

The potential dangers of TFA

There is a number of concerns regarding the safety of HFO refrigerants, including their flammability, potential of hydrogen fluoride formation and formation of trifluoroacetic acid (TFA). In our previous publications we discussed some of these concerns, however the problem of TFA formation was not discussed in detail. This article will therefore focus on TFA formation and its possible effect on environment.

What is TFA?

TFA is short for trifluoroacetic acid, $\text{CF}_3\text{C}(\text{O})\text{OH}$ (Figure 1),- the simplest perfluoroorganic acid available. It is characterized by strong acidity, high dielectric constant, miscibility with water and most organic solvents and relatively low boiling point. Due to its properties it is widely used in organic synthesis as a solvent, catalyst and reagent. Many chemical transformations should be done with the aid of TFA, including rearrangements, functional group deprotections, oxidations, reductions, condensations, hydroarylations and trifluoromethylations [1] [2]

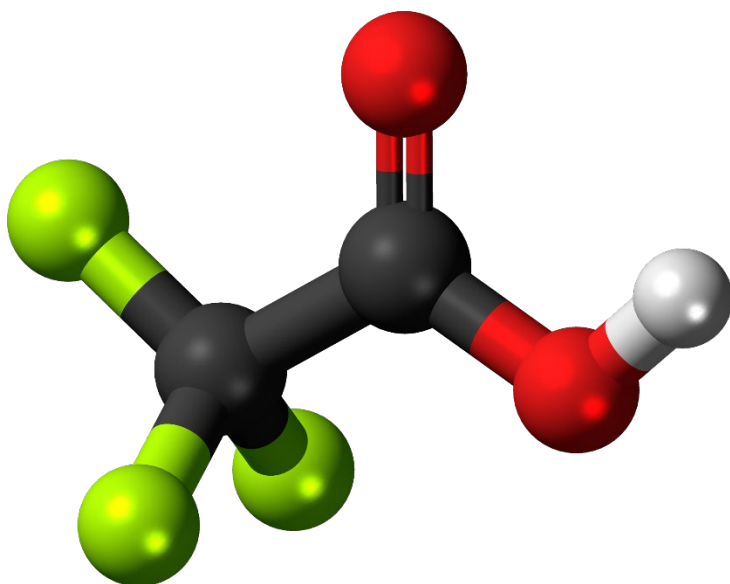


Figure 1 - Molecule of trifluoroacetic acid, TFA, $\text{CF}_3\text{C}(\text{O})\text{O}$ (colour codes: carbon, C: black; hydrogen, H: white; oxygen, O: red; yellow-green: fluorine, F)

Sources of TFA

It is well established that TFA is a globally occurring component of the environment, but uncertainties remain regarding its natural and anthropogenic sources [3]. On one hand, environmental releases of TFA associated to its industrial use are said to be very low [4]. In addition to that, it is also formed from the breakdown of a number of halogenated hydrocarbons, including HFC-134a, HFC-245fa, HFO-1234ze(E), HFO-1234yf [3]. On the other hand, the levels currently existing in the environment cannot be accounted for solely based on anthropogenic sources and imply a long-term, possibly pre-industrial source [4].

The atmospheric degradation of (saturated and unsaturated) HFCs is initiated by their reaction with OH radicals or O_3 , (important only for unsaturated HFCs). The oxygenated products from these reactions are

removed from the atmosphere via deposition and washout processes and may accumulate in oceans, lakes, and other reservoirs.

Hence, TFA - a potential toxic by-product of the atmospheric degradation of fluorocarbons - is removed from the atmosphere by wet deposition and is known to accumulate in certain ecosystems. However, much uncertainty remains in understanding the processes involved in maintaining measured abundances of TFA in today's aquatic environments. While no traces of TFA have been found in the deep ice layers of Greenland (which indicates that there exists no natural source of TFA in fresh water or in the atmosphere) [5], average TFA concentrations in deep ocean waters are above estimated anthropogenic sources thus suggesting natural sources in the ocean [3], probably formed during the eruption of deep-sea volcanoes [5].

Environmental risks of TFA

TFA is a strong acid that is highly resistant to both microbial oxidative and reductive degradation. While biodegradation of TFA has been observed under specific conditions, the relevance of these results to the real world are considered to be doubtful [4]. Therefore it may accumulate on soil, on plants, and in aquatic ecosystems over time and that may have the potential to adversely impact plants, animals, and ecosystems [6]. Overall, TFA has been found to be of very low toxicity in many cases, including algae, higher plants, fish, animals and humans [4]. It was suggested that the health effects caused by the direct inhalational exposure of R-1234yf in atmosphere can be ignored [7].

The lowest threshold for any effects was the reversible effect on growth of one strain of algae, *Selenastrum capricornutum*, which was seen at 0.12 mg/L of sodium trifluoroacetate (corresponds to 0.1 mg/L of TFA). Therefore the concentration of 0.1 mg/L is widely considered as safe concentration and used for comparison in a number of studies [4] [7]. The toxicity limits for other plants and organism have been evaluated using sodium trifluoroacetate [4] and show generally lower toxicity of TFA on a number of species.

Table 1 - Ecotoxicity of sodium trifluoroacetate [4]

	Lowest observed effect concentration	No observed effect concentration
Aquatic organisms		
<i>Selenastrum capricornutum</i> (freshwater green alga)	0.36 mg/l	0.12 mg/L
<i>Phaeodactylum tricornutum</i> (marine alga)		> 117 mg/L
<i>Lemna gibba</i> (duckweed)	600 mg/L	300 mg/L
Terrestrial plants		
Wheat (soil application/root exposure)	10 mg/kg	1 mg/kg
Sunflower (soil application)	1 mg/kg	< 1 mg/kg
Rice (foliar application)		100 mg/l

HFOs can become the main source of TFA

It is estimated that 7-20% of HFC-134a emissions degrades into TFA. In contrast, HFO-1234yf that replaces HFC-134a in many applications reacts much faster and completely decomposes into TFA [3]. It should be noted, that decomposition is not similar for all HFOs, as for instance less than 10% of HFO-1234ze(E) decompose into TFA [6].

Previous studies have predicted the anthropogenic TFA concentrations well within the safe levels, being 1000 times lower than the lowest threshold of 100 µg/L [4]. The studies took into account the emissions of HFCs with generally long lifetimes and therefore assumed that the decomposition takes place after the substances have become well mixed in the atmosphere. Even considering that R1234yf will replace R134a in all mobile air conditioning systems in US, the TFA rainwater concentrations will average at values of 0.89 µg/L and peak at 7.8 µg/L which are still below the safety limit [8].

Considering recent actions to reduce the use of HFCs, it can be expected that the amounts of HFO refrigerant or HFO containing blends will increase in future and replace HFCs in some applications. Several studies therefore predicted TFA levels associated with the replacement of HFC-134a refrigerant with HFO-1234yf. The studies predict peak TFA levels of 1.26-1.70 µg/L that are 60-80 times lower than accepted safe level [6] [9]. The difference of these results compared to the previous study can be explained by much lower lifetime of HFO-1234yf (16.4 days) compared to HFC-134a (13.4 years) that leads to the spatially variable degradation products with more localized peaks and less global transport when compared HFO-1234yf to HFC-134a.

Still, these results can be considered as underestimated as they do not take into account widespread use of HFO-1234yf in other than MAC applications, which gains popularity as a component of many refrigerant blends. Also, considering the TFA concentration variations caused by seasonal precipitation patterns and the possibility that TFA will accumulate in some closed aquatic systems after deposition the ratio between the estimated concentration in surface water and safe concentration limit for aquatic ecotoxicity appears not to be sufficiently large [7].

Overall, preliminary analyses indicate that global replacement of HFC-134a in MAC systems with HFO-1234yf at today's level of use is not expected to produce harmful levels of TFA. But given the use of HFO-1234yf beyond MAC sector, and potential TFA formation from some other HFOs, the potential TFA toxicity to ecosystems is still an open question.

References

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