

CRITICAL REVIEW

View Article Online
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Cite this: *Environ. Sci.: Processes Impacts*, 2021, 23, 1641

Received 22nd July 2021
Accepted 1st October 2021

DOI: 10.1039/d1em00306b

rsc.li/espi

Insufficient evidence for the existence of natural trifluoroacetic acid

Shira Joudan,^a Amila O. De Silva^b and Cora J. Young^{*a}

Trifluoroacetic acid (TFA) is a persistent and mobile pollutant that is present ubiquitously in the environment. As a result of a few studies reporting its presence in pre-industrial samples and a purported unaccounted source, TFA is often claimed to exist naturally. Here, we examine the evidence for natural TFA by: (i) critically evaluating measurements of TFA in pre-industrial samples; (ii) examining the likelihood of TFA formation by hypothesized mechanisms; (iii) exploring other potential TFA sources to the deep ocean; and (iv) examining global budgets of TFA. We conclude 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. We argue the paradigm of natural TFA should no longer be carried forward.

Environmental significance

Trifluoroacetic acid (TFA) is an environmental contaminant that arises from multiple sources, including the degradation of several regulated chemicals. Earlier studies proposed a natural source of TFA to explain the presence of TFA in some environmental samples and the lack of a balanced global budget. This paradigm has been propagated without sufficient evidence. This critical review fully explores the literature and determines that there are no compelling scientific arguments to support the existence of naturally formed TFA. Thus, in the absence of new evidence, natural TFA should not be invoked in any discussions about the production and/or regulation of TFA.

Introduction

Trifluoroacetic acid (TFA; CF_3COOH) has been measured in the environment since the 1990s,¹ but recent advances in analytical techniques are renewing interest in the global ubiquity of TFA.^{2–4} Heightened concerns over per- and polyfluoroalkyl substances (PFAS) have brought TFA into the forefront, with debate on whether or not TFA should be considered a part of the PFAS class.^{5–7} What remains irrefutable is that TFA is a very persistent, very mobile (vPvM) contaminant because of its extremely low reactivity and high water solubility. The vPvM chemicals are subject to increased attention because they can readily move throughout the environment and accumulate, even though their chemical properties (e.g. octanol–water partitioning coefficients) differ from those of traditional persistent organic pollutants.⁸ The bioaccumulation potential of TFA in mammals and fish is typically thought to be lower than more scrutinized PFAS that contain a continuous chain of four or more perfluorinated carbon atoms.^{9,10} Nevertheless, the detection of high TFA levels in human blood and their association with health issues indicate that TFA is bioavailable and has non-

negligible residence time in biota.¹¹ Although TFA is not bioaccumulative in the traditional sense, the high levels in humans are cause for concern (and suggest higher exposure). TFA is phytoaccumulative¹² and has been found in food and beverages.⁴

The TFA paradigm includes the long-held concept that it exists naturally, and only some of its sources are anthropogenic in origin. For example, the European Fluorocarbon Technical Committee (EFCTC) says “the evidence is clear and irrefutable that TFA occurs naturally in large quantities in the environment”.¹³ Similar statements have propagated in academic literature that natural TFA exists, and is widely accepted (e.g. ref. 14–19) but questioned by few (e.g. ref. 20–22). In an effort to better understand the scientific basis for this statement, we sought its origin and corresponding data. The outcome of this objective is that there is inadequate scientific evidence of naturally derived TFA and that the natural TFA paradigm represents a vast overstatement without data to back it up. The question of natural TFA occurrences has not previously been examined in detail, and thus the objective of this work is to critically assess the evidence that TFA occurs naturally. Here, we address some common misinterpretations and limitations of the older TFA research that is often considered the benchmark in newer publications, with the aim to prevent their propagation through new manuscripts. Specifically, we: (i) evaluate published TFA measurements in pre-industrial and other

^aDepartment of Chemistry, York University, Toronto, Ontario, Canada. E-mail: [redacted]@yorku.ca

^bAquatic Contaminants Research Division, Environment and Climate Change Canada, Burlington, Ontario, Canada

environmental samples; (ii) examine the evidence for the proposed natural source; (iii) explore potential sources of TFA to the deep ocean; and (iv) examine the basis for global TFA budgets.

Evaluation of published TFA concentrations in old natural systems

The purported presence of TFA in pre-industrial water samples has been used to suggest TFA is naturally derived. To this end, freshwater and oceanwater samples have been collected, dated, and analyzed for TFA. A major challenge in evaluating the reported measurements is the limited analytical detail provided in these manuscripts, which often did not have Electronic Supplementary Information associated with them. When evaluating quantitative environmental measurements, we require standard figures of merit including limits of detection (LOD) and quantification (LOQ), accuracy, and precision. These are usually developed by determining concentrations in field and laboratory blanks, method recovery efficiency, replicate analysis, standard reference materials and clear data handling methods such as correcting for recovery or background contamination. Our own research using ultra trace analysis of TFA in high Arctic ice caps has underscored the importance of rigorous reporting and efforts to constrain as well as report analytical artefacts.²³ Specifically, we want to know how the sampling was performed, and if any fluorinated materials were used during sample collection, storage, or processing.

Four studies report TFA in pre-industrial freshwater and are summarized in Table 1. The first study was by Jordan and Frank, in which TFA in old groundwater was below LOD whereas TFA in newer groundwater and surface water was 70–320 ng L⁻¹.²³ Berg *et al.* used 15 000 year-old groundwater as a method blank for their measurements of TFA in rainwater and surface waters and did not observe TFA above the detection limit of 5 ng L⁻¹.²⁴ Similarly, Nielsen *et al.* reported no detectable TFA in ~2000 year-old groundwater and ice cores dated to 4191 ± 20 years, with a detection limit of 2 ng L⁻¹.²⁵ Unlike these three papers, Von Sydow *et al.* reported TFA concentrations of 6–56 ng L⁻¹ in 190 year-old Antarctic firn and 5 ng L⁻¹ in glacier ice from Sweden that formed ~500 years ago.²⁶ No obvious relationship was observed between concentration and depth in the firn core. Furthermore, the anthropogenic organochlorine insecticide lindane, and alkyl phosphate flame retardants were noted in the same glacier samples which presents significant concern regarding data quality. Collectively these data suggest that the data quality was hampered by modern contamination or that there were problems in the dating methods used to assign age. Despite these limitations, the authors conclude that based on these data, TFA must have a natural source. Closer scrutiny of the reported analytical methods indicates flaws based on the first principles of quantitative analysis. All sample concentrations were extrapolated below their lowest calibration standard, which was 100 ng TFA into 10 mL water, resulting in a final concentration of 1000 ng mL⁻¹ after sample processing.²⁶ There was no apparent effort to determine whether the linear range of

Table 1 Critical assessment of TFA reporting in pre-industrial freshwater samples

Sample type	Location	Age (from sample collection)	Dated year of samples	TFA (n) ^a	LOD	Notes
Groundwater ²³	Antonien, Kondrau (Bavaria, Germany)	>700	Pre-1300 CE	ND (3)	10 ng L ⁻¹	No information provided about methods for sample collection
	Bayern, Kondrau (Bavaria, Germany)	~200	~1800 CE	23 ± 3 ng L ⁻¹ (5)		
	Thuringer Wald, Kondrau (Bavaria, Germany)	400 ± 60	1596 ± 60 CE	ND (3)		
Groundwater ²⁴	Rennsteig, Kondrau (Bavaria, Germany)	185	1811 CE	13 ± 3 ng L ⁻¹ (3)	5 ng L ⁻¹	Details about sample collection and dating in ref. 27
	Small aquifer in N Switzerland	15 000 ± 1800	13 000 ± 1800 BCE	ND (3)		
Firn ²⁶	Various depths, Maud Land, East Antarctica	~190 to present	~1806–1997 CE	6–56 ng L ⁻¹ (11)	1 ng or 1 ng L ^{-1b}	Fluoropolymer used in sample preparation. LODs and sample concentrations reported below calibration standards
Glacier ²⁶	Marmaglaciare, Sweden	>500	Pre-1500 CE	5 ng L ⁻¹		
Groundwater ²⁵	Grundfoer, Denmark	~2000	~0 CE	ND (3)	2 ng L ⁻¹	
Ice core ²⁵	Summit, Greenland	4191 ± 20	2199 ± 20 BCE	ND (2)		Dated using radiocarbon in dissolved CO ₂ Chemical analysis of ice core from well documented standard archive

^a n = sample replicates; ND = not detected above LOD. ^b The LOD in this paper was unclear, as described in the text.

the calibration curve extended below this calibration standard. The authors define their LOD and LOQ based on their laboratory blanks, but the limited range of calibration standards indicate extrapolation was employed to quantify TFA in the blanks (as well as the samples).²⁶ Overall, our conclusion from these reports is that there is no defensible evidence of any freshwater TFA in the pre-industrial period.

Deep ocean samples that were presumed to be uninfluenced by anthropogenic pollution have been analyzed for TFA and are summarized in Fig. 2. Frank *et al.* reported TFA concentrations consistently $\sim 200 \text{ ng L}^{-1}$ regardless of location or depth, down to 4150 m in the mid-Atlantic Ocean, and down to 2000 m in the Southern Ocean (Antarctica).²⁸ The authors were very thorough in quality control measures during their sampling, wherein field blanks of 400 year-old mineral water were transported throughout the sampling campaign during one year of sampling, and artificial seawater during the next year. The old mineral water, purchased from a commercial supplier, contained the same amount of TFA as both the artificial seawater and deionized water stored in the laboratory ($35 \pm 5 \text{ ng L}^{-1}$, $34 \pm 1 \text{ ng L}^{-1}$, $33 \pm 3 \text{ ng L}^{-1}$, respectively). These concentrations are high, and higher than the pre-industrial freshwater in Table 1. The authors corrected the measured TFA concentrations in ocean water by subtracting the field blank corresponding to the sample, whether it was the 1998 old mineral water, or the 1999 artificial seawater in glass or polypropylene bottles. The authors define their LOD (20 ng L^{-1}) and LOQ (32 ng L^{-1}) as the mean concentration of TFA in deionized water laboratory blanks of (8 ng L^{-1}) plus three times the standard deviation (4 ng L^{-1}) for LOD or plus $6 \times$ the standard deviation for LOQ. It would be more correct to define LOD and LOQ based on the concentrations of TFA in the field blanks because this accounts for the entire sample handling process. The lowest calibration standard was 28 ng L^{-1} , suggesting they reported concentrations in their quality control blanks below their lowest calibration standard; however, the samples were above the lowest calibration standard. In this study, the oldest samples were aged as >60 years old. Their dating was limited by the use of chlorofluorocarbon (CFC) levels in the water, which has a lower limit of 1940, approximately 60 years before the samples were collected. The authors concluded that only a pre-industrial TFA source (*i.e.* natural source) could explain the consistent TFA concentrations measured in waters >60 years old.

Scott *et al.* collected depth profiles from several oceans to provide a more comprehensive picture of global oceanic TFA.²⁹ They observed different trends in TFA depth profiles in different locations, as shown in Fig. 2, with much more variable concentrations than Frank *et al.*,²⁸ including multiple sites with much lower concentrations. For example, in the Atlantic Ocean, TFA ranged from 20 to 200 ng L^{-1} from 23°N , 20°W to 38°N , 73°W . This variability is consistent with more recent analysis of PFAS profiles in ocean sampling across extensive latitudinal gradients.^{30–32} Similar to the work of Frank *et al.*,²⁸ Scott *et al.* reported relatively high concentrations of TFA ($>100 \text{ ng L}^{-1}$) deep into the South Atlantic.²⁹ An additional objective of Scott *et al.* was to test the hypothesis that deep sea vents could be a source of TFA into the ocean, and these results will be

discussed below.²⁹ The works of Frank *et al.*²⁸ and Scott *et al.*²⁹ demonstrate that TFA can be found in the deep ocean. A limitation of these studies was that they did not consider plausible TFA delivery mechanisms from ocean depths representing modern times to the deep ocean.

These same two studies were summarized in a 2016 review paper on TFA that stated “What is clear from these data is that a large amount of the TFA salts in the ocean is from natural rather than human-made sources. However, salts of TFA in surface fresh waters are more likely of anthropogenic origins”.¹⁶ The review paper has been cited for the statement that TFA has some natural origins by scientists,³³ including by those working in the fluorocarbon industry.^{6,13} However, similar to Frank *et al.* and Scott *et al.*,^{28,29} the review did not consider other explanations for the observation of TFA in deep ocean, did not critically assess the analytical methods in those papers, and did not discern the plausibility of the natural mechanism for producing TFA.¹⁶

Another line of evidence for natural TFA used by the fluorocarbon industry¹³ is measurements of TFA from four archived soil samples from Rothamsted Agricultural Research Station, dating from 1865, 1881, 1944, and 1956, which reported concentrations of 0.51, 0.55, <0.1 and 0.35 ng g^{-1} TFA (dry weight), respectively.³⁴ Here, the method details are incongruous whereby the authors report a method limit of detection of 1 ng g^{-1} based on a 10 g sample, suggesting either all of the sample results are below the limit of detection, or they extracted upwards of 100 g of sample. The inconsistency and ambiguity underscore the responsibility of researchers to report rigorous methods, which we have highlighted as a limitation for many early TFA studies. Peer reviewers and journal editors also share a responsibility to insist on the inclusion of rigorous and reproducible methodologies in publications. Additionally, the oldest sample from 1865 contained unexpectedly high concentrations of other haloacetic acids, notably 315 ng g^{-1} dichloroacetic acid, suggesting it was likely contaminated. As demonstrated by early research analyzing TFA in aqueous samples, lab blanks tended to have high TFA concentrations. As such, additional skepticism is incurred by the absence of any reported blanks in this study. Taken together, this stand-alone paper purporting a natural source of TFA in old soil is not supported by sufficient evidence. Overall, the origins of the natural TFA source paradigm are largely based on the observation of TFA in pre-industrial samples, but no studies present a plausible mechanism for formation of TFA from natural sources.

Proposed natural source to deep ocean

Of the thousands of organofluorine molecules found in the environment, the vast majority are solely anthropogenic. Harnisch *et al.*³⁵ observed that several fluorine-containing gases were liberated from the mineral fluorite (CaF_2) upon grinding. The fluorinated gases observed were CF_4 , NF_3 , and SF_6 , along with several CFCs. The presence of CF_4 and other fluorinated gases has been observed in a few studies examining tectonically active areas on the continents.^{36–39} Evidence of enrichment of

fluorinated gases has been sought but not found in other studies of volcanic emissions,^{40–42} indicating the heterogeneous nature of their emission. This heterogeneity has been attributed to the natural variability in fluorine content,^{41,42} which is found primarily in the form of the mineral fluorite. Fluorite is found on continents in deposits typically near major faults or as an accessory mineral in granites,⁴¹ and is not found in the deep ocean. Although CF_4 has been observed to be released from geologic processes, evidence of this occurring in the deep Pacific Ocean was sought but not found.⁴³ Instead, all observed CF_4 could be attributed to dissolution from the atmosphere.⁴³

In the same study in which fluorine-containing gases were measured from crushed fluorite, the authors cite conference presentations of deep ocean observations of TFA (early version of ref. 29) and propose that fluorite “is a source of natural TFA analogous to natural CF_4 ”. There have been no experimental or observational reports of fluorite being a source of TFA under environmental conditions. In addition, the parallel drawn

between TFA and CF_4 ignores basic chemistry. Whereas CF_4 , NF_3 , and SF_6 can all be formed under the anoxic conditions common in magmatic and hydrothermal fluids, production of TFA from fluorite would require an oxygen source for its formation. Observations of CF_4 production solely from continental fluorite does not provide a convincing foundation for TFA production in the deep ocean from anoxic hydrothermal vents. The deep ocean TFA measurements by Scott *et al.* included measurements of four profiles over geologically active areas (Fig. 2) based on the hypothesis that deep sea vents or underwater volcanoes could act as a natural source of TFA.²⁹ Here, we delve into this data and the plausibility of their implications. Three vent profiles were collected in the Pacific Ocean and one in the Mediterranean Sea (Fig. 2). All vent profiles have TFA concentrations within the range reported from depth profiles without vents in the Atlantic, Arctic, and Southern Oceans (Fig. 1). For most vent locations, no measurements exist in a similar location in the absence of vents for direct comparison. One exception is the South Pacific, where a single non-vent depth profile was collected (Fig. 2). The South Pacific non-vent depth profile is distinct from all other ocean profiles (Fig. 1) emphasizing the importance of potential spatial heterogeneity on the interpretation of the data. The South Pacific vent and non-vent depth profiles are shown together in Fig. 2b. If the vents were a significant source of TFA, we might expect higher concentrations of TFA at the deepest depths near the vents, but the profiles do not show this. Overall, the TFA

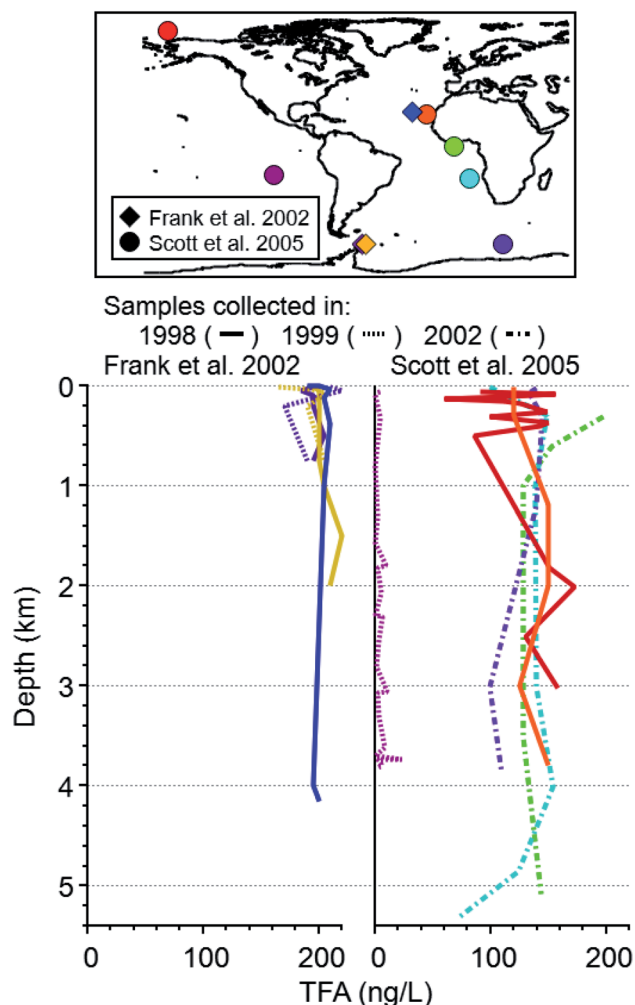


Fig. 1 Ocean depth profiles of TFA concentrations redrawn from Frank *et al.* (left)²⁸ and Scott *et al.* (right).²⁹ For the Scott *et al.*²⁹ data, only profiles with a depth of 1500 m or greater were included. Line colours correspond to sampling locations shown in the top panel, and line styles correspond to year of sample collection.

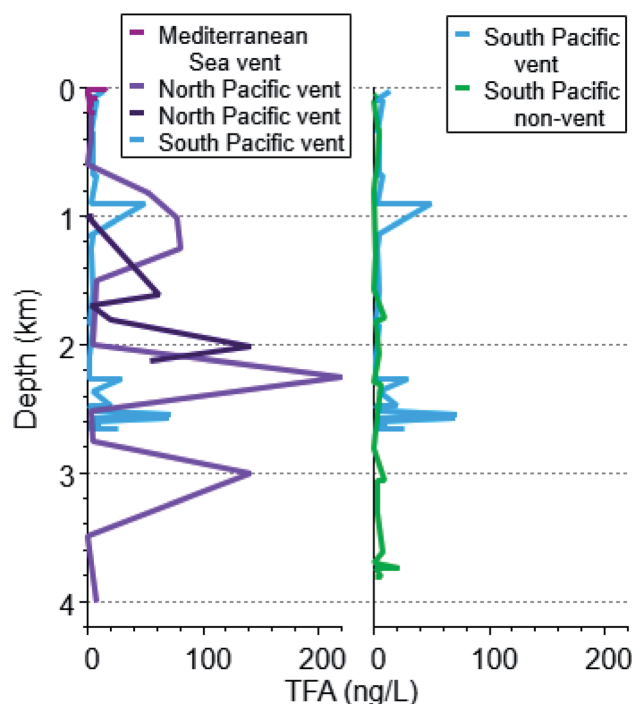


Fig. 2 Profiles measured above vents redrawn from Scott *et al.*²⁹ left panel shows all four vents (note that Mediterranean site is quite shallow). Right panel shows S Pacific vent site vs. S Pacific non-vent site. For all other vent locations, we do not have a non-vent profile for comparison.

depth profiles measured above active vents reported in this single study are not persuasive of a natural TFA source.

Other possible sources to deep ocean

Many anthropogenic pollutants have been found in the deep ocean since the measurement of TFA, including radionuclides,^{44,45} persistent organic pollutants,^{33,46–49} heavy metals,⁵⁰ and microplastics.⁵¹ Other PFAS have also been observed in the deep ocean,^{52,53} including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Deep ocean observations of pollutants with disparate physical properties indicate multiple mechanisms can transport chemicals to the deep ocean on decadal timescales or faster. Three mechanisms, each of which may contribute to TFA in the deep ocean, will be discussed here: (i) meridional overturning circulation; (ii) shelf water cascading; and (iii) sinking of solids. The first potential transport mechanism relates to deep ocean water formation through the meridional overturning circulation, also known as the global conveyor belt. This is well established to carry dissolved gases (e.g. CFCs⁵⁴) to the deep ocean and has been suggested to contribute to deep-ocean observations of POPs (e.g. polychlorinated biphenyls (PCBs),⁴⁸ Fig. 3). Measurements and

models have also shown that meridional overturning circulation delivers PFAS to the deep ocean (Fig. 3).^{52,53} The second potential transport mechanism is through dense water formed on continental shelves that descends along continental slopes or through submarine canyons to deep waters in a process called shelf water cascading.⁵⁵ These intermittent transport events can occur in all the world's oceans⁵⁵ and have been shown to efficiently deliver contaminants, including persistent organic pollutants⁵⁶ and several PFAS,⁵⁷ from coastal regions to the deep sea.⁵⁸ The third potential transport mechanism involves sinking of particles and organisms, which can account for the presence of numerous anthropogenic pollutants in the deepest parts of the ocean. These chemicals include persistent organic pollutants⁴⁶ (e.g. PCBs,^{33,47,49} polybrominated diphenyl ethers,^{33,47} organochlorine pesticides³³), heavy metals,⁵⁰ radionuclides,⁴⁵ and microplastics.⁵¹ Studies have shown that PFAS can accumulate in plankton⁵⁹ and that sinking of plankton can transport PFAS from the surface ocean.³² These proposed mechanisms are all plausible pathways by which TFA could reach the ocean, and thus, the presence of TFA in deep ocean waters does not in itself necessitate invoking a natural source. More marine measurements of TFA, including deep ocean measurements, will help to increase our understanding of potential transport mechanisms.

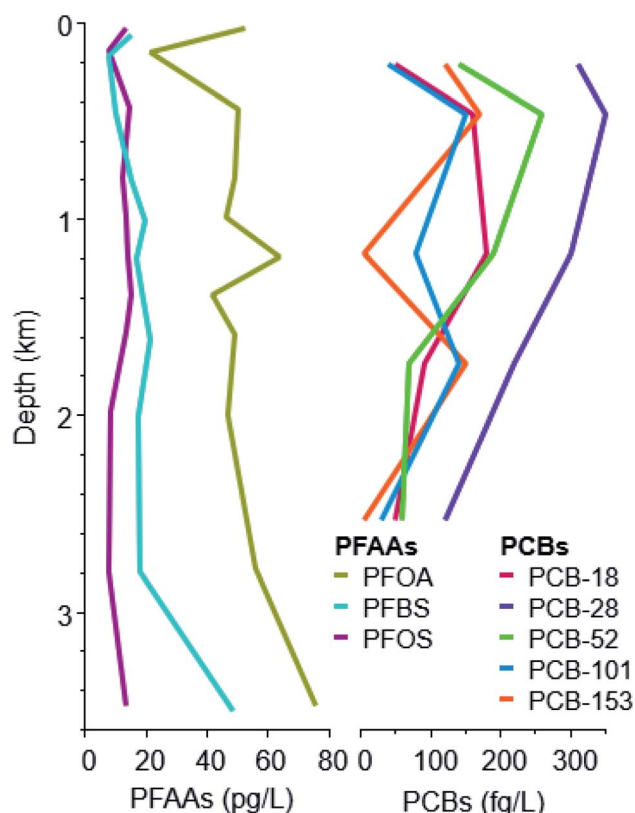


Fig. 3 North Atlantic Ocean depth profiles of persistent compound concentrations. PFAAs (perfluorobutane sulfonate (PFBS), perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA)) measured at 56.6 N, 52.8 W in 2004 and reported in Yamashita *et al.*⁵³ PCBs (PCB-18, -28, -52, -101, -153) measured at 79 N, 4 E for ~1 year from July 2012–2013 and reported in Sun *et al.*⁴⁸

Large fraction of TFA remains unexplained

Finally, arguments have been made that TFA must have a natural source because there is no other explanation for some estimated global burdens. However, until a clear source of natural TFA has been identified and all anthropogenic sources have been completely constrained, an unknown fraction does not itself prove the presence of a natural source. Based on their average reported marine TFA concentrations, Frank *et al.* roughly estimated the total ocean TFA burden using 200 ng L^{-1} and an ocean volume of $1.34 \times 10^{21} \text{ L}$, resulting in a total of 268×10^6 tonnes of TFA in oceans.²⁸ The authors assumed homogeneity of the oceans, which is a vast oversimplification, as shown by other papers discussed herein. This approximation is often used as evidence of natural TFA. Scott *et al.* based their calculated ocean burden on more comprehensive TFA measurements, which divided global waters into different depth profiles and assessed Pacific, Atlantic and Indian Oceans separately, in addition to the Canadian Basin of the Arctic Ocean.²⁹ The authors calculated the total TFA burden using high and low values for Atlantic and Pacific deep water, ultimately reporting a lower total oceanic TFA burden than Frank *et al.* of $(61\text{--}205) \times 10^6$ tonnes. Such estimates are speculative as the calculated TFA burdens are based on extrapolation of uncertain concentrations using unrealistic assumptions of spatial homogeneity throughout the ocean, and that their limited measurements are the most representative. The propagation of error in this workflow results in a highly uncertain burden.

Poor source apportionment of TFA does not specifically support or refute the presence of a natural source. Most anthropogenic contaminants do not have comprehensively characterized budgets, including those with more widespread and simpler measurements. From a wider perspective, the global biogeochemical cycle of elemental fluorine was only first published in 2020.⁶⁰ TFA is released both directly into the environment and indirectly *via* reactive precursors.^{23,61} Some reactive precursors are emitted into the gas phase, where they are oxidized predominantly by hydroxyl radicals to form TFA.⁶² Like other strong acids, TFA is primarily removed by wet and dry deposition.^{14,24} Other precursors are emitted into surface waters, where they are oxidized *via* hydrolysis or *via* biological processes.⁶¹ The long-range transport potential and reactivity of different precursors impact the quantity and location of TFA production, in addition to TFA being transported itself.^{22,62,63} Among the most important atmospheric precursors to TFA are heat transfer fluids, such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), that have been introduced as replacements for CFCs through the Montreal Protocol and subsequent amendments.^{23,64} The atmospheric formation of TFA from these chemicals has been the subject of many studies and the resulting environmental burden is reasonably well constrained.^{16,62}

However, more sources are being identified, such as recently, when a surprising amount of HCFC-133a (CH_2ClCF_3) was found in East Asia, likely as a byproduct of chemical production processes, updating the global emissions of this TFA precursor to 2300 tonnes per year from 2016–2019.⁶⁵ A 2021 paper used a global three-dimensional chemical transport model to investigate the changes in global TFA from the transition of HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$) to a hydrofluoroolefin, HFO-1234yf ($\text{CF}_3\text{-CFCH}_2$), and found that this change resulted in a 33-fold increase in the global burden of TFA when the 2015 emissions were used (*i.e.* 65 tons per year for HFC-134a *vs.* 2200 tons per year for HFO-1234yf).²² Fast reaction of HFO-1234yf to TFA was observed to result in a 250-fold increase of urban surface level TFA concentrations across Europe.²² Zhai *et al.* reported a 17-fold increase of TFA in Beijing's landscape waters over recent years,⁶⁶ and Wu *et al.* suggested there are additional sources of TFA that are not well constrained.⁴⁹ The increase observed in Beijing from 2002 to 2012 ref. 66 was much larger than the increase observed by Pickard *et al.* in remote Arctic ice cores,²³ suggesting local sources and short-lived TFA precursors play an important role. The authors suggested the rapid increase in Beijing was caused by increased usage of the TFA precursor HFC-134a in local automobile air conditioners.⁶⁶

Many other chemicals form TFA in small quantities as byproducts of their synthesis or as degradation products. Fluorotelomer-based chemicals can form small yields of TFA depending on their perfluoroalkyl chain length,⁶⁷ and directly fluorinated high density polyethylene plastic can leach TFA as well as other fluorinated chemicals.⁶⁸ High concentrations of TFA have been reported in Sweden near firefighter training sites, landfills and hazardous waste management facilities, which show the impact of point sources into waterways.² In that study, Björnsdotter *et al.* reported the highest concentration of

14 000 ng L⁻¹ TFA near a fire fighter training facility, where aqueous film forming foams were used.² Although TFA is not an active ingredient in aqueous film forming foams, and to the best of our knowledge, has not been identified in a commercial foam product, this work shows that TFA is coming from aqueous film forming foam contamination either from its presence as a synthetic byproduct and/or the presence of TFA-precursors. Another source of TFA to the environment is the thermolysis of plastics including polytetrafluoroethylene (PTFE).^{69,70} Additionally, many common pesticides and pharmaceuticals contain CF_3 -substituted aromatic groups, which can be precursors to TFA. As of 2020, 18% of pharmaceuticals on the market contain organofluorine for a total of 340 molecules, and 54 of them contain a CF_3 -substituted aromatic group.⁷¹ Also as of 2020, 16% of agrochemicals that have ever been on the market contain organofluorine, for a total of 424 molecules, and 117 of them contain an aCF_3 -substituted aromatic group.⁷² Environmental transformation reactions often result in defluorination of the CF_3 group (*i.e.* F^- is observed), but sometimes TFA forms instead – these two products occur *via* two different reaction mechanism, that are impacted by pH and other conditions.⁷³ Scheurer *et al.* tested the biotransformation of a few suspected TFA-precursors and reported 30–40% conversion to TFA after 60 minutes from three drugs containing CF_3 -substituted aromatic groups: fluoxetine, flurtamone, fluopyram.²⁰ They also reported TFA formation of these three molecules upon ozonation, whereas other pesticides and pharmaceuticals tested whose CF_3 moiety was not on a benzene ring either produced no TFA or small amounts of TFA.²⁰ Another way TFA-precursors have been identified in landfill leachate is by using the total oxidizable precursor (TOP) assay, which identifies TFA-precursors using extreme oxidative conditions in the laboratory.⁷⁴

A mass balance approach to estimate the fraction of TFA in environmental samples that can be traced to anthropogenic sources is not reasonable given the wide range of TFA precursors. Much more work is necessary to fully understand the sources of TFA, which is more possible now with improved analytical techniques. The budgets determined in the late 1990s and early 2000s must be revisited in light of the recent experimental and observational evidence of additional TFA precursors.

Conclusions

Here, we have summarized the ubiquity of TFA throughout the environment, a lack of rigour in TFA measurements highlighting uncertainty on absolute concentrations in older studies, and have proposed plausible mechanisms that can transport TFA into “old” samples. Irrespective of analytical data quality, the presence of TFA in the deep ocean cannot itself be considered evidence of a naturally derived source. There is no data to support a natural geological source of TFA. Recent reports suggest we will continue to find additional novel TFA sources, and we must better constrain known sources to effectively understand its global burden. As scientists, it is our responsibility to ensure the foundation for scientific discussion

is supported by sound science. As discussion about TFA in the environment becomes popular, it is crucial to use correct language based on the most advanced scientific understanding. In probing the natural TFA paradigm, we conclude that based on the current available research, the notion of a natural source of TFA should not be invoked.

Conflicts of interest

There are no conflicts of interest to declare.

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