

Assessment of Possible Transport of Trifluoroacetic Acid from the Oceans to the Atmosphere

Simon L. Clegg

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Simon L. Clegg,
School of Environmental Sciences,
University of East Anglia,
NORWICH NR4 7TJ
U.K.

Contact: s.clegg@uea.ac.uk (and +44 1603 593185)

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Summary

In the *Summary Call for Tender – Transport TFA* (trifluoroacetic acid) that is included as an Appendix to this report it is stated that:

- Establishing if significant quantities of TFA can be transported from the oceans to the land may contribute to a better understanding of TFA deposition. The first step is to understand if significant quantities of TFA are transported to the troposphere from the oceans, with the potential of further transport over land.
- EFCTC would like to understand if any additional TFA can be transported from the oceans to the troposphere, in the same way that HCl is partitioned from aged sea salt aerosol to the troposphere.

For a surface seawater TFA concentration of 150 ng L^{-1} (a factor of 7.8×10^{-9} times that of Cl^-), a literature model of global chlorine cycling suggests that there would be annual flux of TFA to the atmosphere in seasalt aerosol of about 14 tonnes ($1.4 \times 10^4 \text{ kg a}^{-1}$). This is very close the EFCTC's own estimate, which is based upon a slightly higher seawater TFA concentration.

Acidification of seasalt aerosol by dissolution of HNO_3 and from oxidation of dissolved dimethyl sulphide and SO_2 to produce H_2SO_4 results in the expulsion of HCl to the gas phase through the Henry's law equilibrium. Although TFA is a weaker acid than HCl, and its concentration in the aerosol very much lower than that of Cl^- , the same mechanism can in principle apply.

In this report current knowledge of the relevant thermodynamic properties of TFA – the acid dissociation constant and Henry's law constant – is first reviewed. Calculated equilibrium partial pressures of TFA above typical seasalt aerosols over a very wide range of pH are found to be lower than ambient gas phase concentrations (a few ng m^{-3}) by a large margin, except at very low pH. These results imply that acidified seasalt aerosols will *not* be a significant contributor to gas phase TFA except under a very limited set of conditions (low relative humidity, high temperature, polluted conditions, and for the small submicron fraction of the aerosol in which high acidities can be attained, thus limiting the total displacement of TFA).

The behaviour of TFA and HCl were also compared by calculating the equilibrium gas/liquid partitioning as a function of pH and for atmospheric liquid water contents ranging from aerosols in low relative humidity (*RH*) environments to those of cloud and fogwater. The patterns are similar: at atmospheric liquid water contents and pH typical of fog and cloud water the greatest fractions of both substances (approaching 100%) are expected to be in the aqueous phase. This is consistent with them both being removed by wet deposition. Conversely, at moderately acidic and low pH, and atmospheric liquid water contents typical of aerosols, the largest fractions of both total Cl^- and total TFA per m^3 of atmosphere will be found in the gas phase. Of the two acids, TFA has the greater tendency to partition into the gas phase. The predicted balance between gas and aerosol fractions of TFA is consistent with the limited number of atmospheric measurements that have been made.

1. Introduction

Trifluoroacetic acid (TFA) is produced from the breakdown of anthropogenic halocarbons and is

ubiquitous in the environment (WMO, 2022). Brunn et al. (2023) in their review of per- and polyfluorinated alkyl substances (PFAS) summarise sources of TFA and give examples of its rising concentrations in natural waters in Europe. Trifluoroacetic acid has been measured in ocean waters (e.g., Frank et al., 2002; Scott et al., 2005) and is found at all depths. The purpose of this study is to assess whether TFA can be displaced from seasalt aerosols by dissolved acids of which the principal inorganic ones are HNO₃ and H₂SO₄ (from dissolved dimethyl sulphide and SO₂). Seasalt aerosols are generated from the surface of the oceans by wind action and breaking waves (Lewis and Schwartz, 2004), and will therefore contain TFA.

It is well established that the accumulation of nitrate (from HNO₃) and ‘non-seasalt sulphate’ (from H₂SO₄) leads to a Cl⁻ deficit in aged seasalt that is caused by the loss of HCl to the gas phase (e.g., Graedel and Keene, 1995; Su et al., 2022). Modelling of this process (Wang et al., 2019) shows enhanced HCl(g) concentrations – corresponding to HCl loss from the aerosol – chiefly in coastal polluted areas, and in the northern mid-latitudes. Thus, for example, the US east coast, the Atlantic coast of Europe, and the Mediterranean all show strongly enhanced mixing ratios of HCl. Given that TFA is also acidic, it is possible at least in principle that TFA is expelled from acidified seasalt aerosols in the same manner as HCl and therefore constitutes an additional source of gas phase TFA in these and other regions.

The possibility of displacement of TFA from seasalt aerosols is examined here from the perspective of equilibrium thermodynamics, involving consideration of: the concentrations of TFA in seasalt aerosols, aerosol pH, atmospheric liquid water content (from aerosols to cloud water), and the dissociation and Henry’s law constants of TFA that control its speciation and gas/aerosol partitioning. Comparisons are also made with the behaviour of HCl.

2. Thermodynamic properties controlling gas/liquid partitioning

Hydrochloric acid (HCl) is a conventional strong electrolyte and is treated as completely dissociated in aqueous solution. The Henry’s law equilibrium between gas phase HCl and acid solutions containing dissolved Cl⁻, is therefore described in terms of the dissolved H⁺(aq) and Cl⁻(aq) ions, and the gas phase molecule. In contrast, TFA is a weak acid and its dissociation equilibrium in aqueous solutions is treated explicitly. The appropriate Henry’s law equilibrium for TFA is between the undissociated aqueous and gas phase molecules. In the subsections below, the equations for the equilibria and equilibrium constants are presented. In section 3 the data for TFA are reviewed, and some revisions are made to the values presented in the study of Bowden et al. (1996).

2.1 Henry’s law constants

Equilibrium of a conventional strong acid, such as HCl or HNO₃, between gas and aerosol phases is described as follows:



where the equilibrium is between the gas phase molecule and dissociated aqueous ions. The corresponding expression for the Henry’s law constant $K_{\text{H}}(\text{HX})$ is:

$$K_H(\text{HX}) = a\text{H}^+ \cdot a\text{X}^- / f\text{HX}$$

where prefix a denotes activity on the appropriate scale, and $f\text{HX}$ (atm) is the fugacity of HX for which partial pressure ($p\text{HX}$) is usually substituted ($p\text{HX} \approx f\text{HX}$). The Henry's law constants of HCl and HNO₃ are well known, over very wide ranges of temperature (e.g., Carslaw et al., 1995). The activities of the solute species of an aqueous solution are equal their molalities (or mole fractions, or molarities) multiplied by their activity coefficients on the appropriate scale (e.g., Robinson and Stokes, 1970). In the work of Bowden et al. (1996) molalities – moles per kg of pure water solvent – are used so that:

$$a\text{H}^+ = m\text{H}^+ \cdot \gamma\text{H}^+, \text{ and } a\text{X}^- = m\text{X}^- \cdot \gamma\text{X}^- \quad (3)$$

where prefix m denotes molality, and γ is the activity coefficient of the indicated species. Activity coefficients are a measure of the non-ideality of aqueous solutions and are unity by definition for the state of infinite dilution. In the highly concentrated solutions encountered in soluble atmospheric aerosols at moderate to low ambient relative humidities the values of γ can be very different from 1.0 and are estimated using models (e.g., Wexler and Clegg, 2002); Tong et al., 2008).

For TFA and other weak acids, the gas/liquid equilibrium is expressed in terms of the gas phase molecule and the undissociated dissolved acid, so that:



and:

$$K_H'(\text{CF}_3\text{COOH}) = a\text{CF}_3\text{COOH} / p\text{CF}_3\text{COOH} \quad (4\text{b})$$

where $K_H'(\text{CF}_3\text{COOH})$ (mol kg⁻¹ atm⁻¹) is the Henry's law constant of TFA. The prime is used in the symbol K_H' to distinguish it from the form of the constant in the strong acid case. Values of $K_H'(\text{CF}_3\text{COOH})$ were determined experimentally by Bowden et al. (1996), and more recently by Kutsuna and Hori (2008) and are discussed further below.

2.2 The dissociation constant of trifluoroacetic acid

The gas/liquid partitioning of weak acids such as TFA is affected by their degree of dissociation in the aqueous solution. The dissociation reaction of TFA, and the corresponding constant (K_a / mol kg⁻¹) is given by:



$$K_a = a\text{H}^+ \cdot a\text{CF}_3\text{COO}^- / a\text{CF}_3\text{COOH} \quad (5\text{b})$$

2.3 Solubility relationships

The expressions for the equilibrium between gas phase trifluoroacetic acid and the total dissolved acid are given by Bowden et al. (1996) (their section 3.2) and yield:

$$p\text{CF}_3\text{COOH} = m\text{CF}_3\text{COOH}(\text{T}) / [(1 + K_a^*/m\text{H}^+) \cdot K_H'^*] \quad (6)$$

where $CF_3COOH_{(T)}$ is the total acid in the aqueous phase ($CF_3COOH(aq)$ plus $CF_3COO^-(aq)$), and superscript * indicates that the equilibrium constant is a stoichiometric value, which includes the influence of the activity coefficients, hence:

$$K_a^* = K_a \cdot \gamma_{CF_3COOH} / (\gamma_{H^+} \cdot \gamma_{CF_3COO^-}) = (m_{H^+} \cdot m_{CF_3COO^-}) / m_{CF_3COOH} \quad (7)$$

$$K_H'^* = K_H' / \gamma_{CF_3COOH} = m_{CF_3COOH} / p_{CF_3COOH} \quad (8)$$

There does not appear to be any information concerning the values of the activity coefficients of CF_3COOH or CF_3COO^- in aqueous solutions, and all the calculations of gas/liquid partitioning carried out by Bowden et al (1996) assumed values of unity for these species and for H^+ . (This will not lead to any inaccuracy for rain, cloud, and fogwater in which the solutes are very dilute.) The same approach is adopted here.

3. Values of the dissociation and Henry's Law constants of trifluoroacetic acid

The assessment of the pK_a of the acid by Bowden et al. (1996) was based on the literature available at the time, and the most recent reference was Strehlow and Hildebrandt (1990). There does not appear to have been any new work since that date, but searches did find the study of Milne and Parker (1981) which was not considered by Bowden et al. (1996) or by Strehlow and Hildebrandt (1990). The value of the pK_a of CF_3COOH (0.47, invariant with T) adopted by Bowden et al. is a weighted mean of the dissociation constants of Henne and Fox (1951), Kurz and Farrar (1969), and Strehlow and Hildebrandt (1990). The very low quoted uncertainty in the value of Kurz and Farrar (± 0.037 for $K_a = 0.302$) compared to those for the other sources ($K_a = 0.588$ (assumed uncertainty ± 0.1) from Henne and Fox; $K_a = 0.61 \pm 0.25$ from Strehlow and Hildebrandt) causes the mean value of $0.342 \text{ mol dm}^{-3}$ to be close to the Kurz and Farrar value. It now appears that this may be too low.

Milne and Parker (1981) obtained K_a equal to $0.980 \pm 0.003 \text{ mol dm}^{-3}$ (0°C) and $0.650 \pm 0.002 \text{ mol dm}^{-3}$ (25°C) by molar conductivity (see their Table II). They also obtained $1.05 \pm 0.15 \text{ mol dm}^{-3}$ (0°C) from freezing point measurements, although this value appears rather dependent upon assumptions made in the analysis. Milne and Parker discuss other work, and suggest reasonable agreement with their own values. They did not consider the results of Kurz and Farrar (1969) or Henne and Fox (1951).

Bowden et al. (1996) assumed a pK_a that was invariant with temperature because of a lack of consistent values in the literature. This has not really changed. The first two values of Milne and Parker (1981) quoted above together yield a value of ΔH_r of $-11.1 \text{ kJ mol}^{-1}$. This is not in agreement with the work of Kurz and Farrar who found K_a to be essentially invariant with T . Ives and Pryor (1955) obtained ΔH_r of $-0.468 \text{ kJ mol}^{-1}$ for CH_3COOH and $-5.816 \text{ kJ mol}^{-1}$ for CFH_2COOH .

In conclusion, it appears possible that the value of K_a at 25°C is higher than assumed by Bowden et al. (1996), perhaps by a factor of two (to the value of 0.65 mol dm^{-3} of Milne and Parker, 1981). The value of ΔH_r appears to be small and negative, perhaps about -11 kJ mol^{-1} if the K_a values of Milne and Parker are accurate.

Bowden et al (1996) obtained $K_H'(CF_3COOH)$ equal to $(8.95 \pm 0.1) \times 10^3 \text{ mol kg}^{-1} \text{ atm}^{-1}$ at 25°C for a best estimate of the pK_a of the acid of 0.47 from literature data. The enthalpy change for the Henry's

law equilibrium (ΔH_r) was found by Bowden et al. to be -77.6 ± 0.42 kJ mol⁻¹. Because of the nature of the experiments used to determine K_H' (CF₃COOH) there is some dependence upon the value of the pK_a that is adopted. An equation for this dependency, at 25 °C, is given in Table 2 of Bowden et al.

Kutsuna and Hori (2008) also measured K_H' (CF₃COOH) and obtained the smaller value of 5800 ± 700 mol dm⁻³ atm⁻¹ at 25 °C, and ΔH_r equal to -34.2 ± 0.2 kJ mol⁻¹. The method used involved the passage of a gas stream through CF₃COOH test solutions (for equilibration) followed by dissolution of the gas phase acid in aqueous alkali solution and chromatographic analysis to obtain the CF₃COO⁻ concentration and hence partial pressure of the acid in the gas stream. The concentrations of undissociated acid and CF₃COO⁻ in the test solutions were obtained by infra-red spectroscopy.

Can the Henry's law constants of Bowden et al. and Kutsuna and Mori be reconciled? If the K_a of the acid is assumed to be equal to the value of Milne and Parker at 25 °C (hence $pK_a = 0.187$) then the equation relating the experimental K_H' of Bowden et al. to the assumed pK_a of the acid yields a value of 5626 mol kg⁻¹ atm⁻¹, in good agreement with Kutsuna and Hori. The effect of this change in assumed pK_a on ΔH_r is negligible, as it results in a similar shift in K_H' at all T . Bowden et al. (1998) have collected the results of all their measurements of the K_H' of haloacetic acids and their ΔH_r for the Henry's law reaction range from -57.1 to -85.2 kJ mol⁻¹. It is possible that the magnitude of the ΔH_r obtained by Kutsuna and Hori is too low. The revised K_H' of Bowden et al. (1996) at 25 °C (5626 mol dm⁻³ atm⁻¹), combined with ΔH_r of -77.6 kJ mol⁻¹ yields a Henry's law constant of 9.87×10^4 at 0 °C. The equivalent values of Kutsuna and Hori yield K_H' equal to 2.04×10^4 , a factor of 4 difference in the solubility at this temperature.

Table 1. Thermodynamic properties of CF₃COOH and HCl that govern gas/liquid partitioning

CF ₃ COOH		Notes
K_a (25 °C) = 0.65 mol dm ⁻³	$\Delta H_r^\circ = -11.2$ kJ mol ⁻¹	a
K_H' (25 °C) = 5625 mol dm ⁻³ atm ⁻¹	$\Delta H_r^\circ = -77.6$ kJ mol ⁻¹	b

HCl		Notes
K_H (25 °C) = 2.038×10^6 mol ² kg ⁻² atm ⁻¹	$\ln(K_H) = 4.6187 + 5977.5014/T - 0.034017$	c

Notes: for the calculations carried out here the unit moles dm⁻³ (molarity) is treated as being equivalent to moles kg⁻¹ (of pure water, molality).

a – This 25 °C value of the dissociation constant, an ΔH_r° from obtained from the measured K_a of Milne and Parker (1981), their Table II.

b – From Bowden et al. (1996), for an assumed K_a of 0.65 mol dm⁻³, using the equation in the note to their Table 2.

c – From Clegg and Brimblecombe (1990), their Table II. This simplified expression yields results very close to the evaluation of Carslaw et al. (1995).

In conclusion, the study of Milne and Parker (1981) suggests that the dissociation constant of CF₃COOH should be greater than adopted by Bowden et al. (1996), equal to 0.65 mol dm⁻³ instead of 0.339 mol dm⁻³ ($pK_a = 0.47$). The variation of this constant with temperature remains uncertain. If

the greater value of the dissociation constant at 25 °C is accepted then the revised K_H' from the data of Bowden et al. is in excellent agreement with the study of Kutsuna and Hori (2008) at 25 °C. However, enthalpy changes for the Henry's law reaction differ by a factor of two, which makes a large difference to the Henry's law constants at the lower temperatures which will often be of interest when calculating partitioning in the atmosphere.

Recommended values of both equilibrium constants are given in Table 1, together with an expression for the Henry's law constant of HCl which is used in calculations later in this report.

4. Trifluoroacetic acid partitioning in the atmosphere, and comparisons with HCl

The likelihood of TFA being displaced from seasalt aerosols by other acids, and its fate in the atmosphere, can be determined by answering the following questions:

- What would be the equilibrium partial pressures of TFA above acidified seasalt aerosols in equilibrium with typical atmospheric RH , and how do these compare with ambient partial pressures of TFA already in the gas phase?
- How would total TFA (gaseous + soluble particulate) partition between gas and aqueous phases in the atmosphere as a function of pH, and for atmospheric liquid water contents ranging from those typical of aerosols under low RH conditions to those of cloud and fogwater?

4.1 Equilibrium partial pressures of TFA above acidified aerosols compared with ambient concentrations

The concentration of TFA in surface seawater (from which seasalt aerosol is generated) is first required. Trifluoroacetic acid concentrations have been measured by Frank et al. (2002) to be about 200 ng L⁻¹ in the mid-Atlantic and Southern oceans (invariant with depth). Later Scott et al. (2005) measured concentrations in the Arctic, Atlantic and Pacific oceans. Their work shows much greater heterogeneity, consistent with internal ocean sources. Except for the profile measured in the South Pacific, where the concentrations were about 10 ng L⁻¹ or lower, those close to the surface are all of the order of 150 ng L⁻¹ or so (their Figure 2). For these calculations a value of 150 ng TFA L⁻¹ (1.316 nmol L⁻¹) is assumed. The small adjustment to molality-based units (moles per kg of pure water) is ignored, and in the calculations presented here a TFA molality of 1.316×10⁻⁹ mol kg⁻¹ is used.

In an atmosphere of 80% RH the concentrations of the dissolved salts, including TFA, in an aqueous seasalt aerosol are increased by a factor of 7 (relative to salinity 35 seawater), to bring the water activity to equilibrium with the RH . This yields a total TFA molality of 9.2×10⁻⁹ mol kg⁻¹. The equilibrium partial pressure of TFA above the aerosol is related to the total molality, and to the aerosol pH by:

$$pCF_3COOH = mCF_3COOH_{(T)} / [(1 + K_a^*/10^{-pH}) \cdot K_H'^*] \quad (9)$$

where 10^{-pH} is equal to the molality (mH^+) of H⁺ ion in the aqueous aerosol. In the table below are listed calculated pCF_3COOH , and the equivalent in ng m⁻³, for a range of pH at 15 °C and 25 °C:

Table 2. Equilibrium partial pressures of TFA (p_{TFA}) above acidified seasalt aerosol at 80% RH

pH	15 °C		25 °C	
	p_{TFA} (atm)	TFA(g) (ng m^{-3})	p_{TFA} (atm)	TFA(g) (ng m^{-3})
0.0	3.1×10^{-13}	1.5	9.9×10^{-13}	4.8
0.5	1.6×10^{-13}	0.78	5.4×10^{-13}	2.6
1.0	6.4×10^{-14}	0.31	2.2×10^{-13}	1.1
1.5	2.2×10^{-14}	0.11	7.6×10^{-14}	0.37
2.0	7.2×10^{-15}	0.035	2.5×10^{-14}	0.12
3.0	7.2×10^{-16}	0.0035	2.5×10^{-15}	0.012
4.0	7.2×10^{-17}	3.5×10^{-4}	2.5×10^{-16}	0.0012
5.0	7.2×10^{-18}	3.5×10^{-5}	2.5×10^{-17}	1.2×10^{-4}

The calculated partial pressures of TFA are higher, by a factor of 3, at 25 °C. They can be compared with the measured values of gaseous TFA at various locations of only a few ng m^{-3} at most. For example, Zehavi and Seiber (1996) determined total airborne concentrations of TFA of 0.7 to 3.3 ng m^{-3} in Reno, Nevada; and Jordan and Frank (1999) report TFA levels in air of 0.045 to 0.065 ng m^{-3} in Bayreuth, Germany. They cite similar concentrations found in South Africa, Switzerland, and another and site in Germany. Martin et al. (2003) measured total TFA of <0.5 to about 5 ng m^{-3} in southern Ontario over a period of a year, although most values did not exceed 2 ng m^{-3} . The mean mass fraction of TFA in the gas phase in Guelph was found by Martin et al. to be 71%. Total atmospheric concentrations of TFA in Beijing, determined by Wu et al. (2014), were found to be $1.55 \pm 0.56 \text{ ng m}^{-3}$ over the course of a year, with about 85% residing in the gas phase.

The above measured values are only matched or exceeded by the calculated values at extremely low pH: no greater than 1.0 or 1.5 for a TFA gas phase concentration approaching 1 ng m^{-3} at 25 °C, and even lower for the several ng m^{-3} likely needed to exceed ambient concentrations and so cause a flux from the aerosol to the gas phase. What pH values can be attained in acidified seasalt aerosols? The review of atmospheric acidity of Pye et al. (2020) indicates that the pH attained in sea spray aerosols is of the order of 3 to 3.5 (very low values only occurring for fine acid sulphate – organic aerosols). The work of Angle et al. (2021), on the acidity of sea spray aerosol, show that a pH of 3.5 is typical of aerosols of >1 μm diameter, whereas pH 2 is typical of smaller sizes (their figure 1). Angle et al. discuss the ‘buffering’ of the submicron seasalt aerosol at about pH in the unperturbed marine boundary layer by loss of HCl to the gas phase. A short compilation of selected submicron and supermicron marine aerosol pH (Table 1 of Angle et al.) shows that the submicron marine aerosols have pH of ~ 2 down to negative values for polluted regions. On the basis of these data, and the calculated equilibrium partial pressures in Table 2, it appears that loss of TFA is possible from submicron seasalt aerosols, under warm and polluted conditions. However, this fraction of the aerosols is known to constitute only a small fraction of the total mass (e.g., Murphy et al., 2019), so the total displacement of TFA is likely to be small.

Are there any other factors that might cause the acidified aerosol to be a greater source of TFA? At low relative humidities, for which atmospheric aerosols can exist as aqueous droplets supersaturated with respect to dissolved solutes, TFA concentrations will be higher than in the 80% RH example

shown above. For example, at 50% *RH* they would be enhanced by a factor of about 2 which implies a doubling of the equilibrium partial pressures shown above. Non-ideality in the aqueous aerosols (represented by the activity coefficients in equations 7 and 8) might lead to a small increase in the calculated partial pressure but the magnitude of this is difficult to estimate.

Overall, these results suggest that displacement of TFA from seasalt aerosol may only occur where these conditions are met: at low ambient gas phase TFA concentrations (no more than a few ng TFA m⁻³), low *RH*, moderate to high temperatures, polluted conditions, and for the submicron fraction of the seasalt aerosol (which is likely to be the only fraction that is sufficiently acid). Under other conditions – especially high *RH* and low acidity – the aerosol appears likely to be a sink of TFA.

4.2 Comparisons with HCl partitioning

The tendencies of *total* TFA and Cl⁻ (as HCl) to partition between the gas and liquid phases in the atmosphere can be compared by calculating the equilibrium distribution of TFA and HCl between the gas and droplet phases as a function of atmospheric liquid water content and droplet pH. This has been done for 25 °C, and for liquid water contents ranging from those typical of aerosols under dry conditions to cloud water. The values of the equilibrium constants used are taken from Table 1.

For TFA, the ratio R_{TFA} of the moles of CF₃COOH in the gas phase to that in the liquid phase (per m³ of atmosphere) is given by:

$$R_{\text{TFA}} = \{(1000/\text{gW}) / [(1 + K_a^*/10^{-\text{pH}}) \cdot K_H^*]\} \cdot (1/0.02241) \cdot (273.15/T) \quad (11)$$

where gW is the grams of liquid water per m³ of atmosphere, 0.02241 m³ mol⁻¹ is the molar volume of an ideal gas at a standard temperature and pressure, and pH is equal to $-\log_{10}(m\text{H}^+)$ in the droplets. The gas phase fraction of the total, i.e., gas/(gas + aerosol), is equal to $R_{\text{TFA}} / (1 + R_{\text{TFA}})$.

The analogous expression for HCl is:

$$R_{\text{HCl}} = \{(1000/\text{gW}) \cdot 10^{-\text{pH}} / K_H^*\} \cdot (1/0.02241) \cdot (273.15/T) \quad (12)$$

Plots of the gas phase fractions for both acids are shown in Figure 1. At the tops of the plots approximate ranges of atmospheric liquid water content of aerosols, fogs, and cloud drops are indicated. The top right-hand areas on the plots correspond to cloud or fog droplets with a pH roughly in equilibrium with atmospheric CO₂ (about pH 5.5), while the bottom left correspond to aerosol particles under relatively dry conditions that have been acidified by, for example, dissolved HNO₃ and/or H₂SO₄. The solid (blue) lines and associated label “>1%” on the two plots means that in the area below and to the left of the line more than 1% of total HCl (Figure 1a) and TFA (Figure 1b) are partitioned into the gas phase. On the right of that line less than 1% is expected to be in the gas phase. The other lines have analogous meanings. So, for example, the area to the left of the “>90%” dashed (red) line corresponds to acidified atmospheric aerosols and in this region most of the total TFA, and much of the Cl⁻, are expected to be in the gas phase at equilibrium.

It is clear from the figure that both TFA and HCl are scavenged from the atmosphere by cloudwater and rain because both species (>99%) is predicted to be in the liquid phase for pH and atmospheric liquid water contents typical of these conditions. This is consistent with the known behaviour of both acids.

A comparison of the plots for TFA and HCl in Figure 1 also shows that a much greater fraction of the organic compound is predicted to be in the gas phase, compared to HCl, at any given pH and atmospheric liquid water content. Thus only very low concentrations of TFA are expected even in acidified aerosols, and the 150 ng L⁻¹ found in surface seawater and used in the calculations in the previous section falls into this category.

An interesting feature of Figure 1b is that for moderately acidified aerosols the gas phase fraction of total TFA is of the order of 50-90% or so. (Note that there is quite a strong temperature effect: at 0 °C and pH 4 the liquid water value for 50% partitioning of TFA is reduced by about an order of magnitude compared to that at 25 °C shown in Figure 1). This range is consistent with the observations cited earlier, e.g. Martin et al. (2003) and Wu et al. (2014) who measured gas phase fractions in the range noted above.

5. An upper limit to the TFA flux by analogy with HCl

The results above suggest that TFA is unlikely to be displaced from seasalt aerosols by other acids except under a restricted set of conditions. However, it is possible to estimate the sea surface to atmosphere transport of TFA in the seasalt aerosol, and a possible upper limit to the displacement flux of TFA to the gas phase, by simple analogy with Cl⁻.

A surface seawater TFA concentration of 150 ng L⁻¹ is first assumed. One litre (~1 kg) of seawater of salinity 35 contains about 19.3 g Cl⁻ (Millero et al., 2008), and this TFA concentration corresponds to the following TFA:Cl⁻ mass ratio in seawater and seasalt:

$$150 \text{ ng L}^{-1}: 150 \times 10^{-9} / 19.25 = 7.8 \times 10^{-9}:1$$

Historical estimates of seasalt fluxes from the oceans to the atmosphere range from 300 to 30×10³ Tg a⁻¹ (Lewis and Schwartz, 2004). Their estimate is 5000 Tg a⁻¹, with a range of a factor of 4 on either side (i.e., 1250 to 20×10³ Tg a⁻¹). Warneck (1999) lists modern estimates of 1300 Tg a⁻¹ (Andreae, 1995; and Petrenchuk, 1980) in his Table 7.12, but values based upon deposition of seasalt sulphur imply a total mass flux of seasalt of 4800 Tg a⁻¹ (section 10.3.5 of Warneck, 1999).

Table 3. Fluxes of seasalt Cl⁻ and HCl from Wang et al. (2019), and those of TFA by analogy

Substance	Flux	Tg Cl ⁻ a ⁻¹	kg TFA a ⁻¹
Seasalt aerosol	Oceans → atmosphere	1780	1.4×10 ⁴
Seasalt aerosol	Deposition → ocean/land surface	1720	1.3×10 ⁴
HCl	Aerosol → gas phase	52	406 (limit) ^a
HCl	Deposition → ocean/land surface	71 ^b	-

Notes: The fluxes of TFA are based upon an assumed concentration of 150 ng L⁻¹ in surface ocean water.

a – See text for explanation.

b - The dry and wet deposition flux of HCl(g) exceeds the amount that is displaced from the aerosol because there are other sources (see Figure 1 of Wang et al.).

Wang et al. (2019) have modelled the global cycling of tropospheric chlorine. Their results include an estimate of seasalt aerosol generation of 1780 Tg Cl⁻ a⁻¹ or 3230 Tg seasalt a⁻¹, which is in reasonable agreement with other estimates given the wide range noted above. The model of Wang et al. also yields an estimate of the loss of aerosol Cl⁻ to the gas phase as HCl, see Table 3.

Although the calculations presented earlier, and what is known about seasalt aerosol acidification, suggest that under most conditions there will be little or no net flux of TFA from the aerosol to the gas phase, the result of Wang et al. (2019) can be used to suggest an upper limit to the displacement of TFA.

The modelled aerosol to gas phase flux of 52 Tg Cl⁻ a⁻¹ in Table 3, together with a 150 mg L⁻¹ concentration of TFA in surface ocean water and the TFA:Cl⁻ ratio given above, yields a flux of 406 kg TFA a⁻¹. This assumes the same displacement behaviour as HCl, only scaled by the relative concentrations of TFA and Cl⁻ in seawater. The calculations and discussion presented above suggest that real TFA displacement is likely to be no more than a small fraction of this figure, which is itself very small compared with total TFA production, which was estimated by Solomon et al. (2016) to be 2.21×10^7 kg from hydrofluorocarbons and hydrofluoroolefines alone in 2011.

6. Conclusions

The purpose of this report is to determine whether TFA dissolved in seawater, and therefore present in seasalt aerosol generated by wind and breaking waves, is a significant source of TFA to the gas phase under conditions where the aerosol is acidified.

The gas-aerosol partitioning behaviour of TFA, like other weak acids, is controlled by its dissociation and Henry's law constants. The values of these have been reviewed, and some revisions made (relative to the values obtained by Bowden et al. (1996) from their measurements and from a review of the literature). The greatest remaining uncertainties in these quantities concern their variation with temperature. However, these uncertainties seem unlikely to significantly alter the results of the calculated carried out here.

Measurements of ambient gas phase TFA concentrations are quite limited, but mostly of the order of a few ng m⁻³. Calculated values of the equilibrium partial pressures of TFA over acidified TFA-containing aerosols at 80% *RH* are at much lower levels for all except high temperatures (25 °C in these calculations) and very high acidities (typically 0.1 mol kg⁻¹ H⁺ and above). These are only likely to be attained in the submicron fraction of the aerosol which constitutes only a small fraction of the total volume. Lower *RH* would also increase the equilibrium TFA partial pressure above the aerosol. Based on these results, acidified seasalt aerosol is unlikely to be a source of TFA to the gas phase except under a very limited set of conditions (low *RH*, high temperature, and polluted conditions, and for a small fraction of the aerosol, which would limit the total displacement). Otherwise, the aerosol is more likely to be a sink.

The partitioning of TFA between gas and atmospheric liquid phases has also been calculated as a function of pH and atmospheric liquid water content over a six order of magnitude range, encompassing values typical of clouds, fogs, and aerosols. The same calculation has been carried out for HCl, because this has been suggested as a possible analogue for TFA behaviour. A comparison of

the results for the two substances, shown in Figure 1, indicates that for any combination of pH and liquid water content (per m³ of atmosphere) a greater fraction of total TFA would be expected in the gas phase compared to HCl. Measured gas and aerosol concentrations at two land-based sites – which show most of the TFA in the gas phase – appear to be consistent with what is shown in Figure 1. The results in the figure also confirm what is expected: that TFA, like HCl, will partition strongly into cloud and fogwater and will therefore be removed from the atmosphere by wet deposition.

Finally, literature models of global chlorine cycling allow an estimate to be made of the flux of TFA that would be displaced from acidified seasalt aerosol if the behaviour is analogous to that of HCl but scaled according to the concentrations of TFA and Cl⁻ in surface seawater. This hypothetical value, although is unlikely to have practical relevance except possibly as an upper limit, is only 406 kg TFA a⁻¹ globally.

7. References

- Andreae, M.O., 1995. *Climatic effects of changing atmospheric aerosol levels*. In: World Survey of Climatology, Vol. 16, "Future Climates of the World". Elsevier, Amsterdam.
- Angle, K.J., Crocker, D.R., Simpson, R.M.C., Mayer, K.J., Garofalo, L.A., Moore, A.N., Mora Garcia, S.L., Ora, V.W., Srinivasana, S., Farhan, M., Sauer, J.S., Lee, C., Pothier, M.A., Farmer, D.K., Martz, T.R., Bertram, T.H., Cappa, C.D., Prather, K.A., and Grassian, V.H., 2021. Acidity across the interface from the ocean surface to sea spray aerosol. *PNAS* 118: art. no. e2018397118.
- Bowden, D.J., Clegg, S.L. and Brimblecombe, P., 1996. The Henry's law constant of trifluoroacetic acid and its partitioning into liquid water in the atmosphere. *Chemosphere*, 32: 405-420.
- Bowden, D.J., Clegg, S.L. and Brimblecombe, P., 1998. The Henry's law constants of the haloacetic acids. *J. Atmos. Chem.*, 29: 85-107.
- Brunn, H., Arnold, G., Korner, W., Rippen, G., Steinhauser, K.G. and Valentin, I., 2023. PFAS: forever chemicals—persistent, bioaccumulative and mobile. Reviewing the status and the need for their phase out and remediation of contaminated sites. *Environmental Sciences Europe*, 35(1): art. no. 20.
- Carslaw, K.S., Clegg, S.L. and Brimblecombe, P., 1995. A thermodynamic model of the system HCl-HNO₃-H₂SO₄-H₂O, including solubilities of HBr, from <200 K to 328 K. *J. Phys. Chem.*, 99: 11557-11574.
- Clegg, S.L., Brimblecombe, P., 1990. The solubility of volatile electrolytes in multicomponent solutions, with atmospheric applications. In: *Chemical Modelling in Aqueous Systems II*, Eds. Melchior, D.C. and Bassett, R.L., American Chemical Society, Washington, pp. 58-73.
- Frank, H., Christoph, E.H., Holm-Hansen, O. and Bullister, J.L., 2002. Trifluoroacetate in ocean waters. *Environ. Sci. Technol.*, 36: 12-15.
- Graedel, T.E., and Keene, W.C., 1995. Tropospheric budget of reactive chlorine. *Global Biogeochem. Cycles*, 9: 47-77.
- Henne, A.L. and Fox, C.J., 1951. Ionization constants of fluorinated acids. *J. Amer. Chem. Soc.*, 73: 2323-2325.
- Ives, D.J.G. and Pryor, J.H., 1955. The conductometric evaluation of the ionisation functions of the monohalogenoacetic acids. *J. Chem. Soc.*, 2104-2114.
- Jordan, A., and Frank, H., 1999. Trifluoroacetate in the environment. Evidence for sources other than HFC/HCFs. *Environ. Sci. Technol.*, 33: 522-527.
- Kurz, J.L. and Farrar, J.M., 1969. The entropies of dissociation of some moderately strong acids. *J. Amer. Chem. Soc.*, 91: 6057-6062.
- Kutsuna, S. and Hori, H., 2008. Experimental determination of Henry's law constants of trifluoroacetic acid at 278–298 K. *Atmos. Environ.*, 42: 1399-1412.
- Lewis, E.L. and Schwartz, S.E., 2004. *Sea Salt Aerosol Production: Mechanisms, Methods, Measurements and Models - A Critical Review*. Geophysical Monograph 152. American Geophysical Union, Washington, DC, 413 pp.

- Martin, J.W., Mabury, S.A., Wong, C.S., Noventa, F., Solomon, K.R., Alae, M., and Nui, D.C.G., 2003. *Environ. Sci. Technol.*, 37: 2889-2897.
- Millero, F.J., Feistel, R., Wright, D.G. and McDougall, T.J., 2008. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep-Sea Res. I*, 55: 50-72.
- Milne, J.B. and Parker, T.J., 1981. Dissociation constant of trifluoroacetic acid by cryoscopy and conductivity. *J. Solut. Chem.*, 10(7): 479-487.
- Murphy, D.M., Froyd, K.D., Bian, H., Brock, C.A., Dibb, J.E., DiGangi, J.P., Diskin, G., Dollner, M., Kupc, A., Scheuer, E.M., Schill, G.P., Weinzier, B., Williamson, C.J., and Yu, P., 2019. The distribution of sea-salt aerosol in the global troposphere. *Atmos. Chem. Phys.* 19: 4093-4104.
- Petrenchuk, O.P., 1980. On the budget of sea salts and sulphur in the atmosphere. *J. Geophys. Res.*, 85: 7439-7444.
- Pye, H.O.T., Nenes, A., Alexander, B., Ault, A.P., Barth, M.C., Clegg, S.L., Collett Jr., J.L., Fahey, K.M., Hennigan, C.J., Herrmann, H., Kanakidou, M., Kelly, J.T., Ku, I.-T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J.T., Wang, T., Weber, R., Xing, J., Zaveri, R.A., and Zuend, A., 2020. The acidity of atmospheric particles and clouds. *Atmos. Chem. Phys.*, 20: 4809-4888.
- Robinson, R.A. and Stokes, R.H., 1970. *Electrolyte Solutions*, 2nd (Revised). Butterworths, London, 571 pp.
- Scott, B.F., MacDonald, R.W., Kannan, K., Fisk, A., Witter, A., Yamashita, N., Durham, L., Spencer, C. and Muir, D.C.G., 2005. Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans. *Environ. Sci. Technol.*, 39: 6555-6560.
- Solomon, K.R., Velders, G.J.M., Wilson, S.R., Madronich, S., Longstreth, J., Aucamp, P.J., and Bornman, J.F., 2016. Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols. *J. Toxicol. Environ. Health B, Crit. Rev.*, 19:289-304.
- Strehlow, H. and Hildebrandt, P., 1990. The dissociation of trifluoroacetic acid. *Ber. Bunsenges. Phys. Chem.*, 94: 173-179.
- Su, B., Wang, T., Zhang, G., Liang, Y., Lv, C., Hu, Y., Li, L., Zhou, Z., Wang, X., and Bi, X., 2022. A review of atmospheric aging of sea spray aerosols: Potential factors affecting chloride depletion. *Atmos. Env.*, 290: art. no. 119365. 24 pp.
- Tong, C., Clegg, S.L. and Seinfeld, J.H., 2008. Comparison of activity coefficient models for atmospheric aerosols containing mixtures of electrolytes, organics, and water. *Atmos. Environ.*, 42: 5459-5482.
- Wang, X., Jacob, D.J., Eastham, S.D., Sulprizio, M.P., Zhu, L., Chen, Q., Alexander, B., Sherwen, T., Evans, M.J., Lee, B.H., Haskins, J.D., Lopez-Hilfiker, F.D., Thornton, J.A., Huey, G. and Liao, H., 2019. The role of chlorine in global tropospheric chemistry. *Atmos. Chem. Phys.*, 19: 3981-4003.
- Warneck, P., 1999. *Chemistry of the Natural Atmosphere*. International Geophysics Series, Academic Press, 927 pp.

World Meteorological Organisation (WMO), 2022. Scientific Assessment of Ozone Depletion: 2022, GAW Report No. 278, 509 pp., WMO, Geneva.

Wu, J., Martin, J.W., Zhai, Z., Lu, K., Li, L., Jin, H., Hu, J., and Zhang, J., 2014. Airborne trifluoroacetic acid and its fraction from the degradation of HFC-134a in Beijing, China. *Environ. Sci. Technol.*, 48: 3675-3681.

Wexler, A.S. and Clegg, S.L., 2002. Atmospheric aerosol models for systems including the ions H^+ , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , Br^- , and H_2O . *J. Geophys. Res.*, 107: art. no. 4207.

Zehavi, D. and Seiber, J. N., 1996. An analytical method for trifluoroacetic acid in water and air samples using headspace gas chromatographic determination of the methyl ester. *Anal. Chem.*, 68: 3450-3459.

8. Figures

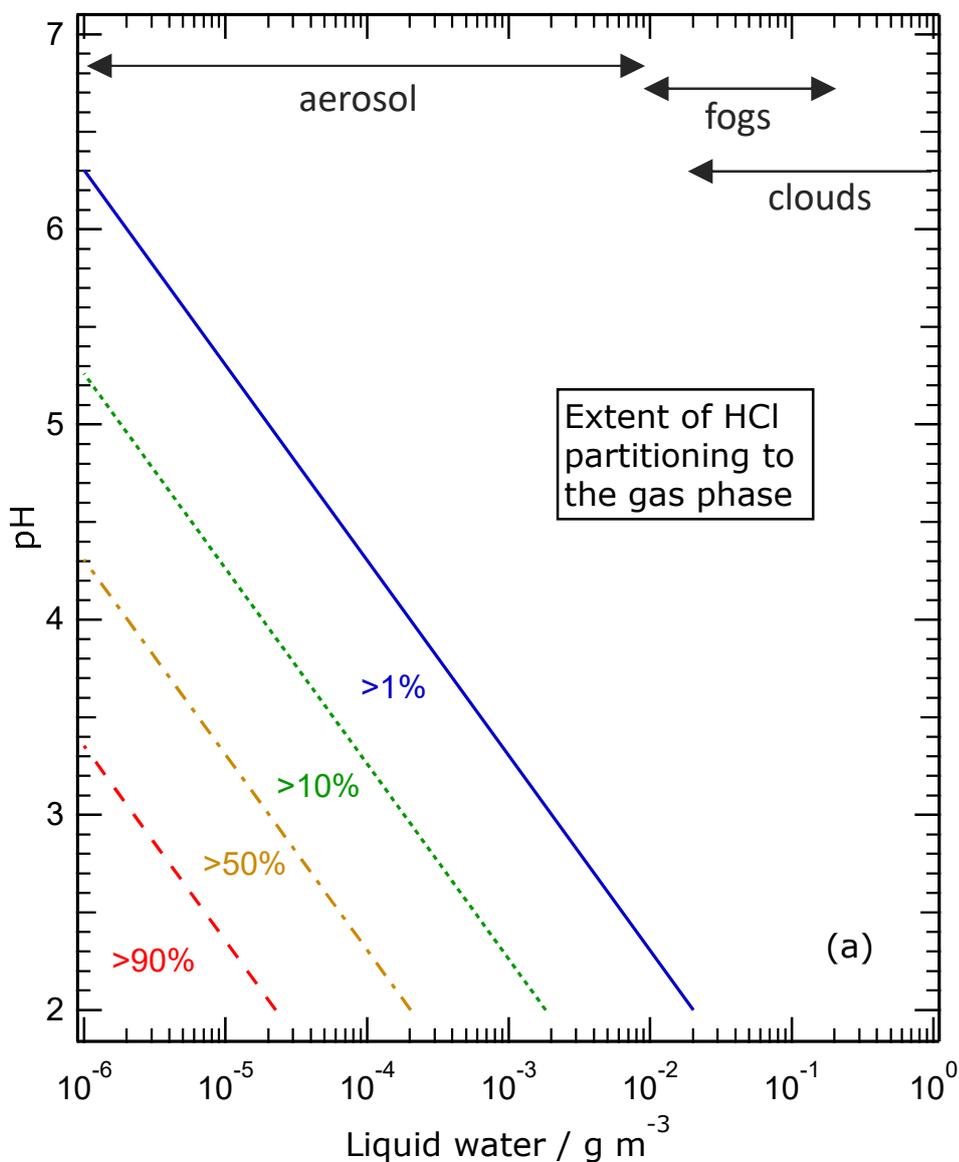


Figure 1a. The extent of HCl partitioning into the gas phase at 25 °C, for various atmospheric liquid water contents as a function of pH ($-\log_{10}(mH^+)$). The quantity to the left of each line is the percentage of total acid in the gas phase along that line. Partitioning to the gas phase increases to the left so that, for example, to the left of the dotted line (green) more than 10% of the acid is expected to be in the gas phase. The approximate ranges of atmospheric liquid water content corresponding to aerosols, fogs and clouds are indicated in the upper part of the plot.

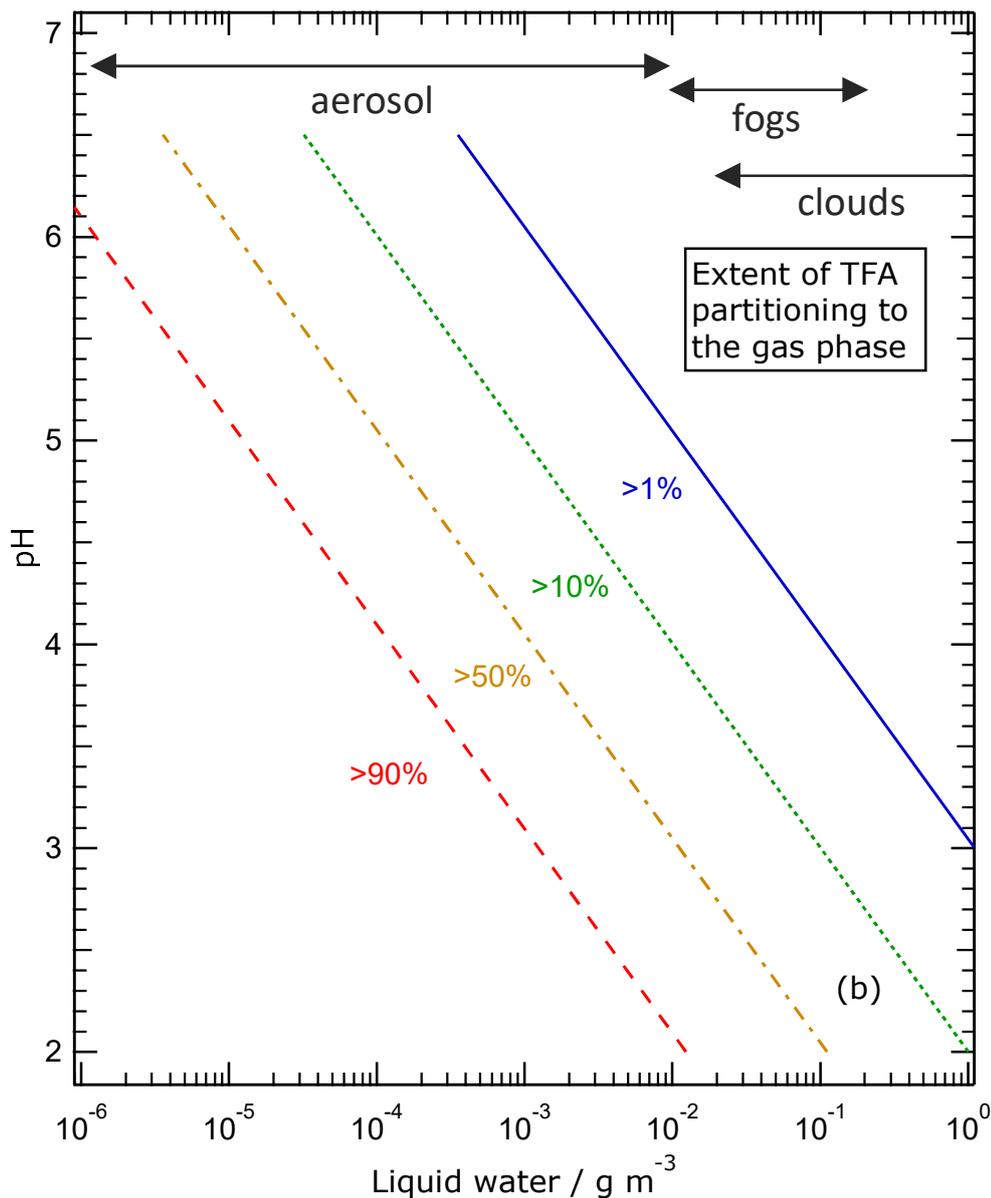


Figure 1b. The extent of TFA partitioning into the gas phase at 25 °C, for various atmospheric liquid water contents as a function of pH ($-\log_{10}(mH^+)$). The quantity to the left of each line is the percentage of total acid in the gas phase along that line. Partitioning to the gas phase increases to the left so that, for example, to the left of the dotted line (green) more than 10% of the acid is expected to be in the gas phase. The approximate ranges of atmospheric liquid water content corresponding to aerosols, fogs and clouds are indicated in the upper part of the plot.

Appendix 1: Background information provided by EFCTC (*Summary Call for Tender – Transport TFA*)

Transport of TFA from the oceans to the troposphere? Including additional information.

Anthropogenic emissions of TFA are a major topic in Europe due to the PFAS restriction proposal. There are significant quantities of TFA in the oceans (61-205 million tonnes, Scott). During the primary generation of sea salt 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. Such a process would only result in about 20 tonnes of TFA being transported to the atmosphere.

We are aware of your expertise for sea salt aerosols¹ and that you co-authored the paper reporting the measurement experimentally of TFA Henry's Law constant in the 1990s. Also, the paper discussed partitioning of TFA into airborne aerosol. The transport of HCl and other inorganic chlorides to the troposphere from SSA has been reviewed.² Oceanic TFA concentrations close to the surface have been measured at about 200ng/L in the Atlantic (Frank³) and 10 ng/L or less in the Pacific (Scott).⁴

EFCTC would like to understand if any additional TFA can be transported from the oceans to the troposphere, in the same way that HCl is partitioned from aged sea salt aerosol to the troposphere. If this can occur, we would be interested if it is possible to estimate or give an indication of the possible magnitude of this transport.

Additional Information

While it is generally accepted that there is a large quantity of naturally occurring TFA in the oceans, this has been disputed by a review paper, "Insufficient evidence for the existence of natural trifluoroacetic acid"⁵ which concludes that "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." Two recent publications have responded to this paper providing evidence that TFA in the oceans must have a natural source. An Inventory of Fluorspar Production, Industrial Use, and Emissions of Trifluoroacetic Acid (TFA) in the Period 1930 to 1999,⁶ concluded that "Significant other industrial uses of fluorides have not been identified, in the period 1930-1999, that could account for the large burden of TFA in the oceans." The Environmental Effects Assessment Panel in its 2022 report⁷, published in 2023, reaches a similar conclusion that TFA in the oceans and endorheic lakes are very unlikely to be all from anthropogenic sources. 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 km³, so that this concentration is equivalent to

¹ Atmos. Chem. Phys., 20, 4809–4888, 2020 and *Commun. Earth Environ.* 2, 93 (2021). <https://doi.org/10.1038/s43247-021-00164-0>

² A review of atmospheric aging of sea spray aerosols: Potential factors affecting chloride depletion <https://doi.org/10.1016/j.atmosenv.2022.119365>

³ Frank, H., Christoph, E. H., Holm-Hansen, O., & Bullister, J. L. (2002) Trifluoroacetate in ocean waters. *Environ. Sci. Technol.*, 36, 12-15. <https://doi.org/10.1021/es0101532>

⁴ Scott, B. F., Macdonald, R. W., Kannan, K., Fisk, A., Witter, A., Yamashita, N., Durham, L., Spencer C., & Muir, D. C. G. (2005). Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans. *Environ. Sci. Technol.*, 39, 6555-6560. <https://doi.org/10.1021/es047975u>

⁵ Joudan, S., De Silva, A. O., & Young, C. J. (2021). Insufficient Evidence for the Existence of Natural Trifluoroacetic Acid. *Environmental Science: Processes & Impacts*, 23, 1641-1649. <https://doi.org/10.1039/D1EM00306B>

⁶ Lindley, A. An Inventory of Fluorspar Production, Industrial Use, and Emissions of Trifluoroacetic Acid (TFA) in the Period 1930 to 1999. *Journal of Geoscience and Environment Protection*, Vol.11 No.3, March 2023 <https://doi.org/10.4236/gep.2023.113001>

⁷ UNEP 2022 Assessment Report of the Environmental Effects Assessment Panel, March 2023, available at <http://ozone.unep.org/science/eeap>

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.

Mechanical transport from the oceans estimated at 20 tonnes of TFA is insignificant. 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 by Frank would translate into a global flux of about 20 tonnes/year. Based on this, deposition of TFA over land is proposed to be solely from anthropogenic sources, which implies TFA deposition over land could potentially be eliminated.

The concentration of TFA in rain from known sources in the mid-1990s was calculated to be <2ng/L.⁸ However, it is also possible that some significant anthropogenic sources of TFA were not identified at that time. The actual TFA concentrations in rainwater, measured in the 1990s, were about two orders of magnitude larger than expected, based on the known anthropogenic sources. 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.⁹ Fog was found to have a higher concentration of TFA than rain.¹⁰

Transport of significant quantities of TFA from the oceans to the land is not supported by measurements of TFA in old ground waters where TFA was either absent or found in low concentrations¹¹ that might be accounted for by some contribution from recent surface waters. However, we are not aware of published information on the transport of TFA in ground and spring waters. TFA rapidly breaks through activated carbon filtration and ion exchangers, after some initial reduction in concentration, in studies for wastewater treatment.¹²

Establishing if significant quantities of TFA can be transported from the oceans to the land may contribute to a better understanding of TFA deposition. The first step is to understand if significant quantities of TFA are transported to the troposphere from the oceans, with the potential of further transport over land. 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).¹³

⁸ 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, DOI: 10.1080/10807039991289644, 1999.

⁹ Kanakidou, M., Dentener, F. J., and Crutzen, P.J.: A global three-dimensional study of the fate of HCFCs and HFC-134a in the troposphere, J. Geophys. Res., 100(D9), 18781-18801, doi.org/10.1029/95JD01919, 1995.

¹⁰ Zehavi, D. and J.N. Seiber, J. N.: An analytical method for trifluoroacetic acid in water and air samples using headspace gas chromatographic determination of the methyl ester, Anal. Chem., 68, 3450-3459, doi.org/10.1021/ac960128s, 1996.

¹¹ Jordan, A. and Frank, H. Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs, Environ. Sci. Technol. 1999, 33, 522-527.

¹² Scheurer, M., Nodler, K. N. et al, Small, mobile, persistent: Trifluoroacetate in the water cycle- Overlooked sources, pathways, and consequences for drinking water supply, Water Research 126 (2017) 460e 471

¹³ World Meteorological Organization (WMO). Scientific Assessment of Ozone Depletion: 2022, GAW Report No. 278, 509 pp.; WMO: Geneva, 2022. Available at <https://ozone.unep.org/science/assessment/sap>