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Annex 1 - EFCTC technical paper TFA and emissions

Contents

Summary

Fluorinated greenhouse gases (F-gases) are a group of industrially-made substances widely used in heat pumps, air conditioners, fridges, freezers and other types of heating and cooling systems and appliances (Most of the F-gases are used as refrigerants in closed RACHP-systems). Small quantities may be emitted in the event of improper handling or unintentional leakage. TFA is a degradation substance of some HFCs HFOs and HCFOs in the atmosphere and it is also naturally occurring.

The scientific annex of this dossier focuses on Trifluoroacetic acid (TFA) and includes the following articles:

1. History of TFA

2. Natural TFA

3. Emissions and atmospheric degradation - TFA yields and deposition

4. Summary of human biomonitoring and health effects of trifluoroacetic acid (TFA)

5. TFA yields from HFCs and HFOs

6. Review Paper: Assessment of human health risks due to environmental exposures to Trifluoroacetic acid (TFA)

Please note that due to the large number of references, a specific list of references is included after each individual article

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TFA (CAS #76-05-1), is a pale, yellow, strongly acidic liquid, with a pKa of 0.23. It is highly volatile and fully water soluble. TFA is a monocarboxylic acid that is the trifluoro derivative of acetic acid. In the environment it is found at extremely low concentrations.

TFA, as described in the first article, was first synthesized in 1922, and industrially used as a solvent and as an intermediate in the synthesis of agrochemicals and pharmaceuticals. In the late 1980s, TFA was first identified as a degradation product of certain organofluorine substances (HCFC-123, HCFC-124, HFC-125, and HFC-134a), and this potential degradation was first discussed by the UNEP Scientific Assessment Panel (SAP) in their 1989 report and by the UNEP Environmental Effects Assessment Panel (EEAP) in their 2002 report.

Besides the anthropogenic sources, TFA has been proven to also arise from natural sources. The objective of the second article is to discuss the conclusions of a number of scientific publications and to explain the evidence that indicates a large quantity of TFA does occur naturally in the oceans, including by referencing to two very recently published sources that were not available to the dossier submitters. Please see related article for references.

The deposition patterns of TFA derived from the degradation of some F-gases (hydrofluorocarbons, HFCs, and hydrofluoroolefins, HFOs) are discussed; subsequently, it dives into the deposition rate and profile linked to atmospheric lifetime of the F-gas and TFA. Moreover, this third section reviews F-gas emissions forecasts using a model (EPEE HFC Outlook EU) that takes into account the latest political orientations and technical developments. Forecasts show how future emissions of HFCs and HFOs are on a down trend to at least 2035 and how this influences TFA deposition. HFC consumption and emissions data shows a REACH restriction for HFCs in the EU will have a very limited effect on the deposition of TFA globally and regionally.

The fourth article discusses the human biomonitoring data of TFA. Biomonitoring for environmental chemicals among general population from the U.S., Canada, Germany and Australia did not report or include TFA. TFA was reported in selected blood samples of the Swedish population, but the concentrations were below the level of quantification (LOQ). High level of TFA was reported among blood samples of volunteer staff and support workers at Nankai University (China); however, the source of TFA is unknown.

The scientific annex is closed by a review of TFA yields from HFCs, HFOs and HCFOs. Trifluoroacetic acid (TFA), CF3C(O)OH, produced by degradation of some halogenated gases has been evaluated extensively in the past few decades. Several HFCs, HFOs and HCFOs produce TFA with molar yields that vary from as low as 1% and up to 100%. Environmental Effects Assessment Panel (EEAP 2022) reviewed the yields of TFA from individual compounds and they are estimated based on evaluations of the available literature. The Science Assessment Panel (SAP 2022) and EEAP 2022 use the same forecasts for HFC and HFO emissions to calculate TFA deposition.

In conclusion, the formation and deposition of TFA from HFCs, HFOs and HCFOs has been widely studied, and results conclude that the current low concentration of TFA produced by the degradation of several HFCs and HFOs is currently judged not to pose a risk to human health or to the environment. Extensive studies for the ecotoxicological effects have demonstrated that TFA from HFCs, HFOs and HCFOs is of no health concern at the measured concentrations and at these concentrations is not

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harmful to ecosystems. TFA occurs naturally in the oceans at concentrations similar to those found in rainwater.

History of Trifluoroacetic Acid

The first synthesis of an organofluorine compound, fluoromethane (CH_3F), was reported in 1862 by Dumas, and organofluorine compounds remained laboratory curiosities until 1930, which saw the first commercial introduction of an organofluorine compound, Freon 12 (CF_2Cl_2). Hence, the history of any significant anthropogenic sources of organofluorine compounds begins in 1930. The early history of organofluorine compounds has been discussed in a review by Okazoe [1].

Trifluoroacetic acid (TFA, $CF_3C(O)OH$) was first synthesized in 1922 by Swarts [2], and was later produced commercially employing the Simon's electrochemical fluorination process, which was developed in the 1940s and patented in 1950 [3]. TFA was first proposed as a degradation product of certain organofluorine substances (HCFC-123, HCFC-124, HFC-125, and HFC-134a) in the late 1980s, and this potential degradation was first discussed by the UNEP Scientific Assessment Panel (SAP) in their 1989 report [4] and by the UNEP Environmental Effects Assessment Panel (EEAP) in their 2002 report [5]. Since that time a number of additional anthropogenic sources of TFA have been identified, such as certain HFOs (an example is HFO-1234yf), certain pharmaceuticals, pesticides and herbicides, and the thermolysis of certain fluoropolymers [6,7]. In addition to anthropogenic sources, natural sources of TFA have also been acknowledged in numerous reports [6-16]. TFA itself was also synthetized and used as a chemical reagent or intermediate product.

It has been discovered that HFC-134a and HFO-1234yf are the most widely employed fluorocarbons producing TFA as an atmospheric degradation product. Atmospheric observations of HFC-134a [17-24] and modelling of tropospheric TFA production from HFC-134a [25-33] have been reported in numerous studies since the 1980s. Instead, atmospheric observation of HFO-1234yf was first reported recently by Vollmer in 2015 [34]. Since then, HFO-1234yf emissions estimates and modelling of subsequent TFA formation have been discussed in a number publications [6,14,35-45].

The 2021 UNEP EEAP Report [15] concluded that "Models indicate that a direct replacement of HFC-134a with HFO-1234yf in refrigeration applications will increase the associated global TFA burden from an annual 65 to 2220 tonnes formed from an equivalent emission of HFO-1234yf (based on emissions in 2015). However, given the low toxicity of TFA (see below), the increase in global environmental concentrations is not expected to significantly impact environmental or human health."

The environmental fate of TFA has been reviewed in detail by Solomon *et al*. [7] and Boutonnet [46]. As pointed out by Solomon *et al*. [7], regardless of the source of TFA in the atmosphere or other compartments in the environment, the ultimate sink is in surface waters. TFA has been found to be ubiquitous, and has been detected in the oceans, surface waters, soil, sediment and certain plants [5,7,45,46]. Solomon *et al*. [7] and Boutonnet [46] both provide extensive risk assessments of TFA, including evaluations of its effects on mammals, terrestrial organisms (plants), and aquatic organisms; DeKant and DeKant have also reviewed the mammalian toxicity of TFA [16]. Boutonnet offers the conclusion that "Based on available data, one can conclude that environmental levels of TFA resulting from the breakdown of alternative fluorocarbons do not pose a threat to the environment." In agreement with the conclusion of Boutonnet, the Solomon *et al*. risk assessment concluded that "the

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current and estimated concentrations of TFA and its salts in the environment that result from the degradation of HCFCs, HFCs and HFOs in the atmosphere do not present a risk to humans and the environment." In their review of TFA mammalian toxicity and human exposures to TFA, DeKant and DeKant [16] concluded that based on recent levels of TFA in water and diet, MoEs (margin of exposures) for human exposures to TFA are well above 100 and do not indicate health risks.

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Natural TFA

The dossier submitters in Annex B (B.1.3.1) reviewed the evidence for the natural occurrence of TFA, referencing key papers that reported a large quantity of TFA in the oceans that also concluded that TFA in oceans have mostly a natural origin, and a paper by Joudan et al., 2000 [1] that concluded the presence of TFA in the deep ocean and lack of closed TFA budget is not sufficient evidence that TFA occurs naturally, especially without a reasonable mechanism of formation. The conclusions from this paper were highlighted in the section summary *"In summary, the number of naturally occurring organic fluorine-containing substances is low compared to other halogenated substances. TFA has been indicated to have natural sources in oceans (underwater vents) but evidence for the existence of natural trifluoroacetic acid is considered insufficient. Oceans are considered the final environmental sink of the substance. However, natural sources for TFA in the oceans have been questioned. TFA in the atmosphere, precipitate, freshwaters and needles of conifers most likely stems from anthropogenic sources. Concentrations of TFA in urban waters and tap water have been increasing over the last decades."*

Additional data, some not available when the restriction dossier was prepared, provide evidence that the quantity of TFA in the oceans must include a large natural burden. Section B.1.3.1 sets out the points from the Joudan et al., 2000 [1] l paper that led the authors to conclude there is not sufficient evidence that TFA occurs naturally. The two most important points, summarised in Section B.1.3.1, are discussed below.

Exploration of other potential TFA sources to the deep ocean

The Joudan et al., 2000 [1] paper states *"A limitation of these studies [Frank and Scott] was that they did not consider plausible TFA delivery mechanisms from ocean depths representing modern times to the deep ocean."* There are three points that address this issue: The age of the deep ocean waters where TFA was found; A comparison between TFA and long chain PFAS concentration profiles in the oceans; and the validity of the transportation mechanisms of TFA to the deep oceans proposed by Joudan et al., 2000 [1].

TFA was detected in the deep arctic ocean, in waters with a reported ^{14}C age of about 1000 years, and oceanic TFA concentrations were determined (Scott et al., 2005). At 3000 m depth in the Canadian Basin of the western Arctic Ocean TFA concentration was measured as 160 ng/L, similar to the concentrations measured in the Atlantic. There have been a number of studies that discuss the Canadian Basin water stratification and water age. The Canada Basin is 3500–3800 m deep and the

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500–1000m thick deep temperature minimum layer (DTML) overlies the Canada Basin bottom water, with the boundary at about 3000 m between DTML and the bottom water[2]. Another paper [3] concluded that "observations have allowed us to speculate that ongoing renewal of the deep Canada Basin is unlikely and the most likely scenario is that the present Canada Basin deep water is the result of a renewal event in the past." An earlier paper concluded that the average age of the Canadian Basin Deep Waters is comparably high at perhaps 400 years [4].

PFAS (≥ C_6) including C_6-C_{12} PFCAs (perfluorinated carboxylic acids) were not found in the deep Arctic Ocean. A recent paper "Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean [5]" determined that PFAS (note the study did not include TFA so does not contradict the Scott measurements) were not found at depths below 250 m in the Arctic Ocean. "The detection of PFASs in the four depth profiles was limited to the 150 m below the surface, except for the North Barents Sea where a PFAS was detected down to 250 m below surface." Samples were taken at depths down to 3000 m [6] "Deep layer water samples (3000 m depth from 4 different stations) were served as field blanks and were found below limits of quantification". The paper states that the lifetime of tracers in Arctic Deep water is about 75 – 300 years.

Estimated total global annual emissions of C_4–C_{14} PFCAs cover the period from 1951, with PFOA based products accounting for most of the emissions in the 1950s and 1960s [7]. Emissions of longer chain PFCAs started about the same time as industrial emissions of TFA.

The Joudan et al., 2000 [1] paper proposes transport mechanisms to account for TFA in the deep ocean and compares TFA, PFAS and POPs in the deep ocean: *"This variability is consistent with more recent analysis of PFAS profiles in ocean sampling across extensive latitudinal gradients."* However, the paper "Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean", discussed earlier, did not find PFAS below 250 m. If TFA and PFAS have similar transport mechanisms then it might be expected that PFAS would also have been found in the deep waters of the Arctic Ocean. Joudan et al., 2000 [1] compared TFA and PFAS depth profiles for the North Atlantic which will both be influenced by the meridional overturning circulation. The mid-Atlantic depth profiles show marked differences for PFAS and TFA. Frank measured TFA concentrations in the mid-Atlantic that were effectively uniform between the surface and 4150 m depth (190 to 210 ng/L at 8 different depths [8]). In contrast, Yamashita[9] found that for PFAS in the mid- Atlantic "*In each of the three Mid-Atlantic water columns, there was a considerable difference in PFAS concentrations between the surface and middle layers of the water column, below 800 m. Concentrations of PFAS were almost negligible in the deepest layers, below 4000 m. The latter finding suggests a lack of direct vertical transport of PFAS from surface to bottom waters*." Similarly, Yamashita comments that for the Labrador Sea, "*approximately 1% of the total emissions of PFOA has been transferred into the deep sea water over the past 60 years. At this rate of distribution, more than 4500 years would be needed for transfer of all of the current emissions of PFOA into the deep sea water in the Labrador Sea."*

In addition, the paper "Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean" also comments that results for PFAS contrast with vertical profiles of PCBs and PBDEs (polybrominated diphenyl ethers) in the Arctic Ocean indicating vertical transport processes are weaker and potentially irrelevant for PFAS, as suggested by some modeling work. This transport mechanism, also discussed by Joudan et al., 2000 [1], should also be irrelevant in the Arctic Ocean for TFA as it is highly hydrophilic

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in contrast to hydrophobic POPs, which partition readily to organic carbon and suspended particles, and particle settling has been suggested to be a dominant transport pathway to deeper water layers for these substances.

Therefore, the mechanisms proposed by Joudan et al., 2000 [1] appear to only explain a tiny fraction of TFA measured in the deep ocean, if any at all.

Examination of global budgets of TFA

The Joudan et al., 2000 [1] paper states *"Finally, arguments have been made that TFA must have a natural source because there is no other explanation for some estimated global burdens. However, until a clear source of natural TFA has been identified and all anthropogenic sources have been completely constrained, an unknown fraction does not itself prove the presence of a natural source."*

It is worth noting that the concentration measurements of TFA in the oceans are not disputed by Joudan et al., 2000 [1]. When discussing the analytical method of Frank, used for the oceanic concentration measurements the paper commented that *"The authors were very thorough in quality control measures during their sampling"*. A supplemental part of the oceanic measurement project for AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) was a comparison of analytical results obtained using the methods employed by the two participating laboratories, the Universität Bayreuth and the University of Nevada, which carried out studies on TFA concentrations in precipitation in California and Nevada in the same period [10].

The large burden of TFA in the oceans (Frank et al.,2002), estimated at 61 - 205 million tonnes (Scott et al., 2005) was measured in the period 1998-2002. An inventory has been published, in 2023, for the period 1930 to 1999, to account for fluorspar consumption by application, identify those uses that result in significant emissions of TFA, and estimate emissions of TFA. The inventory paper concludes that all significant anthropogenic sources of TFA have been accounted for in the period until end 1999. The conclusion from the peer reviewed inventory paper [11] is:

Industrial sources of TFA can only result from the use of fluoride minerals in industrial processes. Major industrial uses of fluorspar started significant expansion from about the same time (1930s). The inventory accounts for most of the fluorspar production (86%) of the 191.9 million tonnes of fluorspar that has been mined in the period 1930 to 1999. In addition, there are many other uses of fluorspar (as HF) that are not as easily estimated but would also not result in the formation of TFA, as these uses are aqueous HF, inorganic, catalysis, solvent, or uses that do not result in substances that could degrade to TFA. Other fluoride minerals were only a minor source of fluoride used for industrial processes in this period, mainly for aluminium production. Industrial emissions of TFA are estimated at 84,000 tonnes until end of 1999, excluding pesticides and pharmaceuticals, and in the range 230,000 to 470,000 tonnes including pesticides and pharmaceuticals. It is difficult to estimate the TFA generation from pesticides due to the various substances used and the uncertain or unknown yield of TFA. Pesticides are most likely the largest source of TFA emissions in the period until 1999, if those pesticides containing a CF_3-group and introduced before 1999, degraded to give 100% yield of TFA. Steel and aluminum production were the two largest consumers of fluoride minerals, predominantly fluorspar, but are not considered to produce TFA, either based on the process conditions, by analysis or the generation of inorganic fluorides. Significant other industrial uses of fluorides have not been

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identified, in the period 1930-1999, that could account for the large burden of TFA in the oceans. An important conclusion from this inventory is that before 1947 extremely limited quantities (if any) of TFA were emitted from industrial sources. However, TFA was detected in the deep Arctic Ocean in waters with a reported ^{14}C age of about 1000 years, with a different study concluding that the waters have a comparably high average age at perhaps 400 years. The inventory for the period 1930-1999 provides complementary evidence that the quantity of TFA (61 - 205 million tonnes) measured in the oceans in the period 1998-2002 must include a large natural burden.

It worth noting that a similar approach (to Scott) has been used to develop an ocean inventory for C_4-C_{14} PFAS [12], however, in contrast to TFA, these substances do not occur naturally. The ocean inventory for each of these PFAS substances is in the range of about 1000 to 15000 tonnes, in contrast to the 61- 205 million tonnes of TFA estimated by Scott. The Scott TFA oceanic burden range calculation approach provides maximum and minimum estimates of the TFA inventories in the major ocean basins. For the Pacific Ocean, values measured to depths down to 4000 m have been used, but the lower 5000 m of the depth has been given a minimal value of 10 ng/L and a maximum value of 175 ng/L. The maximum value for the Atlantic Ocean is calculated by assigning the entire water column a TFA concentration of 175 ng/L. The minimum value is derived by assigning the upper 4000 m a TFA concentration of 175 ng/L and deeper waters, a value of 10 ng/L. The TFA estimates for the Indian Ocean are derived by assuming the entire water column has either a maximum concentration, similar to the Atlantic Ocean, or minimum concentration, similar to the Pacific Ocean.

The Environmental Effects Assessment Panel in its 2022 report [13], published in 2023, reaches a similar conclusion that TFA in the oceans and endorheic lakes are very unlikely to be all from anthropogenic sources. "However, the theory that TFA can be formed from geogenic sources has been challenged. This challenge was partially based on potential analytical errors and lack of information on levels of detection and quantitation, and high variance in concentrations measured in samples at different depths and in different oceanic basins. The authors focused on atmospheric sources of TFA in surface waters and ice, which originates in precipitation and did not consider measurements in other bodies of water such as endorheic lakes and playas located in areas of low precipitation and little fluorochemical industry. One of these locations, the Dead Sea, had a reported concentration of 6400 ng/L. The Dead Sea is in a rift valley with a history of geological faulting and with a volume of 114 km^3, so that this concentration is equivalent to 730 tonnes of TFA. That this amount of TFA (measured in the 1990s) is all from anthropogenic sources is very unlikely, and geogenic sources are more plausible." The report also notes that "Another major unknown in characterising the source of reported concentrations of TFA in the oceans is the degradation half-life of TFA in the environment. As discussed above, TFA is very recalcitrant and is essentially unreactive under normal environmental conditions. If, as seems to be the case, the half-life is likely very long (≈ centuries), very small amounts could accumulate over time to explain the amounts observed in oceans and endorheic basins."

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Emissions and atmospheric degradation of the F-gases (HFCs, HFOs and HCFOs) that are in and out of scope of the restriction proposal; TFA yields and deposition.

This section discusses the F-gas emissions forecast used in the restriction proposal dossier (Annex E), compares it to the UBA forecast based on maximum future use, and explains why both these emissions forecasts overstate the most likely future emissions, which are forecast to be on a down trend to at least 2035 for HFCs and HFOs, using a model (HFC Outlook EU) that takes into account the latest political orientations and technical developments. Importantly, atmospheric monitoring evidence shows that HFC-134a emissions have been overstated in recent years for the European region, which influences the input data for the restriction proposal forecast, particularly for mobile air-conditioning. The EU+UK share of global HFC emissions is rapidly decreasing. Even without additional measures under a revised F-gas regulation, in 2050 the EU (EU+UK) is forecast to contribute only 4% to global

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HFC emissions as CO2e. HFC consumption and emissions data shows a REACH restriction for HFCs in the EU will have a very limited effect on the deposition of TFA globally and regionally.

Data published in 2022 by the Scientific Assessment Panel to the Montreal Protocol, shows an estimated total global atmospheric formation and deposition of 5.8 – 8.1 Tg [1] of TFA from HFCs and HFOs, between 2020 and 2050. Subsequent transfer to the ocean results in average TFA concentrations in sea water projected to increase by 4 - 6 ng/L between 2020 and 2050. This can be compared to the total ocean content of 61–205 Tg of TFA around the year 2000. The HFC Outlook EU model, forecasts 0.19 Tg of TFA generation from HFCs and HFOs between 2000 and 2035. Subsequent transfer to the oceans, would result in an increase of 0.14 ng/L in average oceanic concentration of TFA by 2035. This additional quantity is very minor when compared to the measured oceanic concentrations and estimated oceanic quantities around the year 2000.

Europe does not have any major endorheic basins, (**drainage basins that normally retain water and allow no outflow to other external bodies of water, such as rivers or oceans) which means that almost all TFA deposited in over land in Europe will be transported to the oceans.**

The HFC Outlook Model forecasts emissions of TFA for all HFCs and HFOs at about 9,000 tonnes/year for Europe in 2035, which could result in estimated concentrations of TFA in precipitation averaging less than 330 ng/L to 465 ng/L annually. This can be compared to the UBA target value for TFA in drinking water of 10,000 ng/L (10 µg/L) and the UBA health guidance value for TFA in drinking water of 60,000 ng/L (60 µg/L). A new toxicity test for an aquatic organism, the most sensitive alga (Raphidocelis subcapitata) resulted in a no observed effect concentration (NOEC) of 2.5 mg a.e./L (2,500,000 ng/L or 2500 µg/L), based on inhibition of growth.

Introduction

All the HFCs, HFOs and HCFOs of commercial relevance for refrigeration, foam blowing and technical aerosols in the scope of the restriction proposal degrade in the atmosphere. Their degradation pathways, initiated by reaction with OH radical, and final breakdown products have been determined by experimental studies. Therefore, their breakdown pathways and kinetics, and atmospheric models used to estimate final degradation product yields and TFA deposition profiles are well known.

For each HFC or HFO that degrades to generate TFA, the TFA deposition profile is linked to the TFA yield and atmospheric lifetime of the HFC or HFO. TFA is highly soluble and is scavenged from the atmosphere via rain, fog, and snow, as well as dry deposition. More than 90% of TFA is physically removed from the atmosphere via wet and dry deposition (about 80% via wet deposition and 10% via dry deposition), with an estimated global mean deposition lifetime of about 5–10 days. TFA is also chemically destroyed in the atmosphere by OH. This is estimated to be a minor loss channel (about 6%), (SAP2022) [2].

All the commercially relevant HFCs in scope have atmospheric lifetimes considerably longer than 1 year, which means they are well mixed in the global atmosphere and their final degradation products including TFA are deposited globally. Oceans account for 71% of the global surface area [3], which means that for substances with atmospheric lifetimes >1 year, a large proportion of TFA deposition will occur directly into the oceans. TFA wet deposited over land is mainly transported in surface waters

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to the oceans. The oceans contain a large quantity of TFA that occurs naturally with total quantities estimated to be in the range 61 - 205 million tonnes, measured between 1998-2002[4]. By end 1999, emissions of TFA from industrial sources are estimated as 230,000 to 470,000 tonnes, which is in the range 0.1 to 0.8% of the estimated quantity in the oceans, according to a recent paper, providing complementary evidence that the quantity of TFA in the oceans must include a large natural burden [5].

HFCs consumption and emissions in the EU relative to global

When HFC-134a was identified as a replacement for CFCs in the early 1990s, and TFA was determined to be one of its degradation products, extensive studies were undertaken to understand TFA generation and deposition. According to Kotamarthi et al.,1998 [6], globally averaged concentrations of TFA in rainwater can be easily estimated from mass balance considerations. Local rainwater TFA concentration values deviate from the global averages due to inhomogeneities in OH concentrations and precipitation rates, as well as the long-range transport of gas phase TFA and its precursors. The atmospheric model used shows that the amount of TFA deposited by wet processes (including from HFC-134a) is highest over the tropics and the tropical oceans. Figure 12 in the paper is reproduced here. It is worth noting that this figure also includes TFA deposition from two HCFCs and assumes a much higher yield of TFA from HFC-134a than occurs in practice. Even so, the figure illustrates the TFA deposition patterns for HFCs.

KOTAMARTHI ET AL.: THREE-DIMENSIONAL MODEL

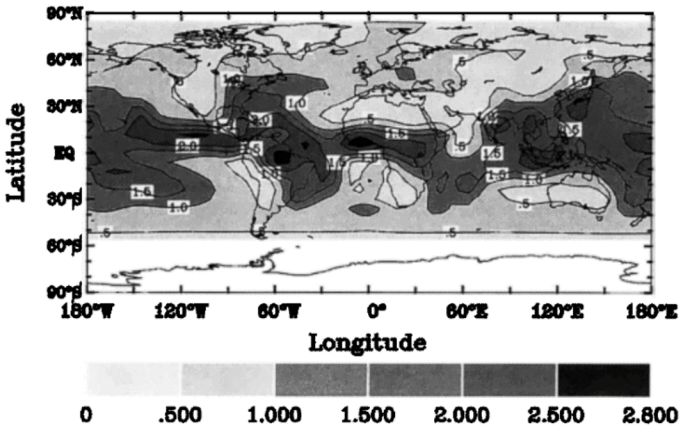

Figure 12. Cumulative amount of TFA deposited by wet processes by the year 2010 at the surface in mg/m^2.

The phase-down of HFCs is regulated by the F-Gas Regulation (Regulation (EU) No 517/2014)) in Europe and by the Kigali Amendment to the Montreal Protocol globally. Due to the relatively low proportion of HFCs used in the EU, compared to global use, any additional restrictions in the EU, imposed as a result of the U-PFAS restriction proposal, will have a very limited effect on the deposition of TFA.

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Required under Article 7 of the Montreal Protocol, its Parties have to provide data on consumption of HFCs. This includes all HFCs in Annex F of the Montreal Protocol and not just those in scope of the U-PFAS restriction proposal, which excludes for example HFC-32 and HFC-152a. The most recent publicly available data [7] shows that the EU + UK accounted for less than 8% (estimated at about 7%) of global HFC consumption on a GWP weighted basis (as CO_2e) in 2020 and 2021. The exact percentage is not available as the USA has not yet reported HFC consumption data due to the timing of its ratification of the Kigali Amendment, which means the global data does not yet include USA. Excluding USA HFC-consumption data, the EU+UK share of consumption is 8% in both years. The current phase-down schedule under the F-gas Regulation is expected to lead to a lower share of global HFC consumption in the future, due to the timing of phase-down requirements, under the Kigali Amendment, for different parties to the Montreal Protocol.

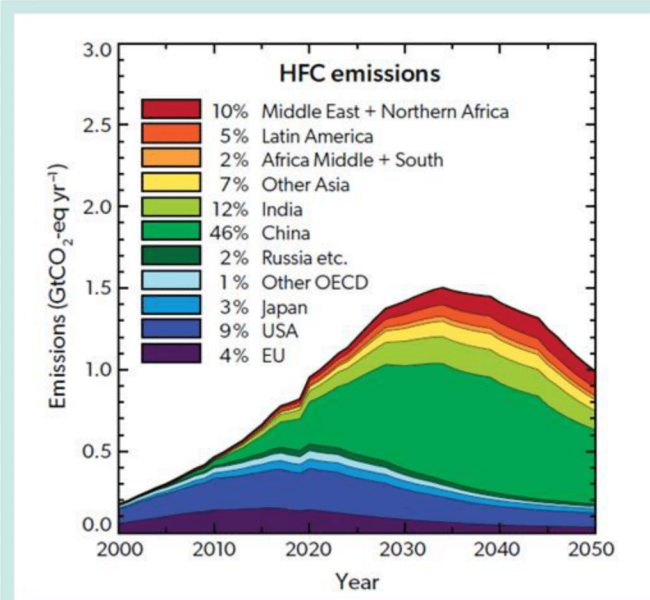

Figure 2-15. Contributions of the HFCs in 11 regions *(left)* and 6

Forecast emissions of HFCs by region are presented in the Scientific Assessment of Ozone Depletion 2022 (SAP2022). SAP2022 Figure 2-15, reproduced here, shows the emissions trends under current regulations, noting that this includes all HFCs in Annex F of the Montreal Protocol and not just those in scope of the U-PFAS restriction proposal. Contributions of the HFCs in 11 regions to the CO_2-eq emissions are from the 2022 Kigali Amendment scenario based on updated observations and reported consumption, national policies, and the provisions of the Kigali Amendment (upper-range scenario). The percentages in the legend refer to the relative contributions in 2050. Emissions of HFCs in the EU are already declining and the F-gas Regulation has led to a reverse and year-on-year decrease of F-gas emissions starting in 2015 [8]. Figure 2-15 shows that the EU+UK share of global HFC emissions is rapidly decreasing. Even without additional measures under a revised F-gas Regulation, in 2050 the EU (EU+UK) is forecast to contribute only 4% to global HFC emissions as CO_2e.

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The use of the individual HFCs follows similar trends in different regions as the main applications are widely used. From HFC consumption and emissions data a REACH restriction for HFCs in the EU will have a very limited effect on the deposition of TFA globally and regionally. The HFCs are being phased-down by the F-gas Regulation and its revision, and globally by the Kigali Amendment, with global emissions forecast to peak in the mid-2030s and then decline.

The use and emissions of HFOs and HCFOs in the EU

HFOs and HCFOs were identified as replacements for HFCs due to their similar safety profiles and their very low GWPs. Their degradation pathways and breakdown products have been investigated and identified, and their TFA yields determined. All the HFOs and HCFOs have very short atmospheric lifetimes measured in days or months. This means that the majority of any TFA produced from emissions of HFOs and HCFOs is deposited regionally. This resulted in more detailed studies being undertaken to determine deposition profiles of TFA.

HFO-1234yf has a 100% molar yield of TFA and an atmospheric lifetime of 12 days and due to it use to replace HFCs, particularly HFC-134a in mobile air-conditioning, several papers have been published for the deposition of TFA from its use. All the other HFOs and HCFOs have very low TFA yields estimated at 2% or 4% [9], depending on the substance.

Future projections for emissions of HFCs and HFOs from mobile air-conditioning for the EU

The main application of HFO-1234yf is in mobile air conditioning, where it replaced HFC-134a. With the European Directive on Mobile air-conditioning systems (MACs), in 2011 it was made mandatory for air conditioning systems in new vehicle types to be filled with a refrigerant with GWP <150; from 2017 all new vehicles were required to use a refrigerant with GWP <150; new vehicles with MAC systems using gases with GWP >150 were not anymore allowed be registered, sold, or able to enter into service in the EU [10]. HFO-1234yf is the refrigerant selected for virtually all new cars. Forecast emissions of HFO-1234yf and HFC-134a for mobile air-conditioning in the restriction proposal are based on the reported emissions required under the United Nations Framework Convention on Climate Change (UNFCCC), using the emission factors applied in the EU Common Reporting Format (CRF) Table. The U-PFAS dossier submitters state [11] that *"The estimate of 14,560 t total emissions of fluorinated gases from MAC with a basis in GHG Inventory data is taken as the main estimate of fluorinated gases from mobile air conditioning in this assessment. Two alternative approaches to the same estimate were explored for comparison, one giving a lower and the other giving a higher emission volume from this sector."* However, as stated by the dossier submitters, this excludes the end-of-life emissions, with an emission factor of 27.26% (2019) reported in the CRF table (2(II)B-Hs2.

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Similarly, the German Environment Agency (Umweltbundesamt, UBA [12]) validated its emissions model by comparison of the emission data from 2000 to 2017 with the National Inventory Reports (NIR) and their data tables in a Common Reporting Format (CRF), which were used to validate the projections of the adapted AnaFgas model; this showed a high degree of agreement. For the year 2018 in Europe, the model used by UBA appears to overstate HFO-1234yf emissions, compared to those derived from observations. The UBA report proposes possible reasons for the discrepancy (see Box 1).

Box 1. Uncertainties for the UBA emissions model (page 189)

A quantitative comparison between observed and simulated concentrations of u-HFC-1234yf for JFJ, MHD and TNS in fully equipped cars results in a scaling factor between the two annual averages in the range of 0.060 to 0.079 (mean 0.068 ± 0.033). Compared to the maximum scenario of Henne et al. (2012), u-HFC-1234yf emissions of approx. 1,300 ± 600 tons (95 % confidence interval), i.e. approx. 1,300 tons for Europe in 2018 are derived from this. These are lower emissions than those determined for the same year in Chapter 3.4 using the AnaFgas model (approx. 3,000 tonnes). The deviations can be explained on the one hand by the reported relatively large uncertainties in the atmospheric determination. It should also be noted that the MHD and JFJ measuring stations are not fully representative of all European u-HFC-1234yf emissions, as they are relatively remote and located in less urban areas. In addition, due to the delayed market launch and the recent full filling of all new passenger cars with u-HFC-1234yf since 2017, emissions are still in a very dynamic growth phase. Therefore, even small time shifts in the model parameters could lead to large relative deviations. The limits of the AnaFgas gas model itself, from which deviations of the calculated emissions from the real ones can result, are explained in Chapter 3.6.2.

According to SAP2022, for Europe, top-down (atmospheric monitoring) HFC-134a emission estimates are significantly lower (51% lower) than the reported HFC-134a emissions in recent years, submitted in the National Inventory Reports [13] (within the period 2008 to 2016). In Europe, new measurements of HFC-134a were carried out on the island of Crete, and were combined with long-term measurements in Ireland, Switzerland, and Italy. These measurements allowed new estimates to be made of emissions from central and western Europe and the eastern Mediterranean. The top-down estimates of aggregated HFC-134a emissions for reporting countries in the domain were 51% (37–69%) lower than the reports to the UNFCCC (18,600 tonnes/year (16,700–20,600) for this domain). The UBA report states total HFC-134a emissions from all applications, not just for MAC, are 28,416 tonnes in 2020 (UBA: Table 24), and about 34,000 tonnes in 2010 (UBA: Figure 14). For 2010, 50% of the UBA HFC-134a emissions is about 17,000 tonnes.

It is worth noting that SAP2022 also reported that for HFC-125 and HFC-143a emissions for Europe, top-down estimated emissions of HFC-125 and HFC-143a in 2013 were smaller than, or consistent with, the reported emissions for central and western Europe and the eastern Mediterranean.

One of the main uses of HFC-134a was mobile air-conditioning, which strongly suggests that emissions from MAC are overstated in the NIR and CRF tables, and this is therefore also expected to apply to HFO-1234yf used in MAC. The U-PFAS restriction proposal references the NIR and CRF for MAC emissions. In addition, forecasting emissions from MAC, based on historical emission factors, is expected to overstate emissions as improvements or changes in technology are not considered. The UBA model assumes an emission rate of 10%/year during the service life, virtually the same as the CRF

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emission factor (e.g. 2018: 9.94% product life factor) used by the restriction proposal, but also includes end-of -life emissions. According to the Montreal Protocol RTOC 2022 Assessment Report [14], leakage rates have decreased for mobile air-conditioning: "*Meanwhile, MAC systems tightness has improved mainly in Europe, US, and Japan, by adopting new hose materials, seals, and other technologies along with more effective coupling designs. In addition, system energy efficiency has increased owing to the development of better heat exchangers, compressors, and control strategies.*" A report from the USA for 50 car and van models, some with dual evaporators, for the model year 2021, reports leakage rates in the range 0.6% to 4.2%, with an average leakage rate of 1.6% and a median leakage rate of 1.25% [15].

Any emission forecasts should also consider the effects of the transition to electric vehicles. This was considerably underestimated in the UBA model [16]. In the EU, virtually all new cars are expected to be electric under the agreed 2035 phaseout of CO_2-emitting cars [17]. Forecasts [18] suggest that by 2040 all new car sales globally could be electric. Therefore, by 2050 as older vehicles are scrapped, the EU vehicle fleet will be virtually all electric. Forecasting emissions of HFO-1234yf through to 2050, based on current technology emission rates and when the mobile air-conditioning technology is undergoing a major transition, appears to be unrealistic and is highly likely to overstate emissions.

Electric vehicle air-conditioning and heat pump systems will, as a minimum, have electric compressors without shaft seals, unlike mechanically driven compressors. For conventional cars, the compressor shaft seal is responsible for about 50% of the refrigerant leakage rate [19] for new vehicles and is a source of increased leakage in older vehicles. Electrically driven compressors, as they do not have a shaft seal, will result in decreased emission rates for new vehicles, and throughout the vehicle lifetime as there is no associated aging factor due to the absence of the shaft seal. Other technology changes may further reduce emissions.

End of life recovery depends to some extent on the remaining refrigerant charge, which, in turn, is highly influenced by the leakage rate, and therefore by the presence or absence of a compressor shaft seal. The requirements of the circular economy will prioritise reducing and reusing materials before recycling them. In the context of refrigerants, HFO-1234yf can be reused following cleaning processes.

Emissions of HFO-1234yf from Mobile Air Conditioners in Europe

A key study for HFO-1234yf emissions from MAC in Europe EU was published in 2012 (Henne et al.) [20]. This simulation assumed that all car air conditioning systems are operated with the refrigerant HFO-1234yf. The study included low and high emissions scenarios, which used different annual leakage rates and end-of-life losses. The model assumed complete replacement of HFC-134a by HFO-1234yf and used predicted vehicle numbers for the year 2020 to calculate emissions. In reality, the complete conversion to HFO-1234yf did not occur but does not invalidate the simulation. Future changes in vehicle numbers or for example changes in leakage rates would affect the derived emissions to some extent. The authors arrived at a total emission level of u-HFC-1234yf for Europe (EU+ Croatia, Norway, Switzerland and Turkey) for 2020 of 11.0-19.2 kilotonnes per year. About 30-40% of these emissions are deposited within Europe in the form of TFA, the rest is transported in the atmosphere towards the Atlantic, Central Asia and Africa.

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However, based on:

- The overstated HFC-134a emissions in the NIR and CRF tables in recent years, used to validate emission models, as MAC is a main use of HFC-134a;
- The recent trends for reduced leakage rates;
- The transition to electric vehicles;

Future emissions from MAC in Europe are expected to be at or below the low emission scenario (11,000 tonnes) used in the Henne et al. study. This includes emissions at end of life, which appear to be excluded by the U-PFAS dossier submitters in their emissions estimate of 14,560 tonnes.

Forecast emissions of in scope HFCs and HFOs to 2070 [21]

U-PFAS Restriction Proposal Dossier: Annex A: Justification for inclusion of in scope and out of scope gases

A.2.1.4. Fluorinated gases

In Annex A, unless specifically explained, fluorinated gases are those gases that are within the definition used for the U-PFAS restriction proposal (see Figure A.5). Fluorinated gases are mainly used as starting materials in the production of fluoropolymers and as heat transfer agent in refrigeration and air conditioning.

Annex A.3.9. Applications of fluorinated gases

A.3.9.1. Uses
Page 63/64: The substances HFC-23 (CHF3), HFC-32 (CH2F2), HFC-152a (CHF2-CH3), HCFC-141b (CCl2F-CH3) and HFO-1132a (CH2=CF2) are not covered by the scope definition of the present U-PFAS restriction proposal due to their chemical structures. However, they are used in blends with other fluorinated gases that are within scope. Besides, the full overall volume of the different applications (including both PFAS and non-PFAS gases) is of relevance as a shift to a different specific gas could affect the whole application volume.
A.3.9.2. Volumes

Page 78: Although some fluorinated gases used in various applications and in considerable overall volumes are outside of the chemical scope of the U-PFAS restriction proposal (e.g. HFC-32), the overall volumes of gases (both PFASs and non-PFASs) for the different applications is of interest as trends and shifts may affect the whole sector use volume as a response to technical or regulatory development. Furthermore, the gases

The forecast emissions for in-scope HFCs and HFOs in the U-PFAS restriction proposal dossier are not obvious, as the forecasts appear to include out of scope gases, with some out-of-scope gases being HFCs and HFOs. The justification for this approach is set out in Annex A (see box),but lacks transparency. It might be interpreted as higher emissions for the in-scope gases and makes it difficult to estimate the emissions of TFA that are generated from some of these gases, as they breakdown in the atmosphere. In addition, it is difficult to compare forecasts from different sources, where the restriction proposal does not appear to include end of life emissions, while the UBA 2021 forecast includes end of life emissions.

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Comparison of U-PFAS Restriction Dossier and UBA forecast emissions

The UBA Report "*Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential*" acknowledges that, in a scenario of maximum future use and emissions of halogenated substitutes, the adoption of technical developments, or measures that could improve the tightness of the systems, or measures to increase the recovery rates, were not taken into account.

It is understood that in the U-PFAS restriction proposal, the same basic emission model was used to the UBA forecasts, even allowing for the exclusion of end of life, which means that similar trends might be expected.

In addition, although the UBA forecast only includes HFCs and HFOs, the other fluorinated gases are relatively minor according to the U-PFAS restriction proposal, Annex A, Dossier Table A.97[22]. From the table comparing both sets of emissions data, it is clear that the UBA worst case scenario emissions have effectively reached a plateau, while the U-PFAS restriction proposal emissions continue to increase, to levels that are significantly above the UBA forecasts. Charts from the UBA report and the restriction proposal dossier data emphasise the differences.

Table: Comparison of Restriction Proposal Dossier and UBA Emissions Forecasts

	2020	2025	2030	2035	2040	2045	2050	2060	2070
PFAS use (the bank)	542,194	598,626	660,931	729,722	805,672	889,527	982,109	1,197,186	1,459,363
PFAS emissions, Excludes End of Life	41,511	45,841	50,602	55,868	61,683	68,103	75,191	91,658	111,731
UBA Emissions HFCs & HFOs Includes End of Life	60,859		62,825		64,524		66,554		

Data sources: 1. U-PFAS restriction proposal, *Annex E, Table E.84 [23]. Projected yearly PFAS use and emissions in the fluorinated gases sector of the EEA in tonnes (mean values based on market data), which states Tonnage and emission estimates also include applications of fluorinated gases in mobile air conditioning and in transport refrigeration. 2. UBA 2021.*

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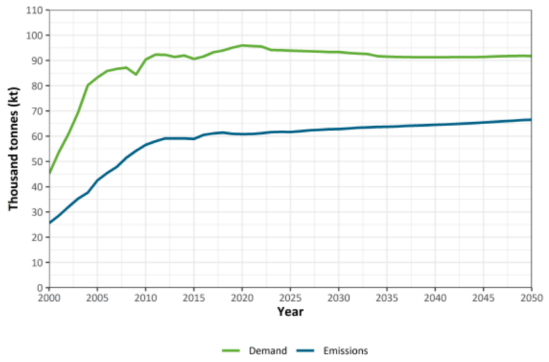
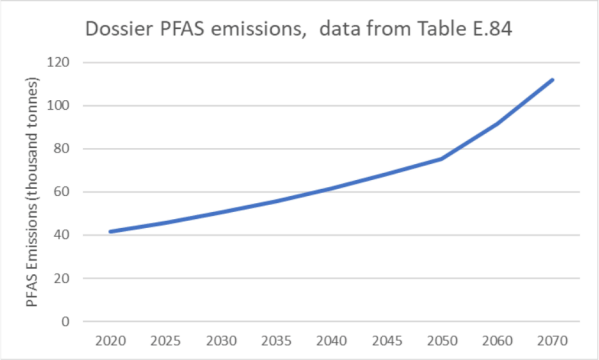
UBA Figure 12: Demand and emissions of HCFCs, HFCs, u-HFCs and u-HCFCs in the EU-28 in metric kilotonnes for the period 2000 to 2050 for the "u-HFC and u-HCFC maximum scenario".



Emissions data from Table E.84, see also in Figure E.12. Appears to include non-PFAS gases and may exclude end-of-life



It has already been demonstrated that current and future emissions from one of the main applications (mobile air-conditioning) are/will be lower than those in the UBA and restriction proposal dossier.

The EPEE HFC Outlook EU model

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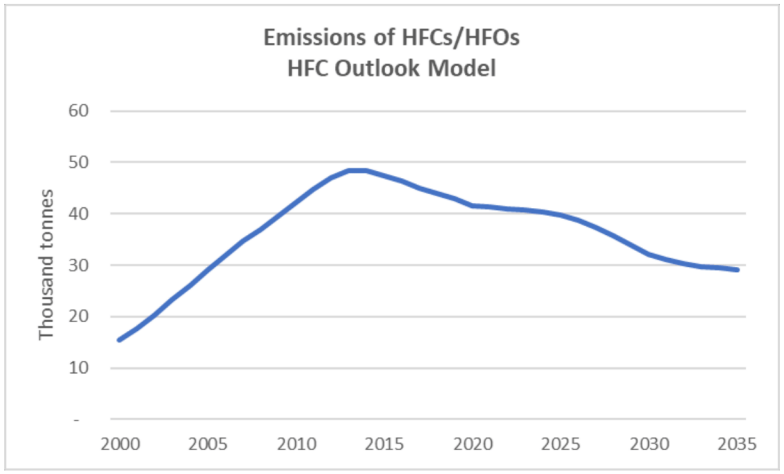

The EPEE HFC Outlook EU model [24], developed by Gluckman Consulting, carries out detailed modelling of the future markets for refrigerants in the EU+UK and takes into account the latest political orientations and technical developments. The HFC Outlook EU model is highly regarded, and parallel models are used beyond EU borders. The UN has worked with EPEE and Gluckman Consulting to create country specific models to help Montreal Protocol Article 5 countries prepare their F-Gas reductions plans. The HFC Outlook EU projections are built bottom-up, providing an analysis of the stock of equipment in more than 50 HFC market sub-sectors. This includes the RACHP sectors and also non-RACHP HFC applications such as MDIs, technical aerosols and foams.

The HFC Outlook EU model has been used to provide forecasts of consumption for individual HFCs and HFOs, and emissions from their use until 2035. Consumption and emissions of HFCs and HFOs from this model can be compared with the forecasts by UBA and those presented in the Restriction Proposal Dossier. Important points from this comparison are:

- Emissions of HFO-1234yf in 2035 are less than the low emission scenario (11,000 tonnes) used in the Henne et al. study for mobile air-conditioning in Europe and include emissions from its use in other HVACR applications.
- Emissions of HFO-1234yf are significantly lower than the UBA forecasts for HFO-1234yf emissions in the period until 2035 and are less than one quarter of the emissions forecast by the UBA for 2035. This is not unexpected as the UBA forecast has a scenario of maximum future use and emissions of halogenated substitutes, the adoption of technical developments or measures that could improve the tightness of the systems or measures to increase the recovery rates were not taken into account under this maximum scenario.
- For the period 2008 to 2016, the HFC Outlook EU model does not underestimate emissions for HFC-134a. It shows higher emissions for HFC-134a in Europe when compared to the top-

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down HFC-134a emissions reported in SAP2022, but lower emissions when compared to UBA data.

- Total emissions for HFO-1234ze(E), HFO-1336mzz and HCFO-1233zd(E) are significantly lower than these forecast by the UBA, and in 2035 are less than one quarter of the UBA forecast.
- This version of the HFC Outlook EU model forecasts total emissions of HFCs and H(C)FOs [in scope and out of scope] of about 29,000 tonnes (EU-27) in 2035, compared to the UBA forecast of 62,825 tonnes in 2030 and 64,524 tonnes in 2040 (EU-27+UK).
- The restriction proposal dossier forecasts 55,868 tonnes of F-gas emissions in 2035. This forecast appears to include out of scope F-gases but excludes end-of life emissions.

In summary, the Restriction proposal dossier and the UBA emissions forecasts are based on a similar model. The model, as used by UBA, is a maximum emissions scenario, which, by definition, will overstate emissions as it does not consider the adoption of technical developments. Top-down emissions show that reported emissions of HFC-134a are overstated for Europe in recent years, which will influence emissions forecasts by UBA and the restriction proposal dossier. The HFC Outlook EU model takes into account the latest political orientations and technical developments and forecasts significantly lower emissions for HFCs and HFOs, which are forecast to be on a downward trend at least until 2035.

Global and European Regional TFA generation and deposition

The SAP2022 Assessment Report forecasts the global generation and deposition of TFA by 2050, based on the assumption that that 50% of the future emissions of low-GWP alternatives are related to HFOs, from which it is assumed that 50% is HFO-1234yf, with a conversion rate of 100% to TFA. The calculation also assumes that the formation of TFA from HFC-134a is based on its expected mixing ratio of HFC-134a and its lifetime of 14 years. Conversion rates from the destroyed HFC-134a amounts to TFA were 7–20%. From the data presented, with an estimated total atmospheric formation and deposition of 5.8 – 8.1 Tg [25] of TFA between 2020 and 2050, and subsequent transfer to the ocean, average TFA concentrations in sea water are projected to increase by 4 - 6 ng/L between 2020 and 2050, assuming a total ocean volume of 1.37×10^9 km^3. This can be compared to the total ocean content of 61–205 Tg of TFA around the year 2000 reported in Scott et al. (2005) [26], based on measuring varying concentrations in different ocean parts, or the 274 Tg of TFA reported in Frank et al. (2002) [27], based on a measured constant concentration of 200 ng/L. Scott et al. measured oceanic concentrations of 10 ng/L to 160 ng/L.

The UBA scenario of maximum future use and emissions of halogenated substitutes, which did not consider the adoption of technical developments or measures that could improve the tightness of the systems or measures to increase the recovery rates, forecasts 1.38 Tg of TFA generation from HFCs and HFOs between 2000 and 2050 for Europe. Subsequent transfer to the oceans would result in an

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increase of 1 ng/L in average oceanic concentration of TFA by 2050. This additional quantity is relatively minor when compared to the measured oceanic concentrations and estimated oceanic quantities around the year 2000.

The HFC Outlook EU model, using the EEAP2022 Assessment Report [28] yields of TFA for each HFC and HFO, forecasts 0.19 Tg of TFA generation from HFCs and HFOs between 2000 and 2035. Subsequent transfer to the oceans would result in an increase of 0.14 ng/L in average oceanic concentration of TFA by 2035. This additional quantity is very minor when compared to the measured oceanic concentrations and estimated oceanic quantities around the year 2000. This estimate ignores the approximately 6% of TFA that is destroyed in the atmosphere. The model forecasts about 9,000 tonnes of TFA emissions for Europe in 2035. This is considerably lower than the UBA forecast of 40,364 tonnes in 2030 and 47,691 tonnes in 2040.

Sensitivity Analysis: The EEAP2022 report [29][1] discusses the yield of TFA from individual HFC and HFO substances. For some substances such as HFC-134a, a range is quoted, with the yield of TFA depending on conditions and for these the central estimate was used. However, for some substances, there is uncertainty about the TFA yield, with upper theoretical limits quoted. For these substances, applying the upper limit TFA yields has a minor effect on the HFC Outlook EU model forecast for TFA emissions in 2035, which would be about 10,000 tonnes. Similarly, the model forecasts, using the TFA upper limits, 0.25 Tg of TFA generation from HFCs and HFOs between 2000 and 2035. Subsequent transfer to the oceans would result in an increase of 0.18 ng/L (i.e. similar to the above) in average oceanic concentration of TFA by 2035.

Transportation of TFA deposited over land, to the oceans

Europe does not have any major endorheic basins, (**drainage basins that normally retain water and allow no outflow to other external bodies of water, such as rivers or oceans), which means that almost all TFA deposited in over land in Europe will be transported to the oceans.**

This is analogous to the transportation of chloride, from sea salt aerosol deposition over land, back to the oceans.

The Annual Cycle of Sea Salt [30]:[2] Extract from paper about river run off "*Petrenchuk (1980) estimates that the river runoff of sea salt is 300–400 Tg yr. This should equal what is deposited over*

[1] UNEP 2022 Assessment Report of the Environmental Effects Assessment Panel, March 2023, available at http://ozone.unep.org/science/eeap see Chapter 6 Appendix

[2] Modeling the Annual Cycle of Sea Salt in the Global 3D Model Oslo CTM2: Concentrations, Fluxes, and Radiative Impact, A. Grini, G. Myhre, J. K. Sundet, and I. S. A. Isaksen, Journal of Climate, 2002, Volume 15, 1717, American Meteorological Society

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land (as nothing is assumed accumulated on land). Using yearly river data of 35.6x10^3 km^3 and an average chlorine concentration in rivers of 6.4 - 7.8 mg/L Petrenchuk (1980) finds 230–280 Tg/yr of chlorine. This should be approximately the same as the chlorine deposited over land from sea salt aerosols. Our model deposits 161 Tg/yr of sea salt over land, corresponding to 88 Tg/yr of chlorine. Given the uncertainties and assumptions made in such a comparison the estimates compare reasonably well. The comparison assumes that river concentration of chlorine is constant, that we have a steady state in chlorine at land, that no chlorine evaporates from the aerosols, and that the only way the chlorine can escape from land to ocean is by rivers."

TFA concentrations in European rainfall

The U-PFAS restriction dossier, in Annex B, reports on TFA concentrations measured in surface waters and rain (B.4.2.7. Monitoring of specific PFASs in environmental samples and Table B.78). Forecasts of the contribution of some HFCs and HFOs to the concentration of TFA in rain in Europe and other regions have been published. TFA is highly soluble and is scavenged from the atmosphere via rain, fog, and snow, as well as dry deposition. Some fraction of the TFA dissolved in cloud water can partition back into the gas phase when the cloud water evaporates. More than 90% of TFA is physically removed from the atmosphere via wet and dry deposition (about 80% via wet deposition and 10% via dry deposition), with an estimated global mean deposition lifetime of about 5–10 days. TFA is also chemically destroyed in the atmosphere by OH. This is estimated to be a minor loss channel (about 6%), (SAP2022) [31].

The Henne et al study [32] modelled the contribution of HFO-1234yf to TFA rainfall concentrations using high and low emissions scenarios. It has already been shown that future emissions from mobile air-conditioning (MAC) in Europe are expected to be at or below the low emission scenario (11,000 tonnes) used in the Henne et al. study. The low emissions scenario calculated concentrations of TFA in precipitation averaging 330 ng/L to 465 ng/L annually, and an annual maximum of 1260 ng/L.

The HFC Outlook Model forecasts emissions of TFA for all HFCs and HFOs at about 9,000 tonnes/year for Europe in 2035. The European emissions of HFC and HFOs that can breakdown to form TFA are dominated by the ultra-low GWP HFOs and HCFOs in 2035. For each substance that degrades to generate TFA, the TFA deposition profile is linked to the TFA yield and atmospheric lifetime of the substance. However, the HFOs and HCFOs that breakdown to give low yields of TFA have short atmospheric lifetimes, with two being similar to HFO-1234yf. While a complete atmospheric model for Europe would be required to provide a more accurate assessment, TFA rainfall concentrations due to emissions of HFCs and HFOs from Europe in 2035 can be roughly estimated by using the Henne et al. study rainfall concentrations. Emissions of about 9,000 tonnes of TFA (HFC Outlook Model) could result in estimated concentrations of TFA in precipitation averaging less than the low emissions scenario from the Henne et al. study (330 ng/L to 465 ng/L annually) in 2035.

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The UBA report [33] and the HFC Outlook Model forecasts show that the combined contribution to TFA emissions in Europe of the HFOs 1234ze, HFO-1336mzz and HCFO-1233zd are very minor in the period until 2035, due to their low yield of TFA formation and their forecast low emissions.

The estimated concentrations of TFA in precipitation averaging less than 330 ng/L to 465 ng/L (0.33 µg/L to 0.47 µg/L) in 2035 can be compared to the UBA target value for TFA in drinking water of 10,000 ng/L (10 µg/L) and the UBA health guidance value for TFA in drinking water of 60,000 ng/L (60 µg/L) [34].

The EEAP 2022 Assessment Report [35] summarises a new toxicity test for an aquatic organism. This was a retest of the most sensitive alga (Raphidocelis subcapitata). The study protocol followed OECD guideline 201 and effect values were based on growth. A no observed effect concentration (NOEC) of 2.5 mg a.e./L (2,500,000 ng/L or 2500 µg/L) was reported based on inhibition of growth.

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10. Directive2006/40/EC relating to emissions from air-conditioning systems in motor vehicles and amending Council Directive 70/156/EEC.

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11. Restriction proposal dossier Annex B page 268.

12. UBA Final report *Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential* | Umweltbundesamt

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14. 2022 TOC Refrigeration, AC and Heat Pumps Assessment Report page 189, available at Technology and Economic Assessment Panel (TEAP) | Ozone Secretariat (unep.org)

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Summary of human biomonitoring and health effects of trifluoroacetic acid (TFA)

Human biomonitoring data of TFA, as well as its temporal trend, is limited. Biomonitoring for environmental chemicals among general population from the U.S., Canada, Germany and Australia did not report or include TFA. TFA was reported in selected blood samples of the Swedish population, but the concentrations were below the level of quantification (LOQ). High level of TFA was reported among blood samples of volunteer staff and support workers at Nankai University (China); however, the source of TFA is unknown.

The German Environment Agency (UBA) recently proposed that plants could serve as biomonitoring tool to evaluate the presence and trend of TFA in the terrestrial environment.

Studies that report association between human biomonitoring of TFA and health effects are limited. A recent study from China reported **a protective effect** between ultra-short chain PFAS, which included TFA, and glycemic biomarkers linked to increased risk of diabetes.

Specific studies:

Human biomonitoring databases from:

(1) the U.S. Centers for Disease Control and Prevention (CDC) National Health and Nutrition Examination Survey (NHANES) from 1999 through 2018 (NHANES 2023 [7]);

(2) Canadian Health Measures Survey (CHMS 2023 [3]) from 2007 to 2017;

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(3) German Environmental Specimen Bank from 2009 to 2019 (Gockener 2020 [6]); and

(4) human serum samples between 1975 and 1995 in Australia (Nilsson 2023 [8]) were reviewed, TFA was either not reported or not measured.

TFA was detected in human blood samples in three recent studies. Two of these studies are from Sweden (Aro *et al.* 2019, 2021 [1], [2]), and all the measured concentrations were below the level of quantification (LOQ) with poor recovery in the blood samples.

For the first study (Aro *et al.,* 2021, [2]), 148 blood samples (92 samples or 62% were detected for TFA) were obtained from people who donated blood with unknown source of TFA exposure between 2018 and 2019. The sum of ultra-short chain PFAS (PFEtS, PFPrS excluded non-quantifiable TFA and PFPrA) made up of 0.2% of the composition for 63 individual PFASs detected. In the second Swedish study (Aro et al., 2019 [1]), 20 blood samples were obtained from individuals living in a municipality of Ronneby, who have known to been exposed to PFASs via consumption of PFAS contaminated drinking water from firefighting foams used at a nearby military airport. The blood samples were from October 2014. One sample was detected for TFA but it was below LOQ. The perfluoroalkyl carboxylic acid (PFCA) and sulfonic acid (PFSA) precursors had a negligible contribution to the sum of 63 PFASs measured. Results from these 2 studies are not generalizable to the larger population of Sweden.

The third study is from China (Duan *et al.,* 2020 [4]). Blood samples were obtained from 294 volunteer staff and support workers at Nankai University (China) with unknown source of TFA exposure. The geometric mean of TFA is 7.21 ng/mL (detection rate: 97%) which is made up of 17.2% of the composition of the 21 individual PFASs detected. The source of TFA exposure among this specific study population could come from many sources such as laboratory reagent, by-product in the chemical synthesis process, and degradation of pharmaceuticals and plant protecting agents with tri-fluoromethyl moieties. The measurements were taken at one point in time and among selected study population; therefore, the results are not generalizable to the larger population of China.

A recent study funded by the German Environment Agency (Freeling *et al*., 2022 [5]) reported plants as a biomonitoring tool to evaluate the presence and trend of TFA in the terrestrial environment. Tree leaf samples (European beech, Lombardy poplar, Norway spruce, and Scots pine) from the German Environmental Specimen Bank (ESB) were analyzed for TFA from 1989 to 2020. The sampling sites represented major ecosystem types in Germany. The study assumed that the major source of TFA in the studied plant matrices was atmospheric deposition. The authors reported that there is a positive temporal trends of TFA in archived plants over the last 3 decades (**Figure 1**).

Figure 1: Temporary concentration trends of TFA in archived plants (Freeling et al., 2022 [5])

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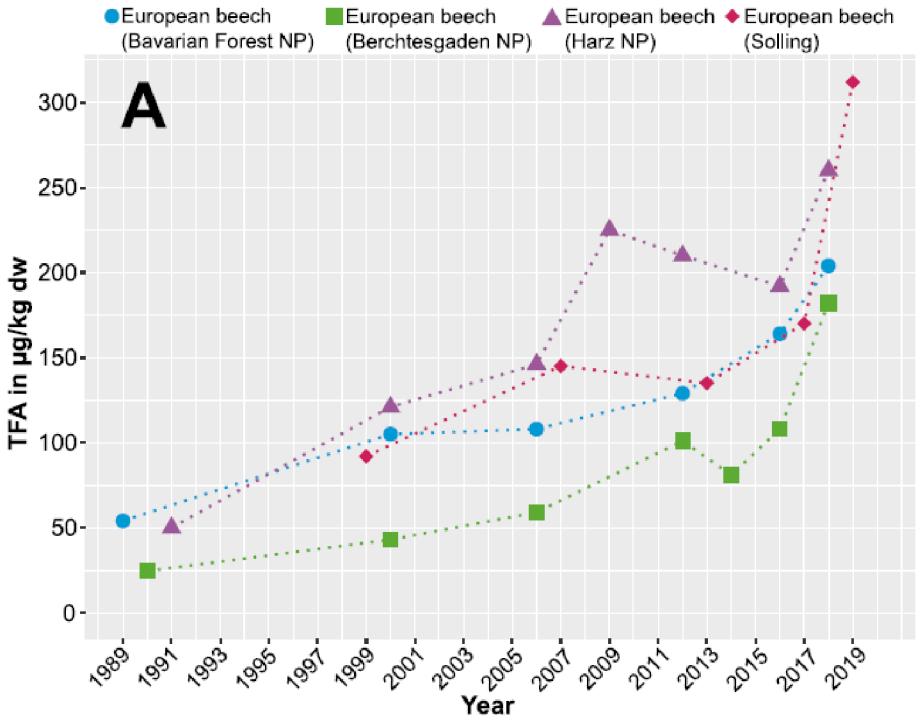

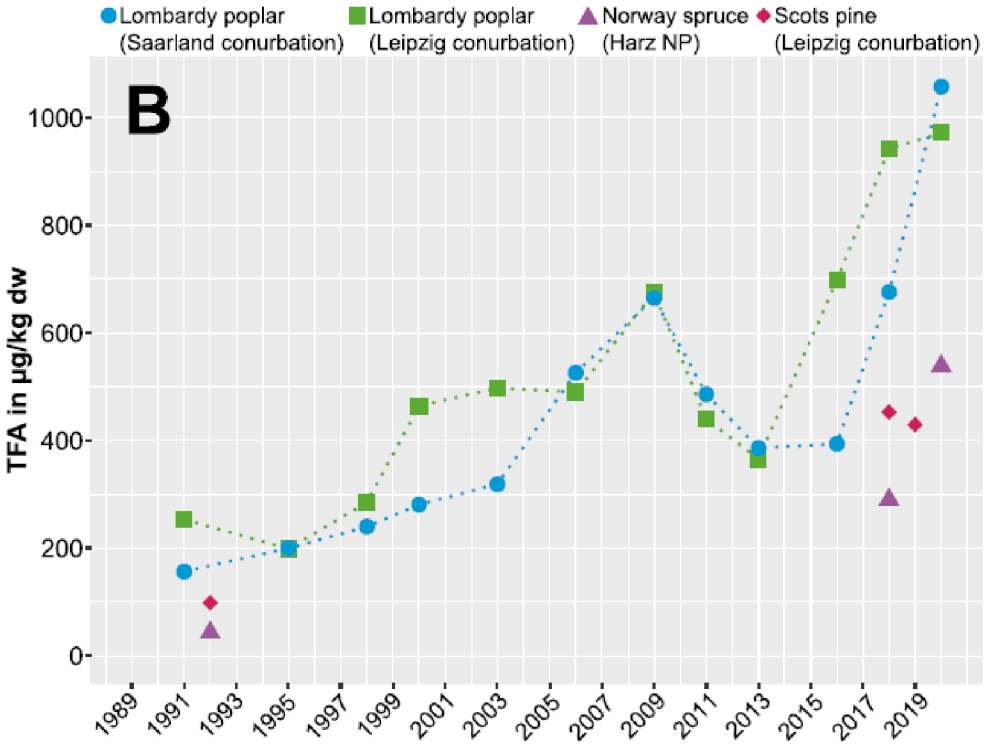

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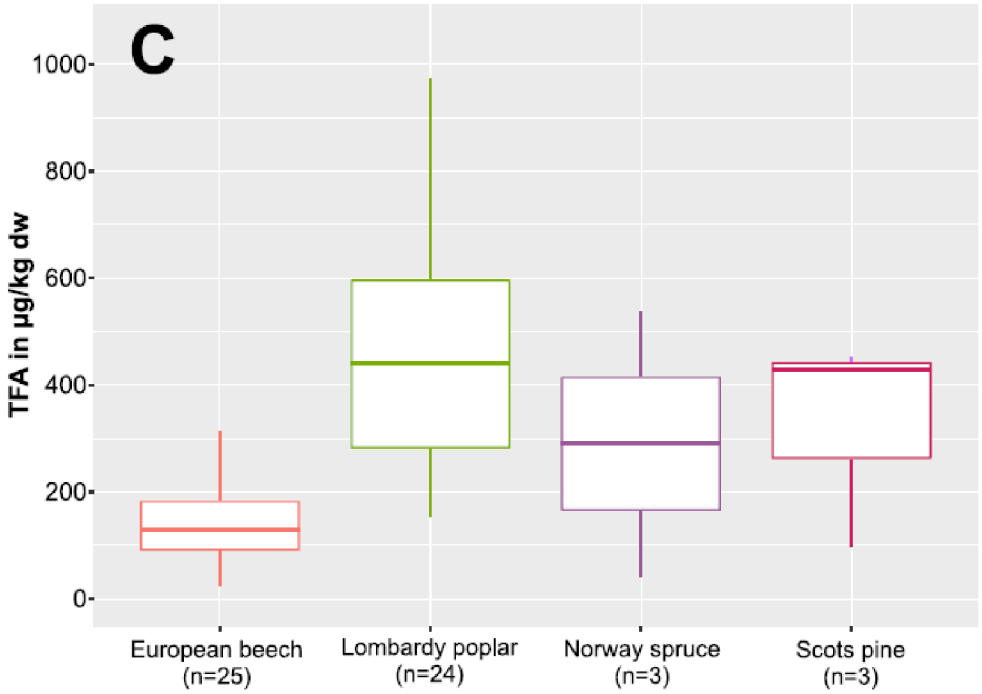

A recent study from China (Duan et al., 2020) reported sum ultra-short chain perfluoroalkyl carboxylic acids (∑PFCAs C2-C3: TFA & PFPrA) was **inversely** associated with glycemic biomarkers linked to increased risk of diabetes. It is a **protective effect** between ∑PFCAs C2-C3 and HbA1c level in adjusted model with an estimate of -0.014 (95%CI: -0.027,-0.001) and p value = 0.037. The same inverse association for individual substance of TFA and PFPrA was not statistically significant at p value=0.05 among highly exposed population for TFA (median=8.46 ng/ml). This is a cross sectional study conducted among volunteer staff and support workers at Nankai University (China), the study results are not generalizable, and causality could not be inferred.

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TFA yields from HFCs, HFOs and HCFOs

Trifluoroacetic acid (TFA), $CF_3C(O)OH$, produced by degradation of some halogenated gases has been evaluated extensively in the past few decades (see reviews by SAP 2022 [1], EEAP 2022 [2], Burkholder et al., 2015 [3] and Wallington et al. 2015 [4]). Several HFCs, HFOs and HCFOs produce TFA with molar yields that vary from as low as 1% and up to 100%. EEAP 2022 reviewed the yields of TFA from individual compounds and they are estimated based on evaluations of the available literature. These are shown in the figure reproduced in part from EEAP 2022 [5]. Error bars in the figure represent both experimental uncertainties and upper and lower yield ranges due to competing reaction channels that depend on environmental conditions.

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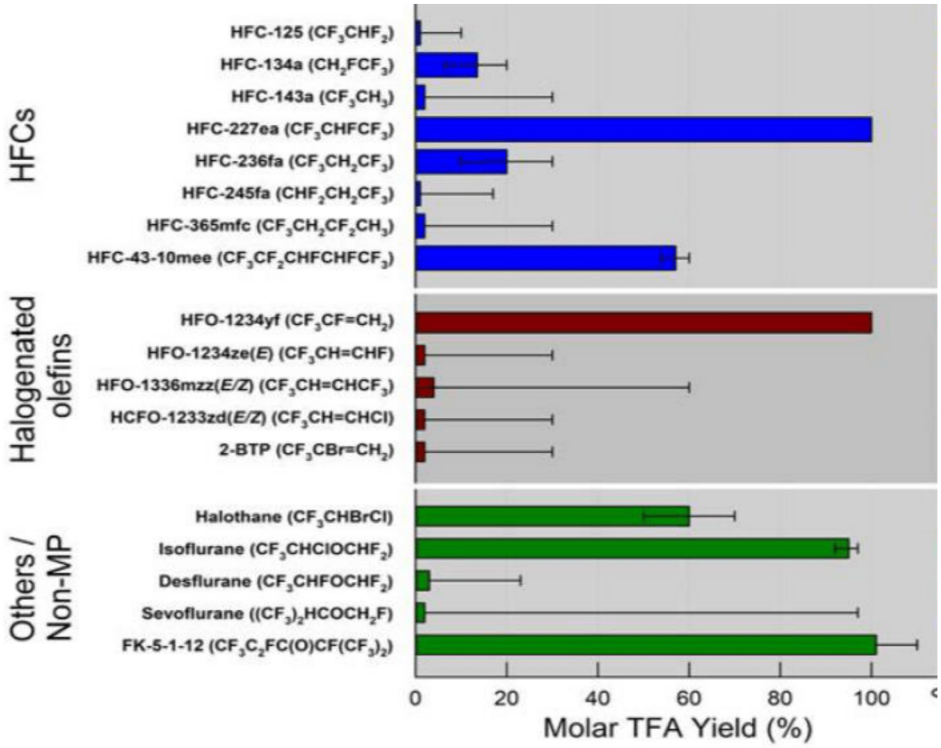

Figure: TFA yields from HFCs, and HFOs, as adopted from 2022 EEAP report (Chapter 6 Figure 12 page 282). *The category 'Others/Non-MP' are not relevant to this discussion.*

HFCs, HFOs and HCFOs that yield TFA will typically oxidize, either by OH radical- or sunlight-initiated oxidation, to either trifluoroacetyl fluoride ($CF_3C(O)F$) or trifluoroacetaldehyde ($CF_3C(O)H$). For example, HFC-134a and HFO-1234yf lead to trifluoroacetyl fluoride, as an atmospheric oxidation intermediate. $CF_3C(O)F$, once formed, will convert to 100% TFA, within days, via aqueous phase chemistry in clouds or water droplets.

EEAP 2022 cites estimated TFA yields for HFOs and HCFOs as: HFO-1234yf, 100%; HFO-1234ze(E), 2%; HFO-1336mzz(E/Z), 4%; HCFO-1233zd(E), 2%. HFO-1234ze(E), HFO-1336mzz(E/Z), and HCFO-1233zd(E) degrade in the atmosphere via CF_3CHO. The atmospheric degradation of HFC-143a, HFC-245fa and HFC-365mfchas CF_3CHO as an intermediate product. For HFC-125, a minor reaction pathway can lead to a low yield of TFA. HFC-134a has a TFA yield estimated at 7–20 % depending on conditions [6]. The yield of TFA from CF_3CHO may depend on whether it remains in gaseous form.

According to EEAP 2022 Section SI 4.1.3: "Current understanding of the atmospheric fate of CF_3CHO suggests that its atmospheric fate is dominated by destruction by photolysis resulting in an atmospheric lifetime of the order of two days (Chiappero et al., 2006 [7]). Photolysis of CF_3CHO leads

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to CF_3 and CHO radicals which cannot contribute to the formation of TFA (Sulbæk Andersen & Nielsen, 2022 [8]). The rate of reaction of CF_3CHO with OH radicals is slow (atmospheric lifetime of approximately 20 days), and thus of less importance in the fate of CF_3CHO. Any oxidation of CF_3CHO initiated by OH radicals will produce CF_3CO radicals, which undergo reaction with O_2 to yield acyl peroxy radicals, $CF_3C(O)O_2$. These acyl peroxy radicals can react with HO_2, NO, or NO_2. Reaction of $CF_3C(O)O_2$ with HO_2 radicals can lead to the formation of TFA (39% yield) (Hurley et al., 2006 [9]). Finally, on contact with liquid water, CF_3CHO can produce aldehyde hydrates (gem-diols). These can, at least in the gas-phase, react with OH radicals (lifetime of approximately 90 days) and present an efficient way of generating TFA (Sulbæk Andersen et al., 2006 [10]). The latter two processes are likely minor fates for CF_3CHO. The importance of formation of TFA from the reaction of OH with CF_3CHO was indirectly accessed by Sulbæk Andersen et al. (Sulbæk Andersen, Schmidt, et al., 2018 [11]) in a global modeling study of HCFO-1233(zd). This model, which did not include potential CF_3CHO-hydrate formation, suggested a 2% yield of TFA from CF_3CHO. The contribution to TFA from CF_3CHO hydrate formation and processing remains highly uncertain (Franco et al., 2021 [12]. Sulbæk Andersen et al., 2006 [13]). Assuming that uptake into cloud water and hydration is efficient, effectively converting CF_3CHO into TFA on a timescale of 5 days (only limited by transport limitations, i.e., the lower limit for the time taken for transport into clouds (Wallington et al., 1994 [14]), then a maximum TFA yield of 27% can be expected from the hydrate formation [24]. **Thus, the TFA yield from processing of CF_3CHO is estimated at 2% with an upper theoretical limit of ~ 30%**."

The degradation routes for $CF_3C(O)H$ are summarized in the table, which explains why the hydrate route has significant uncertainty, but also why it is likely to be a relatively minor degradation route.

Summary of degradation routes for $CF_3C(O)H$

Degradation Route	Atmospheric Lifetime	Reaction	Comment
Major: Photolysis	0.92-2.5 days [15]; 19 hours [16]	$CF_3CHO + h\nu \rightarrow CF_3 + CHO$	Does not form TFA, with HF and CO_2 as final products.
Minor: Hydroxyl radical OH	20 [17] -26 days [18]	$CF_3CHO + OH \rightarrow CF_3CO + H_2O$	Produces low yield of TFA following further reaction of the acyl radical (CF_3CO). The low yield of TFA is influenced by atmospheric concentration of NOx. In the presence of excess NOx, no TFA was detected [19]
Minor: Hydration then OH radical	Homogeneous gas-phase reaction with H_2O occurs slowly, if at all.	$CF_3CHO + H_2O \Leftrightarrow CF_3CH(OH)_2$ $CF_3CH(OH)_2 + OH + O_2 \rightarrow CF_3COOH$	The hydrate is in equilibrium with CF_3CHO [22] Estimated atmospheric lifetime for reaction of

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	Typical lifetime around 5 [20] -15 days [21] for contact with water-rich media such as clouds		$CF_3CH(OH)_2$ with OH of approximately 90 days [23]. The 90 days lifetime is long enough to allow competition from the likely dehydration under low humidity conditions and subsequent fast loss via photolysis. If the hydrate reacts with OH, the yield of TFA is 100%.

Note: The lifetime of each HFO/HCFO and location of emissions does affect to some extent where CF_3CHO will be formed and, under what conditions it will decompose to other products.

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5. EEAP 2022, Chapter 6, Figure 12 page 282

6. EEAP 2022, Chapter 6, Appendix, SI 4 Estimated molar yields (%) of TFA from ODS replacements. Section SI 4.1.3 discusses CF3CHO, and the degradation of each substance is discussed.

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Review Paper: Assessment of human health risks due to environmental exposures to Trifluoroacetic acid (TFA)

A recently published hazard and risk assessment[3] reviews the mammalian toxicity of TFA and human exposures to assess the margin of exposures (MoE) (see note 1). This is particularly timely, due to its relevance to the public consultation for the U-PFAS restriction proposal. The paper concludes that the potential of TFA to induce acute toxicity is very low and oral repeated dose studies in rats have identified the liver as the target organ with mild liver hypertrophy as the lead effect. Biomarker analyses indicate that TFA (trifluoroacetic acid) is a weak peroxisome proliferator in rats. TFA administered to rats did not induce adverse effects in an extended one-generation study and in a developmental toxicity study or induce genotoxic responses. 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.

The review summarizes the available mammalian toxicity data on trifluoroacetate and integrates this information with potential human exposures to trifluoroacetate based on the measured concentrations of TFA in water and food using the margin of exposure methodology. The paper also explains that the liver is the target organ following repeated oral administration of TFA and that the effects of TFA on liver are generally mild and consistent with a PPAR-alpha mode of action. This mode of action is not considered relevant to humans, as human liver, in contrast to rodents, does not respond to PPAR alpha activation by initiating cell proliferation. Note also that there were no changes in thyroid hormones, nor were there any adverse effects on reproduction or development.

The paper considers that a highly conservative approach is applied by UBA regarding the presence of contaminants in drinking water in Germany. The margin of exposures (MoEs) regarding potential exposures of the general population to TFA from drinking water are very large and orders of magnitude above the required MoE > 100 even when using the highest measured concentrations of TFA in surface water as a surrogate for drinking water levels. Drinking water, based on the highest

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concentration (4.8 µg TFA/L) detected in environmental water samples taken from 2014 to 2022, as reported in the review paper, results in a 62,500 margin of exposure compared to the No Observed Adverse Effect Level (NOAEL) of 10 mg/kg bw/day in rats, identified in the review paper as the applicable NOAEL.

Risks of exposure to TFA in aquatic organisms

Environmental Effects Assessment Panel 2022[4] reported one new toxicity test for an aquatic organism. This was a retest of the most sensitive alga (*Raphidocelis subcapitata*). The study protocol followed OECD guideline 201. Effect values were based on growth. A no observed effect concentration (NOEC) of 2.5 mg acid equivalent/L (2,500,000 ng/L) was reported based on inhibition of growth. The detailed report of the study was reviewed by ECHA and was classified as "*reliable without restriction*", hence it has been used here in the characterisation of the toxicity of TFA to aquatic organisms. "The margin of exposure between the distribution of no observed effect concentrations (NOEC) of trifluoroacetic acid salt from a range of studies and the observed and expected concentrations in the oceans and endorheic basins is several orders of magnitude and is indicative of *de minimis* risk."

TFA toxicity data and drinking water guidance value for TFA in Germany

The German drinking water guidance value or German Health Orientation Value (GOW) for TFA has evolved and increased as more TFA toxicity data has become available with the UBA most recently increasing the allowable guidance limit in 2020.[5] A chronic (long term - 1 year) drinking water study in rats used high concentrations of TFA, between 100,000 and 2 million times higher than the average concentration found in rainwater in 2018-2019. No effects were found at the lower concentration (the NOEL, no-observed effect level, i.e., no changes compared to a control group). The GOW was set by applying a safety factor of 100 to the NOEL, taking into account human body weight and everyday water consumption, and then adding an additional safety factor of 10 to allow TFA from drinking water to contribute a maximum of 10% to the tolerable daily intake (TDI) of TFA. The GOW for TFA is 60 µg/L in drinking water.

[4] Montreal Protocol on Substances that Deplete the Ozone Layer UNEP 2022 Assessment Report of the Environmental Effects Assessment Panel available at http://ozone.unep.org/science/eeap.

[5] Trifluoressigsäure (TFA)–Gewässerschutz im Spannungsfeld von toxikologischem Leitwert, Trinkwasserhygiene und Eintragsminimierung. Erläuterungen zur Einordnung des neuen Trinkwasserleitwerts von 60 µg/L. 20. Oktober 2020. Umweltbundesamt www.umweltbundesamt.de

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