in nature. However, presence of any compounds in the environment, whether synthetic or otherwise, does not necessarily imply harm. There are multiple sources of TFA in the environment, one of which is the degradation of refrigerant of R-1234ze(E). However, it is not an eco-toxic compound at relevant concentrations, and the reason for this is that TFA does not materially adsorb to surfaces; whether it is, or is not, classified as a PFAS has no relevance to its toxicity because PFAS species do not all behave alike. Hanson et al. [6] project that environmental concentrations to 2100 will remain at "orders of magnitude lower than the thresholds of toxicity". Current attacks upon the use of fluorinated refrigerants, including R-1234ze(E), on the grounds that they partially degrade in the atmosphere to TFA are wholly unjustified.

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