Naturally Occurring TFA

The evidence is that TFA occurs naturally in the environment

The evidence is clear and irrefutable that TFA occurs naturally in large quantities in the environment. Over 200 million tonnes are present in the oceans, both coastal and deep-ocean seawater, having apparently accumulated over many million years from chemical reactions in or around sub-sea volcanic vents. The occurrence of other fluorinated organic substances that occur naturally is also well established, for example CF_4 is naturally present in granites and fluorites in the continental crust.

Norwegian Environment Agency, 2017, Study on Environmental and Health Effects of HFO Refrigerants, Norwegian Environment Agency Report No. No. M-917|2017, Oslo, Norway.

"Hydrothermal vents are suggested as one of the natural sources of TFA in the oceans with data indicating that a large amount of the TFA salts in the ocean are from natural rather than anthropogenic sources (Solomon et al, 2016[1]). It has been suggested that more than 95% of the TFA salts found in the oceans are naturally produced (UNEP EEAP, 2014[2])."

Oceans

"The concentrations of TFA in the Mid-Atlantic and the Southern Ocean off Elephant Island were all close to 200 ng a.e./L [footnote 1] at depths ranging from the surface to 4150 m. Those measured at various depths in the Western and Eastern Arctic, North Atlantic, and North and South Pacific were all ≤200 ng a.e./L and some were as low as 1 ng a.e./L. To conclude, a value of 200 ng a.e./L is considered to be a representative value for TFA concentrations in the oceans (Solomon et al, 2016[1] and references therein)."

IPCC/TEAP Special Report: Safeguarding the Ozone Layer and the Global Climate System 2005 Chapter 2: Chemical and Radiative Effects of Halocarbons and Their Replacement Compounds pages 154-155

"TFA has been observed in varying concentrations in surface waters (oceans, rivers and lakes) and in fog, snow and rain-water samples around the globe, for example, in the USA, Germany, Israel, Ireland, France, Switzerland, Austria, Russia, South Africa and Finland (see references in Nielsen et al., 2001[3]). TFA appears to be a ubiquitous component of the contemporary hydrosphere. TFA is reported in concentrations of about 200 ng/L in ocean water down to depths of several thousand meters (Frank et al., 2002[4]). If 200 ng/L is the average concentration of TFA in all ocean water, the oceans contain around 3*108 t of TFA *(note Frank estimated 268 million tonnes, more recently described as over 200 million tonnes).* **With an anthropogenic contribution of 10,266 t/yr [footnote 2] it would have taken approximately 3400 years to achieve the present TFA concentration in ocean waters; therefore, industrial sources cannot explain the observed abundance of TFA in ocean water.** High TFA concentrations in the Dead Sea and Nevada lakes, of 6400 ng/L and 40,000 ng/L, respectively, suggest long-term accumulation over centuries and the existence of pre-industrial sources of TFA (Boutonnet *et al.*, 1999[5]). However, TFA was not found in pre-industrial (>2000 years old) fresh water taken from Greenland and Denmark (Nielsen *et al.*, 2001[3]). Therefore, although it appears that there is a significant natural source of TFA, the identity of this source is unknown."

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1   **Explanatory note on units:** a.e. is TFA acid equivalent as the TFA is present in the oceans as salts. Other extracts do not state a.e. but this can be assumed. ng L-1, ng l-1 ng/L and ng/l are all used in different sources quoted but this has been standardised here to ng/L, except in the table reproduced from the Boutonnet Risk Assessment.

2   The anthropogenic contribution, for example from HFC-134a, can be calculated from the atmospheric concentration of HFC-134a in a given year and its annual decomposition rate to TFA.

"TFA is a ubiquitous natural component of the hydrosphere, with many sources beyond the halocarbons controlled under the Montreal Protocol (e.g., Scheurer et al., 2017[6]). It is present in ocean water, even at great depths and in remote locations, at a concentration of approximately 200 ng /L (Solomon et al., 2016[1]). In surface freshwater, TFA levels are typically 10–300 ng/L. TFA is stable in the environment and accumulates in terminal water bodies such as salt lakes. TFA levels in the Dead Sea have been reported to be 6,400 ng/L (Boutonnet *et al.*, 1999[5]). Currently, the oxidation of HFC-134a makes the largest contribution from ODS replacements to TFA formation. The global background atmospheric concentration of HFC-134a is approximately 100 ppt. Assuming a 7–20% molar yield of TFA (Wallington *et al.*, 1996[7]), rainout as the sole atmospheric fate of TFA, and annual global precipitation of 5 x 1017 liters Warneck and Williams (2012[8]) give an estimate of 20–50 ng/L for the current average TFA concentration in global precipitation [footnote 3] resulting from HFC-134a degradation. Local concentrations will be higher or lower than the global average depending on local precipitation volumes and photochemical activity. **The concentrations of TFA observed in rainwater typically substantially exceed those that can be accounted for by HFC-134a degradation, indicating the presence of significant sources other than HFC degradation** (Frank *et al.*, 1996[9]; McCulloch and Lindley, 2003[10]; Wu *et al.*, 2014a, b[11,12])."

Historical perspective from the 1990s

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

"According to Elliott (1994)[13], trifluoroacetic acid is manufactured by only three companies." "The quantities involved are relatively small — of the order of 1000 metric tons per year."

"Industrial use is limited and environmental releases are very low. Some additional TFA will be formed from the breakdown of a few halogenated hydrocarbons, most notably HFC-134a (CF_3CH_2F), HCFC-124 (CF_3CHFCl), and HCFC-123 (CF_3CHCl_2). **As these substances have only been produced in limited commercial quantities, their contribution to environmental levels has been minimal.** Surprisingly, environmental measurements in many of diverse locations show existing levels of 100 to 300 ng/L in water with one site (Dead Sea) having a level of 6400 ng/L. These levels cannot be accounted for based on current atmospheric sources and imply a long-term, possibly pre-industrial source."

"Environmental trifluoroacetate can also be produced during the oxidation of several organofluorine compounds released to the atmosphere by human activities. Halothane and isoflurane anaesthetics, which have been in use since the 1970s, yield trifluoroacetate. Also, some of the fluorocarbon alternatives to CFCs decompose in the atmosphere to form trifluoroacetate (NASA, NOAA, and AFEAS, 1995[14]) and, while these sources are currently small, they could become significant in the future and merit the closer scrutiny given below."

"Concentrations of trifluoroacetate observed in the air, in precipitation and in surface waters in Europe are several orders of magnitude larger than the known source fluxes would allow (Frank *et al.*, 1996[9]). Similar concentrations have been observed in contemporary water and air samples from Nevada, USA; Canada; Australia and South Africa (Zehavi and Seiber, 1996[15]; Frank and Klein, 1997[16]; Grimvall *et al.*, 1997[17]), suggesting that there is one or more large unknown source of environmental trifluoroacetate. The sizes of the fluxes of the known source gases are not in doubt; their concentrations calculated from estimated emissions are consistent with observations, and additional contemporary sources, substantially larger than those known, must be invoked to explain the observed environmental concentrations of trifluoroacetate."

"Surface water in and around Reno, Nevada, showed far higher concentrations of trifluoroacetate using a comparable, but different, analytical method (Zehavi and Seiber, 1996[15]). The highest concentration that was recorded exceeded that in the Dead Sea (Frank *et al.*, 1996[9]) by a factor of 6. **In both cases, if the samples of the receiving waters and the rivers feeding them are representative, accumulation over many hundreds of years would be necessary to account for the observations."**

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3   The concentrations of TFA in global precipitation (eg rain) cannot be related to the absolute concentration found in the oceans; TFA can be transported to the atmosphere by sea spray aerosol and then precipitated (see the section on this subject). The global precipitation in 2012 is estimated as 5 x 1017 litres (*reference 8*) and the volume of water in the oceans is estimated as 1.33 billion km[3] (https://oceanservice.noaa. gov/facts/oceanwater.html), which is about 2700 times the annual global precipitation. The concentration of TFA in rainwater due to HFC-134a is calculated from the atmospheric concentration of HFC-134a in any given year, its annual decomposition rate to TFA and the global precipitation.

"The current [1990s] potential sources of trifluoroacetic acid would provide, at most, 2800 metric tons per year distributed throughout the world."

Concentrations in the oceans in the 1990s: "Table 4 shows the seawater concentrations recorded by Frank and co-workers[9,16] for samples from the Baltic and North Seas and the Atlantic and Pacific Oceans."

Boutonnet

Table 4. Seawater analyses (Frank et al., 1996; Frank and Klein, 1997).

Location	Sample date	TFA determination		
		ng·l⁻¹	n	S.D.[a]
North Sea (Husum, Germany)	7 Jul 95	90	4	17
Baltic Sea (Warnemünde, Germany)	8 Jul 95	40	3	26
N. Atlantic (Ile d'Yeu, France)	7 Sep 95	250	3	70
N. Atlantic (Mace Head, Ireland)	7 Sep 95	70	4	26
S. Atlantic (Cape Pt., South Africa)	18 Oct 95	160	3	3
S. Pacific (Noosa Heads, Australia)	22 April 96	200	3	26

[a]S.D. is the Standard Deviation of n analyses.

"While the whole of the world has not been covered by the [1990s] sampling program, it is apparent that trifluoroacetic acid is a ubiquitous contaminant of surface waters over a large part of the earth's surface. It is also present in air and rain samples and in samples of old ice."

Old Soil Samples Containing TFA

From Comparison of Haloacetic Acids in the Environment of the Northern and Southern Hemispheres B. F. Scott, C. Spencer, J. W. Martin, R. Barra, H. A. Bootsma, K. C. Jones, A. E. Johnston, and D. C. G. Muir *Environ. Sci. Technol.*, 2005, 39 (22), 8664-8670• DOI: 10.1021/es050118l

"The results for the four archived U.K. soil samples (from Rothamsted Agricultural Research Station), for the years 1865, 1881, 1944, and 1956, are shown in Table 3 [extracts of Table 3 shown below]." "Throughout the time that the samples were in the Rothamsted archive they remained sealed and they were transferred in new, cleaned containers." "No degradation of TFA would be expected given its known stability under normal environmental conditions."

TABLE 3. Concentrations of HAAs (Haloacetic acids) in Archived Samples (ng/g Dry Weight)

compound	1865	1881	1944	1956
TFA	0.51	0.55	<0.1	0.35

Transport of sea spray aerosol

The world's oceans constitute a significant TFA reservoir (estimated at over 200 Tg) and the generation of sea salt aerosol by mechanical action of wind on the sea surface is well known. It is postulated that this provides a mechanism for transportation of significant quantities of TFA over considerable distances, further even than sea salt aerosol. This represents a variable background concentration of TFA in the environment that supplements any generated by decomposition of fluorocarbons.

The EFCTC paper '*Transport of naturally occurring trifluoroacetic acid (TFA) by sea salt aerosol*' can be downloaded here.

Unexpected Contributions of Sea Spray and Lake Spray Aerosol to Inland Particulate Matter, Nathaniel W. May, Matthew J. Gunsch, Nicole E. Olson, Amy L. Bondy, Rachel M. Kirpes, Steven B. Bertman, Swarup China, Alexander Laskin, Philip K. Hopke, Andrew P. Ault, and Kerri A. Pratt; Environ. Sci. Technol. Lett., **2018**, *5* (7), pp 405–412 **DOI:** 10.1021/acs.estlett.8b00254

The transport of sea spray aerosol over long distances has been reported in this paper:

"Sea spray aerosol (SSA) and lake spray aerosol (LSA) from wave breaking contribute to particulate matter (PM) in coastal regions near oceans and freshwater lakes, respectively. However, SSA and LSA contributions to atmospheric aerosol populations in inland regions are poorly understood because of difficulties differentiating them from other inland sources when using bulk particle measurements. Herein, we show that SSA and LSA episodically contribute to atmospheric aerosol populations at a rural site in northern Michigan >700 and >25 km from the nearest seawater and Great Lakes sources, respectively."

The *1999 Environmental Risk Assessment of Trifluoroacetic Acid, Human and Ecological Risk Assessment* states that TFA was found in precipitation in remote areas in the mid-1990s, which is consistent with transport by sea spray aerosol.

"Similarly to their surface water determinations, Zehavi and Seiber (1996[15]) reported levels of TFA in rain and fog that were high but consistent with the measurements of Frank *et al.* (1996[9]). Grimvall and co-workers [17] have shown not only that TFA is widely distributed — from Arctic to Antarctic — at low concentrations, but that it was present in precipitation in the Swedish Arctic some 400 years ago. The levels in old ice from the Mårmo Glacier are similar to present day concentrations." *And* "**The significance of the discovery of low concentrations of TFA in precipitation in remote areas is that it indicates a geographically dispersed source. With an atmospheric lifetime (towards rainout) of a few weeks, it would not be possible for TFA that is generated in the northern hemisphere to be present in southern hemispherical precipitation.**"

Other related natural fluorocarbons from abiotic sources

A wide range of fluorinated compounds occur naturally in the environment, with many detected in the vents of volcanoes. Naturally Occurring Organofluorines Chapter · July 2005 DOI: 10.1007/10721878_5

"Stoiber *et al.*[18] were the first to report in 1971 the presence of organofluorine compounds, including some CFCs, in the volcanic gases from the fumaroles of the Santiaguito volcano in Guatemala. In addition to detecting methane, hydrogen fluoride, hydrogen chloride, and about 30 other organic compounds, these workers identified tetrafluoroethylene, hexafluoropropene, chlorodifluoromethane, chlorotrifluoroethylene, dichlorofluoromethane, trichlorofluoromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane. **The authors suggest that these compounds 'probably resulted from reactions of hydrocarbons with hydrogen fluoride and hydrogen chloride, inorganic halides or halide containing minerals under high temperature conditions which prevailed at the source.** The most likely sources of organic compounds are probably sediment or fossil soil layers beneath the volcano'. Unfortunately, quantitative measurements were not carried out, but the organic compounds were separated and identified by gas chromatography-mass spectrometry."

Tetrafluoromethane (CF_4) is occurs naturally in the environment. Tetrafluoromethane in the deep North Pacific Ocean Article *in* Geophysical Research Letters · July 2008 DOI: 10.1029/2008GL034355

"Since the atmospheric lifetime of CF_4 is very long, the preindustrial natural atmospheric abundance of CF_4 may be explained by relatively minor natural emissions from the solid Earth. CF_4 is naturally present in granites and fluorites in the continental crust [Harnisch and Eisenhauer, 1998[19]; Harnisch et al., 2000[20]], and Deeds et al. [2008 [21]] have shown that **CF_4 liberated by weathering and alteration is transported out of the continental lithosphere to the atmosphere by groundwater fluid flow**. If similar CF_4 emissions occur from the oceanic mantle, crust, or overlying sediments, then CF_4 would be expected to accumulate in the deep ocean, especially in the deep Pacific where water residence times are long, in a manner analogous to the accumulation of dissolved crustal and mantle helium in the deep Pacific [e.g., Lupton, 1998[22]]."

And

"The continental lithospheric flux of CF_4 to the atmosphere is estimated at $(1–5)\times10^4$ moles of CF_4 per year [Deeds et al., 2008] [21]. If an oceanic source of CF_4 exists it is therefore at most only about 4% of the continental flux, **indicating that weathering and alteration of the continental crust are the dominant sources of natural CF_4 to the atmosphere** [Harnisch and Eisenhauer, 1998 [19]]. This is consistent with the lack of detectable amounts of CF_4 in mafic rocks [Harnisch and Eisenhauer, 1998 [19]; Harnisch et al., 2000 [20]] and volcanic gases [Jordan et al., 2000 [23]; Frische et al., 2006 [24]], which suggest that neither the oceanic crust nor the mantle are significant sources of CF_4."

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