Transport of naturally occurring trifluoroacetic acid (TFA) by sea salt aerosol

Abstract: *The concentrations of trifluoroacetic acid and its salts (TFA) observed in air and rain at a time (1990s) when the introduction of TFA into the atmosphere, either directly or through decomposition of fluorocarbons was insignificant, were about two orders of magnitude larger than expected from fluorocarbon decomposition. Additional sources, substantially larger than the known anthropogenic sources, are needed to explain the historically observed environmental concentrations of trifluoroacetate in rain and surface waters. 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.*

Introduction

There is now clear evidence that trifluoroacetic acid and its salts (TFA) occurs naturally in large quantities in the environment. However, in 1991, a research programme was undertaken to determine the environmental fate of TFA in response to concerns that significant amounts would be formed in the atmospheric decomposition of some hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) that were then becoming used as replacements for chlorofluorocarbons (CFCs). This programme (Boutonnet et al., 1999) included a comprehensive analysis of the concentrations of TFA in the air, precipitation, surface waters and the oceans. The TFA concentrations measured were unexpected; a large natural reservoir of TFA had not been anticipated, having apparently accumulated over many million years from chemical reactions in or around sub-sea volcanic vents (Frank et al., 2002). Almost 300 Tg of TFA (trifluoroacetic acid and its salts) were estimated as present in the oceans (Frank et al., 1996), both coastal and deep-ocean seawater, more recently the quantity was revised to "over 200 Tg" (Frank et al., 2002), This is consistent with the wide range of fluorinated compounds that occur naturally in the environment, with many detected in the vents of volcanoes (Gribble, 2005).

The concentration of TFA in rain from known sources in the mid-1990s was calculated to be <2ng L^{-1} (Boutonnet et al., 1999). The actual TFA concentrations in rainwater, measured in the 1990s, were about two orders of magnitude larger than expected. For example, the measured concentration at Bayreuth, Germany in 1995 and 1996 averaged 100 ng L^{-1}, but the expected concentration of trifluoroacetic acid in rain from known sources was less than 1/60th of that observed (Kanakidou et al., 1995). Fog was found to have a higher concentration of TFA than rain (Zehavi and Seiber, 1996). In addition, the discovery of low concentrations of TFA in precipitation in remote areas indicated a geographically dispersed source. Snow at Queen Maud Land, Antarctica in 1996 contained 2 and 9 ng L^{-1} of TFA for different samples (Grimvall et al., 1997).With an atmospheric lifetime (towards

rainout) of a few weeks, it would not be possible for TFA that was generated in the northern hemisphere to be present in southern hemispherical precipitation.

Furthermore, the concept of a significant source unrelated to fluorochemicals use is reinforced by its presence in old soil samples. Four archived soil samples from the Rothamsted Agricultural Research Station (UK) for the years 1865, 1881, 1944 and 1956 show TFA concentrations of 0.51, 0.55, <0.1 and 0.35 ng g^{-1}, respectively (Scott et al., 2005).

There is a need to explain the, albeit variable, distribution of TFA in atmospheric precipitation and surface waters and this paper presents a suggested mechanism for transport of TFA from the sea to be deposited over land in rainfall, with subsequent return to the sea in run off through rivers.

Transport of TFA by Sea Salt Aerosol

The generation of sea salt aerosol by mechanical action of wind on the sea surface is well known. The net flux is calculated at 1785 Tg yr^{-1} of chloride ion from the marine boundary layer (Erickson et al.,1999). This is the quantity that is carried into the free troposphere and can be subsequently deposited onto the Earth's surface. Immediately in the atmosphere, the aerosol composition changes as a result of the dynamic equilibria between evaporation (of the water content and other volatile components, such as TFA) or accumulation of water and absorption of atmospheric gases that affect acidity (for example carbon dioxide, sulphur dioxide or ammonia) and dry or wet deposition of the particles. As a consequence of the chemical equilibria, 7.6 Tg yr^{-1} of HCl is calculated to be deposited on the Earth's surface (Erickson et al., 1999).

During the primary generation of the aerosol, which 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 sea. With an average salt content of 3.5% wt in seawater, the 200 ng L^{-1} TFA determined (Frank et al.,1996) would translate into a global flux of about 20 Mg yr^{-1}. However, based on the global annual rainfall, this quantity of TFA if uniformly distributed, would result in < 0.1 ng L^{-1} in rain, which is insufficient to explain the concentrations measured in the 1990s. If evaporation of TFA occurs within the marine boundary layer during generation of the aerosol, the quantity of TFA introduced into the atmosphere could be very much larger. In the 1990s the concentrations of TFA present in rainwater and run-off were about two orders of magnitude larger than the TFA to be expected from decomposition of fluorocarbons at that time (Kanakidou et al., 1995). Based on the global water cycle described (van der Leeden, 1975) and a subjective average of the measured concentrations of 100 ng L^{-1}, some 3.8 Gg yr^{-1} of natural TFA would be returned to the sea as run-off.

In the particles of sea salt aerosol, TFA is subject to the same chemical and physical influences as the chloride ion, but with arguably different outcomes. The changes in the aerosol tend to direct the chloride ion towards dry deposition in the particles and wet deposition in rain; chloride ion is not present as a vapour and the 0.4% deposited as HCl remains in the liquid phase. TFA, on the other hand, does have a small but significant vapour pressure over simulated sea salt aerosol and can partition into the gas phase. It does not react with atmospheric hydroxyl radical and is removed by dissolution in fog or rain and subsequent wet deposition (Bowden et al., 1996; Kutsunaand Hori, 2008).

Over land, it has been shown recently that the reaction of Criegee intermediates with TFA in the gas phase is extremely rapid (Chhantyal-Pun et al., 2017). Criegee intermediates are present in the atmosphere as a result of the reaction of ozone with alkenes and play an important role in atmospheric chemistry over landmasses with vegetation, where biogenic emissions of alkenes (e.g., isoprene and terpenes) are significant and ozone is available. Reactive loss of TFA via reaction with Criegee intermediates could be an important loss mechanism for TFA, and it has not been accounted for in atmospheric models of TFA deposition. Inclusion of this new gas-phase chemistry in atmospheric models could decrease the projected deposition of TFA over landmasses (by as much as a factor of two), However this does not invalidate the postulated mechanism for transport by sea salt aerosol, indeed the additional loss process augments the need for such natural transport.

The sea salt aerosol mixture of solid and liquid particles is transported up to several hundred kilometres inland and concentrations are calculated to be significantly elevated over, for example, Europe as far as Russia; Australia; the Amazon basin of Brazil and the Pacific seaboard of the USA (Sofiev et al., 2011). The concentrations of TFA observed in air and rain in Bayreuth, Germany (Frank et al,, 1996); rain at Mace Head, Ireland and Gdansk, Poland (Grimvall et al., 1997); fog at Davis and Santa Rosa, California, USA and rain at Reno, Nevada, USA (Zehavi and Seiber, 1996) are all consistent with its transport in the aerosol and accompanying air mass. The measurements were carried out at a time when the introduction of TFA into the atmosphere, either directly or through decomposition of fluorocarbons, was insignificant (Boutonnet et al., 1999).The table shows rainfall concentrations for locations about 400 km or more from the nearest coastline (from Boutonnet et al., 1999). Excluding Antarctica, 58% of land zones are within 500 km of the coast (Kummu et al., 2016).

Rainfall TFA concentrations for locations about 400 km or more from the nearest coastline

Location	Approx. distance to nearest coast	TFA concentration in rainfall ng L^{-1}	Date of analysis
Bayreuth, Germany	500 km	100 average	March 1995 to October 1996
Alpthal, Switzerland	400 km	80	September 1995
Zurich, Switzerland	400 km	50	September 1995
Reno, Nevada, USA	400 km	31, 34-37, 90	September 1994 & July 1995

Summary

The atmospheric lifetime of TFA before it is rained out is of the order of a few weeks (Boutonnet et al., 1999), meaning that TFA can be transported over considerable distances from the position where it was transferred into the atmosphere from the ocean surface; 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. Thus, there are background concentrations of TFA in the atmosphere, precipitation and surface water that augment any anthropogenic generation, such as that reported in surface water in Beijing (Wu et al., 2014). The background

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concentration has been shown to be highly variable and would depend on differences in generation of the sea salt aerosol, influenced by wind speed and temperature, differences in precipitation, with fog having a higher concentration than heavy rainfall, and differences in geographical location relative to the sea.

The European FluoroCarbons Technical Committee is a Cefic Sector Group that monitors legislation related to HFCs (hydrofluorocarbons), and HFOs (hydrofluoro-olefins) in the EU and at global level. Fluorocarbons are used as feedstock, as refrigerants, as solvents and as blowing agents for insulation plastic foams.

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