EFCTC
EUROPEAN FLUOROCARBONS
TECHNICAL COMMITTEE

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SPECIAL REVIEW ON …

Understanding TFA

29 August 2016

TFA (trifluoroacetic acid and its salts) is a breakdown product of some fluorocarbons, is naturally occurring in the environment and resistant to further degradation (breakdown). This EFCTC Special Review is intended to provide an easy to understand summary of the 'TFA story' and provides links to more detailed supporting information.

1. What is TFA?

→ *TFA is a naturally occurring substance which is stable in the environment and resistant to further degradation (breakdown). TFA is also produced by the breakdown of some fluorocarbons.*

The stable form of TFA in the environment is the trifluoroacetate ion (CF_3COO^-) which will be combined with counter-ions such as sodium, in seawater, or calcium or ammonium inland, to form neutral salts. However, "TFA" is used as shorthand for trifluoroacetic acid and its salts.
TFA is also produced by the breakdown of some HCFCs, some HFCs and some HFOs in the atmosphere (see appendix). Currently the largest fluorocarbon source of TFA is HFC-134a; HFO 1234yf is expected to become another fluorocarbon source, while other HFOs like 1234ze (E) or 1233zd (E) are not a source of TFA.

2. How much TFA is present naturally in the environment?

→ *Over 200 million tonnes are present in the oceans, both coastal and deep-ocean seawater. To determine if underwater vents could contribute to the TFA concentrations in the oceans, profiles were taken over three vents in the Pacific and Mediterranean Oceans. The results suggest that some deep-sea vents may be natural sources of TFA (1). More than 95% of TFA found in the oceans is naturally produced. See fact sheet on TFA.*

TFA is not confined to the oceans. It was found in samples of fog, rain, river and lake water analysed during the 1990s. The TFA concentrations measured were far in excess of those that could occur as a result of atmospheric oxidation of man-made fluorocarbons.

TFA is also found in soil samples, including in an archived soil sample from 1865. Generally, soil retention of TFA is poor: it appears to be held in soil by adsorption and not by irreversible binding. Therefore, TFA will ultimately enter the aqueous environment.

TFA appears to be very resistant to degradation (breakdown) by non-biological physicochemical processes. Its light-absorption properties make it resistant to photochemical breakdown. Other physicochemical loss processes that have been studied are extremely slow under environmental conditions. TFA salts are highly soluble and will not precipitate from solution at concentrations expected in the environment. Thus, the stability and solubility of TFA suggest that it will tend to remain dissolved in water.

(1):Scott B.F., R.W. Macdonald, K. Kannan, A. Fisk, A. Witter, N. Yamashita, L. Durham, C. Spencer and D.C.G. Muir, Trifluoroacetate (TFA) Profiles in the Arctic, Atlantic and Pacific Oceans, Environ. Sci. Technol., 39, 6555-6560, 2005.

An overall environmental risk assessment has been conducted on the basis of the data generated by studies in the 1990s. The results of the risk assessment and several review articles are published in the peer-reviewed literature. Further information about TFA can be found at www.afeas.org.

3. A natural cycle transporting sea salt and TFA from the oceans

→ *Although the source of TFA deposited over land has not been confirmed, the concentrations and locations are consistent with transport of TFA from the oceans in much the same way as sea salt (as an aerosol).*

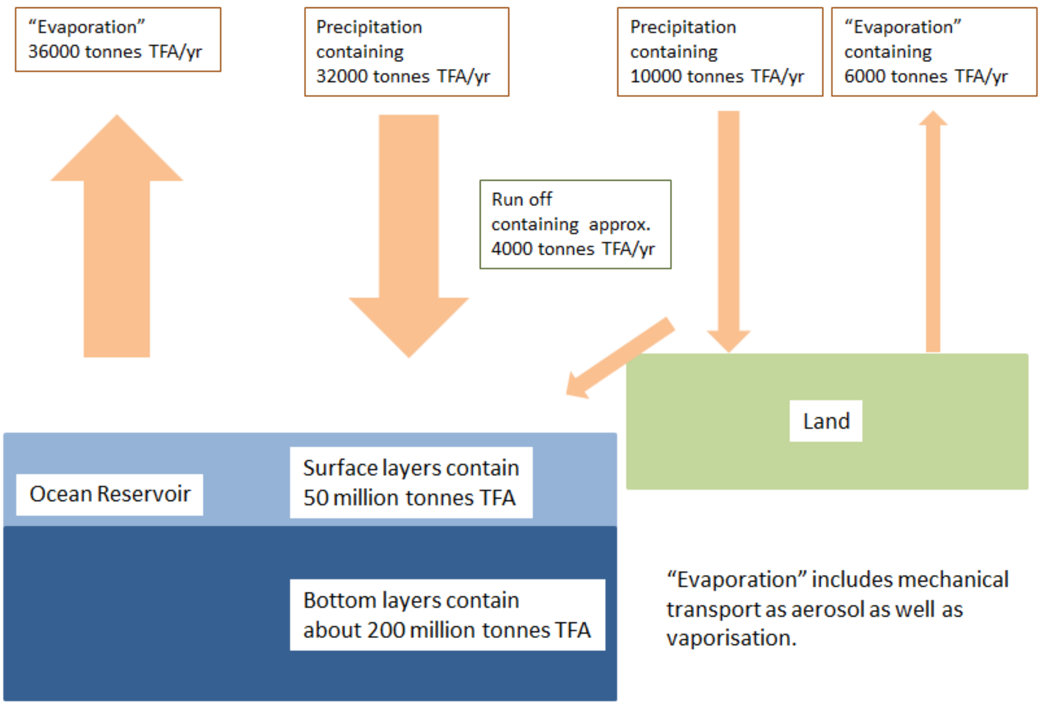
The generation of sea salt aerosol by mechanical action of wind on the sea surface is well known. The aerosol is removed from the global atmosphere mainly by wet deposition, with the sea salt aerosol being transported up to several hundred kilometres inland.

Because the primary generation of the aerosol is essentially a mechanical process at the sea surface, the quantity of TFA transported into the atmosphere should scale simply by its concentration relative to that of the chloride ion in the aerosol. This could result in a TFA transport into the atmospheric aerosol of 36,000 tonnes annually. Much of this will be precipitated back into the oceans and it is estimated that about 4000 tonnes is precipitated over land globally. The total estimated precipitation over land of about 10,000 tonnes includes 6000 tonnes "evaporated" from the land.

The atmospheric lifetime of TFA before it is rained out is of the order of two weeks, meaning that TFA can be transported over considerable distances from the position where it was transferred into the atmosphere; further even than sea salt aerosol, for which the equivalent lifetime is less than one week.

Once rained out it is eventually transported back to the oceans through water run-off from the land.

Global TFA Natural Cycle



"Evaporation" includes mechanical transport as aerosol as well as vaporisation.

4. What is the potential impact of TFA?

→ *In addition to run-off into the oceans, the TFA deposited on land and water has the potential to accumulate in terminal water bodies (e.g. lakes) and in plant material. Based on the relative insensitivity of aquatic organisms to TFA, predicted concentrations of TFA in terminal water bodies are not expected to impair aquatic systems significantly. The toxicity of TFA to algae, higher plants, fish, crustaceans, animals and humans has been evaluated. It was found to be of very low toxicity to all of these organisms.*

Tests have shown that mammals are not affected by TFA at concentrations many thousands of times higher than expected in the environment. With humans, some fluorinated drugs break down in the human body to form trifluoroacetate, which is rapidly excreted. Tests with fish and crustaceans show these organisms are also highly resistant to TFA. Because TFA has very low affinity for lipids (fatty materials), there is no potential for passive accumulation in fatty tissues, even after long exposure at low levels.

Microorganisms that have been tested do not actively concentrate TFA from the environment. TFA does not inhibit the growth of bacteria and most of the algae tested, even at high concentrations. The growth of one species of algae was inhibited by TFA, but only at concentrations about 1000 times above those expected in rain and snow.

AFEAS-sponsored research (see www.afeas.org) has shown that plants take up TFA through the roots as well as through leaf surfaces. Trifluoroacetate has no known toxicity to plants at the concentrations at which it is expected to be deposited in rain and snow. In prolonged exposure, however, at concentrations several thousands of times greater than these levels, TFA inhibits plant growth and development.

Overall the toxicity of TFA has been evaluated in stream mesocosms, algae, higher plants, fish, animals and humans. It has been found to be of very low toxicity in all of these systems.

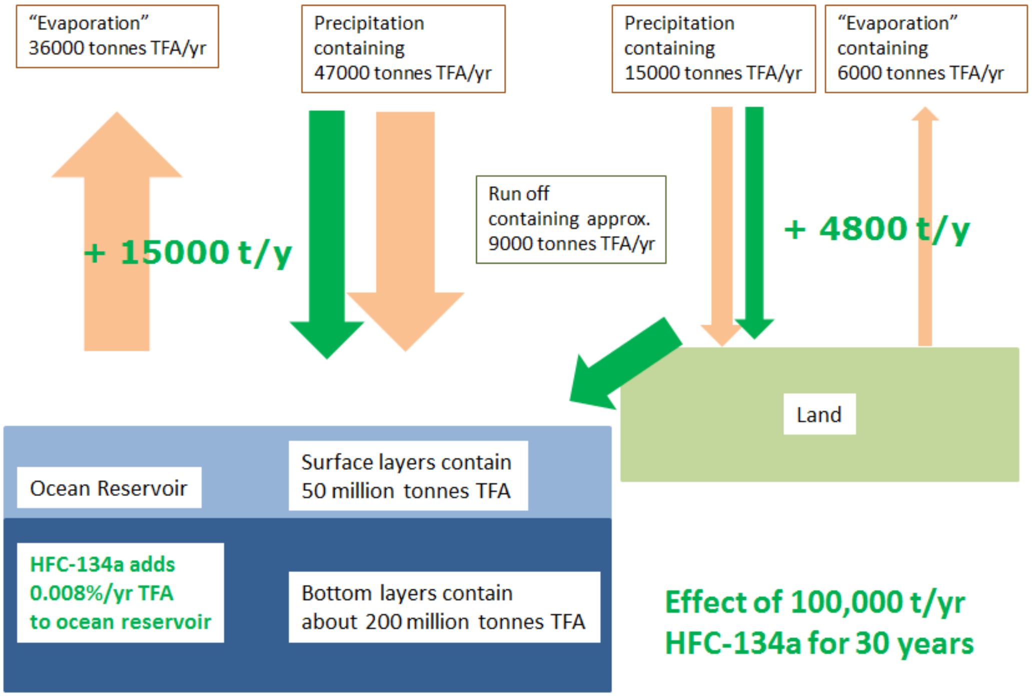
For more detailed information see:

Boutonnet J.-C, Bingham P., Calamari D., de Rooij C., Franklin J., Kawano T., Libre J.-M., McCulloch A., Malinverno G., Odom J.M., Rusch G.M., Smythe K., Sobolev I., Thompson R. and Tiedje J. M.
Environmental Risk Assessment of Trifluoroacetic Acid,
Human and Ecological Risk Assessment 5(1):59-124 (1999).

5. The contribution of some HCFCs, HFCs, HFOs to the TFA cycle

→ *Some, but not all HCFCs, HFCs and HFOs containing the CF_3-C group can breakdown to TFA in the atmosphere. The yield of TFA can vary depending on how many breakdown pathways there are. The yield of TFA from HFC-134a (the largest volume commercial HFC) is about 20%, whereas HFO-1234yf (the replacement for HFC-134a in car air-conditioning) breaks down completely to TFA.*

Effect of HFC-134a on Global TFA cycle

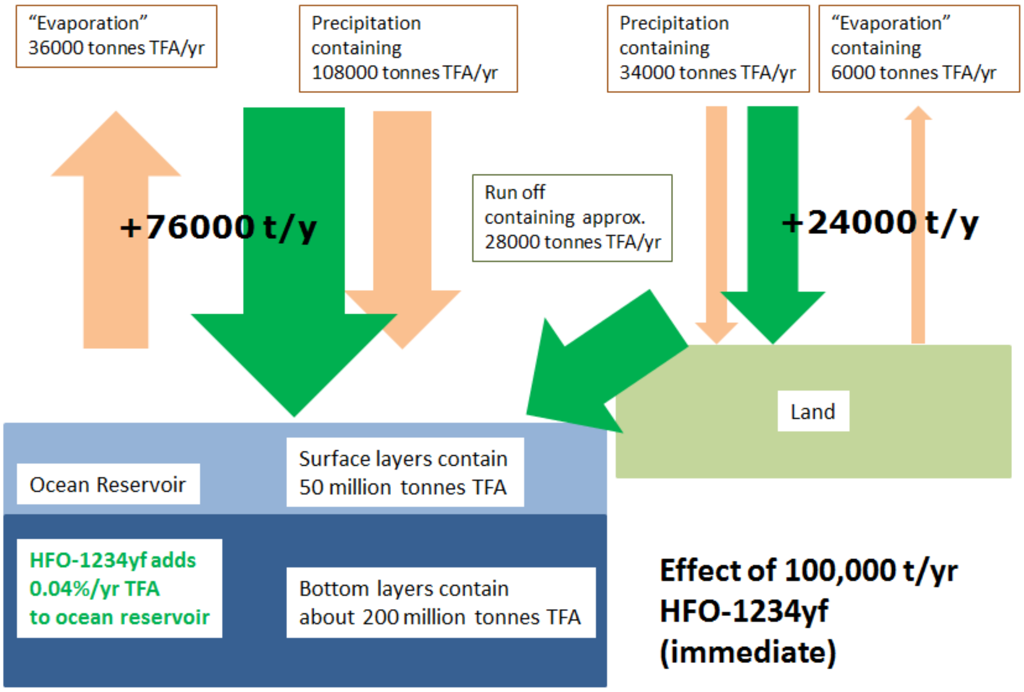


To compare HFC -134a and HFO-1234yf on the TFA cycle, emissions of 100,000 tonnes/year have been used. This is a similar to the estimated emissions of HFC-134a from mobile air-conditioning globally and HFO-1234yf is replacing HFC -134a in this application.

The effect of 100,000 tonnes /year of HFC-134a emissions on the TFA cycle can be estimated. It would increase the precipitation of TFA over the land globally by 4800 tonnes. Because of the atmospheric lifetime of HFC-134a (13.4 years), breakdown in the atmosphere is relatively slow, it takes about 30 years of continuous emissions for the atmosphere to reach a steady state (where the amounts removed by atmospheric oxidation become equal to the emissions of HFC-134a).
In contrast to HFC-134a, the atmospheric oxidation of HFO-1234yf is almost immediate (a few days) and each molecule of HFO-1234yf yields a molecule of TFA. As the molecular weights are the same, each tonne of HFO-1234yf results in one tonne of TFA. An emission of 100,000 tonnes/yr of HFO-1234yf would result in an immediate increase of 24,000 tonnes/yr of TFA deposited in precipitation to land. To allow a simple comparison to HFC-134a it has been assumed that the split between deposition to land and to the sea is not affected by the short lifetime of HFO-1234yf.

More detailed analyses have been carried out under point 6.

Effect of HFC-134a on Global TFA cycle



Effect of 100,000 t/yr HFO-1234yf (immediate)

6. What is the potential impact of TFA due to HCFCs, HFCs, HFOs?

→ *The risk from the environmental levels of TFA acid due to the continuing emissions of HCFCs and HFCs was assessed, and concluded that they do not pose a threat to the environment. Recent assessments of the potential risk from using HFO-1234yf in mobile air conditioning reached the same conclusion; that no threat is posed to the environment.*

The lowest threshold for any effects of TFA was the reversible effect on growth of one strain of algae, Raphidocelis subcapitata (formerly known as Selenastrum Capricornutum), which was seen at 0.12 mg/l. There is a 1000-fold difference between the no-effect concentration for these algae and the projected environmental levels of TFA from HFCs and HCFCs (0.0001 mg/l). Based on available data, it has been concluded that environmental levels of TFA resulting from the breakdown of alternative fluorocarbons do not pose a threat to the environment.

Recent assessments of the potential risk from using HFO-1234yf in mobile air conditioning reached the same conclusion; that no threat was posed to the environment. The anticipated TFA concentration in rainwater is expected to be much lower (generally by a factor of 1000) than the minimum concentration that has been shown to cause a biological effect.

HFC-134a degrades slowly to TFA when released to the atmosphere, whereas HFO-1234yf which is replacing it in automobile air-conditioning has a much shorter atmospheric lifetime than HFC-134a (10 days vs. 13.4 years). Switching to shorter-lived HFO-1234yf will change the geographic patterns of formation and deposition of TFA. Recent studies have modelled the use patterns for mobile air-conditioning in the USA[1], the EU[2] and Japan[3] and the deposition pattern of TFA based on rainfall and prevailing winds.

The study for the EU assessed a worst case European HFO-1234yf emission and subsequent TFA formation and distribution scenario, and the calculated TFA levels remain an order of magnitude below safe limits. Their conclusions imply that the aquatic concentrations will remain well below the no-effect level of the most sensitive algae, even in the most extensive HFO 1234yf European use conditions in mobile air conditioning.

The North American study concluded that after fifty years of emissions of HFO-1234yf, the predicted concentrations of TFA in North American surface water are likely to range between 1 and 15 µg/l, resulting in concentrations 60-1000 times smaller than the nominal ecotoxicological endpoint of 0.1 mg/l for sensitive aquatic species.

In conclusion, the accumulation of TFA in the environment can be regarded as a minor concern overall.

"........ projected future increased loadings of TFA to playas, land-locked lakes, and the oceans due to continued use of HCFCs, HFCs, and replacement products are still judged to present negligible risks for aquatic organisms and humans. "[4].

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[1] Luecken D.J., Waterland R.L., Papasavva S., Taddonio K.N., Hutzell W.T, Rugh J.P. and Andersen S.O., *Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), A Potential Greenhouse Gas Replacement*, Environmental Science & Technology 44:343–348 (2010).

[2] Henne S., Shallcross D.E., Reimann S., Xiao P., Brunner D., O'Doherty S., Buchmann B., *Future Emissions and Atmospheric Fate of HFC-1234yf from Mobile Air Conditioners in Europe*, Environmental Science & Technology 46 (3):1650-8 (2012).

[3] Kajihara H., Inoue K., Yoshida K. and Nagaosa R., *Estimation of environmental concentrations and deposition fluxes of R-1234-YF and its decomposition products emitted from air conditioning equipment to atmosphere*, Proceedings 2010 International Symposium on Next-generation Air Conditioning and Refrigeration Technology, 17-19/2/2010, Tokyo, Japan.

[4] Environmental effects of ozone depletion and its interactions with climate change: 2014 assessment.
Published as: Madronich S., Shao M., Wilson S. R., Solomon K. R., Longstreth J. D. and Tang X. Y., *Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with changing climate: implications for human and environmental health*, Photochemical & Photobiological Sciences 14:149-69 (2015).

APPENDIX HFC and HFO atmospheric breakdown and TFA formation

HFC/HFO	TFA Formation	Reference
HFC-125	No TFA formation	Edney E.O. and D.J. Driscoll, *Chlorine Initiated Photooxidation Studies of Hydrochlorofluorocarbons (HCFCs) and Hydrofluorocarbons (HFCs): Results for HCFC-22 ($CHClF_2$); HFC-41 (CH_3F); HCFC-124 ($CClFHCF_3$); HFC-125 (CF_3CHF_2); HFC-134a (CF_3CH_2F); HCFC-142b ($CClF_2CH_3$); and HFC-152a (CHF_2CH_3)*, International Journal of Chemical Kinetics 24:1067-81 (1992).
HFC-152a		
HFC-134a	Minor TFA formation (<20%)	Møgelberg T.E., Sehested J., Wallington T.J., Nielsen O.J., *Atmospheric chemistry of HFC-134a: kinetics of the decomposition of the alkoxy radical CF_3CFHO*, International Journal of Chemical Kinetics 29:209-17 (1997). Wallington T.J., Hurley M.D., Fracheboud J.M., Orlando J.J., Tyndall G.S., Sehested J., Møgelberg T.E. and Nielsen O.J., *Role of excited CF_3CFHO radicals in the atmospheric chemistry of HFC-134a*, Journal of Physical Chemistry 100(46):18116-22 (1996).
HFC-143a	No TFA formation	Nielsen O.-J., Gamborg E., Sehested J., Wallington T.J. and Hurley M.D., *Atmospheric chemistry of HFC-143a: Spectrokinetic investigation of the $CF_3CH_2O_2$ radical, its reaction with NO and NO_2 and the fate of CF_3CH_2O*, Journal of Physical Chemistry 98:9518-25 (1994).
HFC-227ea	TFA formation (100%)	Møgelberg T.E, Sehested J., Bilde M., Wallington T.J. and Nielsen O.-J., *Atmospheric Chemistry of CF_3CFHCF_3 (HFC-227ea): Spectrokinetic Investigation of the $CF_3CFO_2 \bullet CF_3$ Radical, its Reactions with NO and NO_2, and Fate of the $CF_3CFO \bullet CF_3$ Radical*, Journal of Physical Chemistry 100, 8882-9 (1996).
HFC-236fa	No TFA formation	Møgelberg T.E., Platz J., Nielsen O.-J., Sehested J. and Wallington T.J., *Atmospheric Chemistry of HFC-236fa: Spectrokinetic Investigation of the $CF_3CHO_2{*}CF_3$ Radical, its Reaction with NO, and the Fate of the $CF_3CH \bullet CF_3$ Radical*, Journal of Physical Chemistry 99:5373-8 (1995).
HFC-365mfc	No TFA formation	Wallington T.J. and O.-J. Nielsen, *Atmospheric Photooxidation of Gas Phase Air Pollutants*, in: Environmental Photochemistry Part II, The Handbook of Environmental Chemistry Volume 2M, 119-160, Springer-Verlag, Heidelberg, (2005).
HFC-43-10mee	Minor TFA formation	
HFO-1234yf	TFA formation (100%)	Hurley M.D., Wallington T.J., Javadi M.S. and Nielsen O.-J., *Atmospheric chemistry of $CF_3CF{=}CH_2$: Products and mechanisms of Cl atom and OH radical initiated oxidation*, Chemical Physics Letters 450:263–267 (2008).
HFO-1234ze	No TFA formation	T.J. Wallington, M. P. Sulbaek Andersen, O. J. Nielsen, Atmospheric Chemistry of Short-Chain Haloolefins: Photochemical Ozone Creation Potentials (POCPs), Global Warming Potentials (GWPs), and Ozone Depletion Potentials (ODPs), Chemosphere, 129, 135, 2015over many
HFO-1225ye	TFA formation (100%)	Hurley M.D., Ball J. C. and Wallington T. J., Atmospheric Chemistry of the Z and E Isomers of $CF_3CF{=}CHF$; Kinetics, Mechanisms, and Products of Gas-Phase Reactions with Cl Atoms, OH Radicals, and O_3, Journal of Physical Chemistry A 111(39):9789 -95 (2007).

The European FluoroCarbon Technical Committee is a Cefic Sector Group that monitors the constantly changing legislation related to HFCs (hydrofluorocarbons), PFCs (perfluorinated carbons) and SF_6 (sulphur hexafluoride), CFCs (chlorofluorocarbons), HCFCs (hydrochlorofluorocarbons), in the EU and at global level.
Fluorocarbons are used as feedstock, as refrigerants, as solvents and as blowing agents for insulation plastic foams.