Insufficient evidence for the existence of natural trifluoroacetic acid

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Abstract

12   Trifluoroacetic acid (TFA) is a persistent and mobile pollutant that is present ubiquitously in the
13   environment. As a result of a few studies reporting its presence in pre-industrial samples and a
14   purported unaccounted source, TFA is often claimed to exist naturally. Here, we examine the
15   evidence for natural TFA by: (i) critically evaluating measurements of TFA in pre-industrial
16   samples; (ii) examining the likelihood of TFA formation by hypothesized mechanisms; (iii)
17   exploring other potential TFA sources to the deep ocean; and (iv) examining global budgets of
18   TFA. We conclude that the presence of TFA in the deep ocean and lack of closed TFA budget is
19   not sufficient evidence that TFA occurs naturally, especially without a reasonable mechanism of
20   formation. We argue the paradigm of natural TFA should no longer be carried forward.

Environmental significance

22   Trifluoroacetic acid (TFA) is an environmental contaminant that arises from multiple sources,
23   including the degradation of several regulated chemicals. Earlier studies proposed a natural
24   source of TFA to explain the presence of TFA in some environmental samples and the lack of a
25   balanced global budget. This paradigm has been propagated without sufficient evidence. This
26   critical review fully explores the literature and determines that there are no compelling scientific
27   arguments to support the existence of naturally formed TFA. Thus, in the absence of new
28   evidence, natural TFA should not be invoked in any discussions about the production and/or
29   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 of 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 phytoaccumulative[12] 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. [14–19]) but questioned by few (e.g. [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 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 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

71 field and laboratory blanks, method recovery efficiency, replicate analysis, standard reference
72 materials and clear data handling methods such as correcting for recovery or background
73 contamination. Our own research using ultra trace analysis of TFA in High Arctic ice caps has
74 underscored the importance of rigorous reporting and efforts to constrain as well as report
75 analytical artefacts.[23] Specifically, we want to know how the sampling was performed, and if
76 any fluorinated materials were used during sample collection, storage, or processing.

77   Four studies report TFA in pre-industrial freshwater and are summarized in Table 1. The
78 first study was by Jordan and Frank, in which TFA in old groundwater was below LOD whereas
79 TFA in newer groundwater and surface water was 70-320 ng/L.[24] Berg et al. used 15,000-year-
80 old groundwater as a method blank for their measurements of TFA in rainwater and surface
81 waters and did not observe TFA above the detection limit of 5 ng/L.[25] Similarly, Nielsen et al.
82 reported no detectable TFA in ~2000-year-old groundwater and ice cores dated to 4191 ± 20
83 years, with a detection limit of 2 ng/L.[26] Unlike these three papers, Von Sydow et al. reported
84 TFA concentrations of 6-56 ng/L in 190-year-old Antarctic firn and 5 ng/L in glacier ice from
85 Sweden that formed ~500 years ago.[27] No obvious relationship was observed between
86 concentration and depth in the firn core. Furthermore, the anthropogenic organochlorine
87 insecticide lindane, and alkyl phosphate flame retardants were noted in the same glacier samples
88 which presents significant concern regarding data quality. Collectively these data suggest that
89 the data quality was hampered by modern contamination or that there were problems in the
90 dating methods used to assign age. Despite these limitations, the authors conclude that based on
91 these data, TFA must have a natural source. Closer scrutiny of the reported analytical methods
92 indicates flaws based on the first principles of quantitative analysis. All sample concentrations
93 were extrapolated below their lowest calibration standard, which was 100 ng TFA into 10 mL
94 water, resulting in a final concentration of 1000 ng/mL after sample processing.[27] There was no
95 apparent effort to determine whether the linear range of the calibration curve extended below this
96 calibration standard. The authors define their LOD and LOQ based on their laboratory blanks,
97 but the limited range of calibration standards indicate extrapolation was employed to quantify
98 TFA in the blanks (as well as the samples).[27] Overall, our conclusion from these reports is that
99 there is no defensible evidence of any freshwater TFA in the pre-industrial period.

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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)	LOD	Notes
Groundwater[24]	Antonien, Kondrau (Bavaria, Germany)	>700	Pre-1300 CE	ND (3)	10 ng/L	No information provided about methods for sample collection.
	Bayern, Kondrau (Bavaria, Germany)	~200	~1800 CE	23 ± 3 ng/L (5)		
	Thuringer Wald, Kondrau (Bavaria, Germany)	400 ± 60	1596 ± 60 CE	ND (3)		
	Rennsteig, Kondrau (Bavaria, Germany)	185	1811 CE	13 ± 3 ng/L (3)		
Groundwater[25]	Small aquifer in N Switzerland	15000 ± 1800	13,000 ± 1800 BCE	ND (3)	5 ng/L	Details about sample collection and dating in[28]
Firn[27]	Various depths, Maud Land, East Antarctica	~190 to present	~1806-1997 CE	6 – 56 ng/L (11)	1 ng or 1 ng/L*	Fluoropolymer used in sample preparation. LODs and sample concentrations reported below calibration standards.
Glacier[27]	Marmaglaciaren, Sweden	>500	Pre-1500 CE	5 ng/L		
Groundwater[26]	Grundfoer, Denmark	~2000	~ 0 CE	ND (3)	2 ng/L	Dated using radiocarbon in dissolved CO_2.
Ice core[26]	Summit, Greenland	4191 ± 20	2199 ± 20 BCE	ND (2)		Chemical analysis of ice core from well documented standard archive.

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

Deep ocean samples that were presumed to be uninfluenced by anthropogenic pollution
have been analyzed for TFA and are summarized in Figure 2. Frank et al. reported TFA
concentrations consistently ~ 200 ng/L regardless of location or depth, down to 4150 m in the
mid-Atlantic Ocean, and down to 2000 m in the Southern Ocean (Antarctica).[29] 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 ± 5 ng/L, 34 ± 1 ng/L, 33 ± 3 ng/L, respectively).
These concentrations are high, and higher than the pre-industrial freshwater in Table 1. The

116   authors corrected the measured TFA concentrations in ocean water by subtracting the field blank
117   corresponding to the sample, whether it was the 1998 old mineral water, or the 1999 artificial
118   seawater in glass or polypropylene bottles. The authors define their LOD (20 ng/L) and LOQ (32
119   ng/L) as the mean concentration of TFA in deionized water laboratory blanks of (8 ng/L) plus
120   three times the standard deviation (4 ng/L) for LOD or plus 6x the standard deviation for LOQ. It
121   would be more correct to define LOD and LOD based on the concentrations of TFA in the field
122   blanks because this accounts for the entire sample handling process. The lowest calibration
123   standard was 28 ng/L, suggesting they reported concentrations in their quality control blanks
124   below their lowest calibration standard; however, the samples were above the lowest calibration
125   standard. In this study, the oldest samples were aged as >60 years old. Their dating was limited
126   by the use of chlorofluorocarbon (CFC) levels in the water, which has a lower limit of 1940,
127   approximately 60 years before the samples were collected. The authors concluded that only a
128   pre-industrial TFA source (i.e. natural source) could explain the consistent TFA concentrations
129   measured in waters >60 years old.

130   Scott et al. collected depth profiles from several oceans to provide a more comprehensive
131   picture of global oceanic TFA.[30] They observed different trends in TFA depth profiles in
132   different locations, as shown in Figure 2, with much more variable concentrations than Frank et
133   al.,[29] including multiple sites with much lower concentrations. For example, in the Atlantic
134   Ocean, TFA ranged from 20 to 200 ng/L from 23 °N, 20 °W to 38 °N, 73°W. This variability is
135   consistent with more recent analysis of PFAS profiles in ocean sampling across extensive
136   latitudinal gradients.[31–33] Similar to the work of Frank et al.,[29] Scott et al. reported relatively high
137   concentrations of TFA (>100 ng/L) deep into the South Atlantic.[30] An additional objective of
138   Scott et al. was to test the hypothesis that deep sea vents could be a source of TFA into the
139   ocean, and these results will be discussed below.[30] The works of Frank et al.[29] and Scott et al.[30]
140   demonstrate that TFA can be found in the deep ocean. A limitation of these studies was that they
141   did not consider plausible TFA delivery mechanisms from ocean depths representing modern
142   times to the deep ocean.

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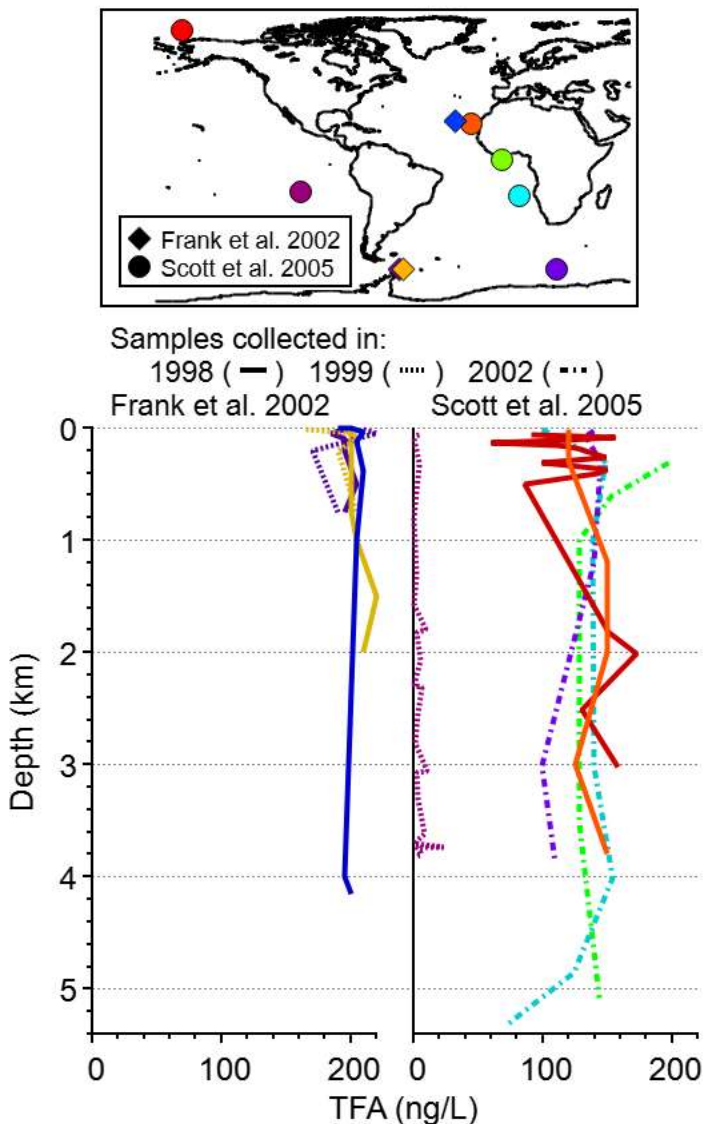
Figure 1. Ocean depth profiles of TFA concentrations redrawn from Frank et al. (left)[29] and Scott et al. (right).[30] For the Scott et al.[30] data, only profiles with a depth of 1500 m or greater were included. Line colours correspond to sampling locations shown in the top panel, and line styles correspond to year of sample collection.

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,[34] including by those working in the fluorocarbon industry.[6,13] However, similar to Frank et al. and Scott et al.,[29,30] 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]

158   Another line of evidence for natural TFA used by the fluorocarbon industry[13] is
159   measurements of TFA from four archived soil samples from Rothamsted Agricultural Research
160   Station, dating from 1865, 1881, 1944, and 1956, which reported concentrations of 0.51, 0.55,
161   <0.1 and 0.35 ng/g TFA (dry weight), respectively.[35] Here, the method details are incongruous
162   whereby the authors report a method limit of detection of 1 ng/g based on a 10-g sample,
163   suggesting either all of the sample results are below the limit of detection, or they extracted
164   upwards of 100 g of sample. The inconsistency and ambiguity underscore the responsibility of
165   researchers to report rigorous methods, which we have highlighted as a limitation for many early
166   TFA studies. Peer reviewers and journal editors also share a responsibility to insist on the
167   inclusion of rigorous and reproducible methodologies in publications. Additionally, the oldest
168   sample from 1865 contained unexpectantly high concentrations of other haloacetic acids, notably
169   315 ng/g of dichloroacetic acid, suggesting it was likely contaminated. As demonstrated by early
170   research analyzing TFA in aqueous samples, lab blanks tended to have high TFA concentrations.
171   As such, additional skepticism is incurred by the absence of any reported blanks in this study.
172   Taken together, this stand-alone paper purporting a natural source of TFA in old soil is not
173   supported by sufficient evidence. Overall, the origins of the natural TFA source paradigm are
174   largely based on the observation of TFA in pre-industrial samples, but no studies present a
175   plausible mechanism for formation of TFA from natural sources.

Proposed natural source to deep ocean

177   Of the thousands of organofluorine molecules found in the environment, the vast majority
178   are solely anthropogenic. Harnisch et al.[36] observed that several fluorine-containing gases were
179   liberated from the mineral fluorite (CaF_2) upon grinding. The fluorinated gases observed were
180   CF_4, NF_3, and SF_6, along with several CFCs. The presence of CF_4 and other fluorinated gases has
181   been observed in a few studies examining tectonically active areas on the continents.[37–40]
182   Evidence of enrichment of fluorinated gases has been sought but not found in other studies of
183   volcanic emissions,[41–43] indicating the heterogeneous nature of their emission. This heterogeneity
184   has been attributed to the natural variability in fluorine content,[42,43] which is found primarily in
185   the form of the mineral fluorite. Fluorite is found on continents in deposits typically near major
186   faults or as an accessory mineral in granites,[42] and is not found in the deep ocean. Although CF_4
187   has been observed to be released from geologic processes, evidence of this occurring in the deep
188   Pacific Ocean was sought but not found.[44] Instead, all observed CF_4 could be attributed to
189   dissolution from the atmosphere.[44]

190   In the same study in which fluorine-containing gases were measured from crushed
191   fluorite, the authors cite conference presentations of deep ocean observations of TFA (early
192   version of [30]) and propose that fluorite *"is a source of natural TFA analogous to natural CF4."*
193   There have been no experimental or observational reports of fluorite being a source of TFA
194   under environmental conditions. In addition, the parallel drawn between TFA and CF_4 ignores
195   basic chemistry. Whereas CF_4, NF_3, and SF_6 can all be formed under the anoxic conditions
196   common in magmatic and hydrothermal fluids, production of TFA from fluorite would require
197   an oxygen source for its formation. Observations of CF_4 production solely from continental
198   fluorite does not provide a convincing foundation for TFA production in the deep ocean from

199 anoxic hydrothermal vents. The deep ocean TFA measurements by Scott et al. included
200 measurements of four profiles over geologically active areas (Figure 2) based on the hypothesis
201 that deep sea vents or underwater volcanoes could act as a natural source of TFA.[30] Here, we
202 delve into this data and the plausibility of their implications. Three vent profiles were collected
203 in the Pacific Ocean and one in the Mediterranean Sea (Figure 2). All vent profiles have TFA
204 concentrations within the range reported from depth profiles without vents in the Atlantic,
205 Arctic, and Southern Oceans (Figure 1). For most vent locations, no measurements exist in a
206 similar location in the absence of vents for direct comparison. One exception is the South
207 Pacific, where a single non-vent depth profile was collected (Figure 2). The South Pacific non-
208 vent depth profile is distinct from all other ocean profiles (Figure 1) emphasizing the importance
209 of potential spatial heterogeneity on the interpretation of the data. The South Pacific vent and
210 non-vent depth profiles are shown together in Figure 2b. If the vents were a significant source of
211 TFA, we might expect higher concentrations of TFA at the deepest depths near the vents, but the
212 profiles do not show this. Overall, the TFA depth profiles measured above active vents reported
213 in this single study are not persuasive of a natural TFA source.

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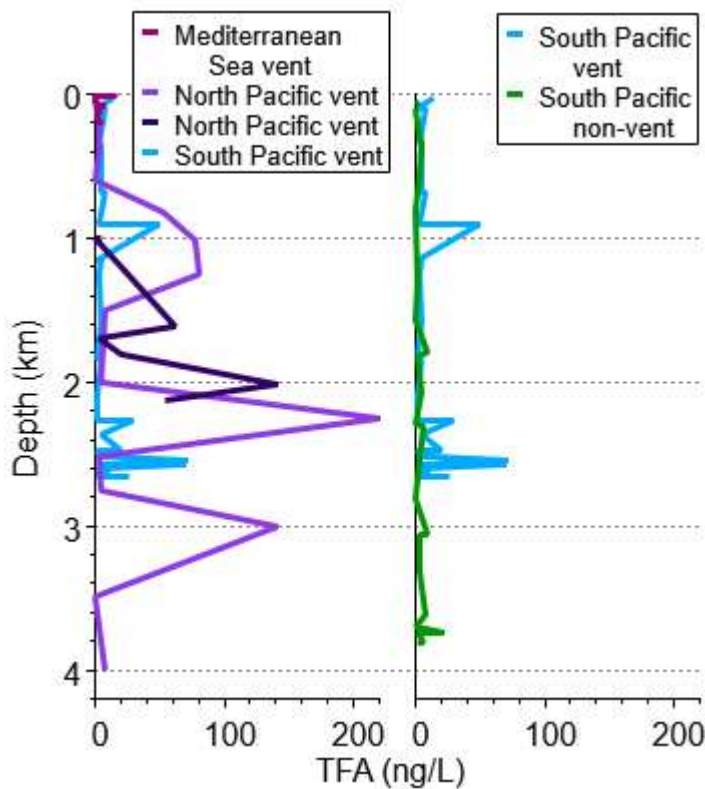
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216 **Figure 2**. Profiles measured above vents redrawn from Scott et al.[30] Left panel shows all four
217 vents (note that Mediterranean site is quite shallow). Right panel shows S Pacific vent site vs S
218 Pacific non-vent site. For all other vent locations, we do not have a non-vent profile for
219 comparison.

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Other possible sources to deep ocean

Many anthropogenic pollutants have been found in the deep ocean since the measurement of TFA, including radionuclides,[45,46] persistent organic pollutants,[34,47–50] heavy metals,[51] and microplastics.[52] Other PFAS have also been observed in the deep ocean,[53,54] 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 conveyer belt. This is well established to carry dissolved gases (e.g. CFCs[55]) to the deep ocean and has been suggested to contribute to deep-ocean observations of POPs (e.g. polychlorinated biphenyls (PCBs),[49] Figure 3). Measurements and models have also shown that meridional overturning circulation delivers PFAS to the deep ocean (Figure 3).[53,54] 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.[56] These intermittent transport events can occur in all the world's oceans[56] and have been shown to efficiently deliver contaminants, including persistent organic pollutants[57] and several PFAS,[58] from coastal regions to the deep sea.[59] 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 pollutants[47] (e.g. PCBs,[34,48,50] polybrominated diphenyl ethers,[34,48] organochlorine pesticides,[34]), heavy metals,[51] radionuclides,[46] and microplastics.[52] Studies have shown that PFAS can accumulate in plankton[60] and that sinking of plankton can transport PFAS from the surface ocean.[33] 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.
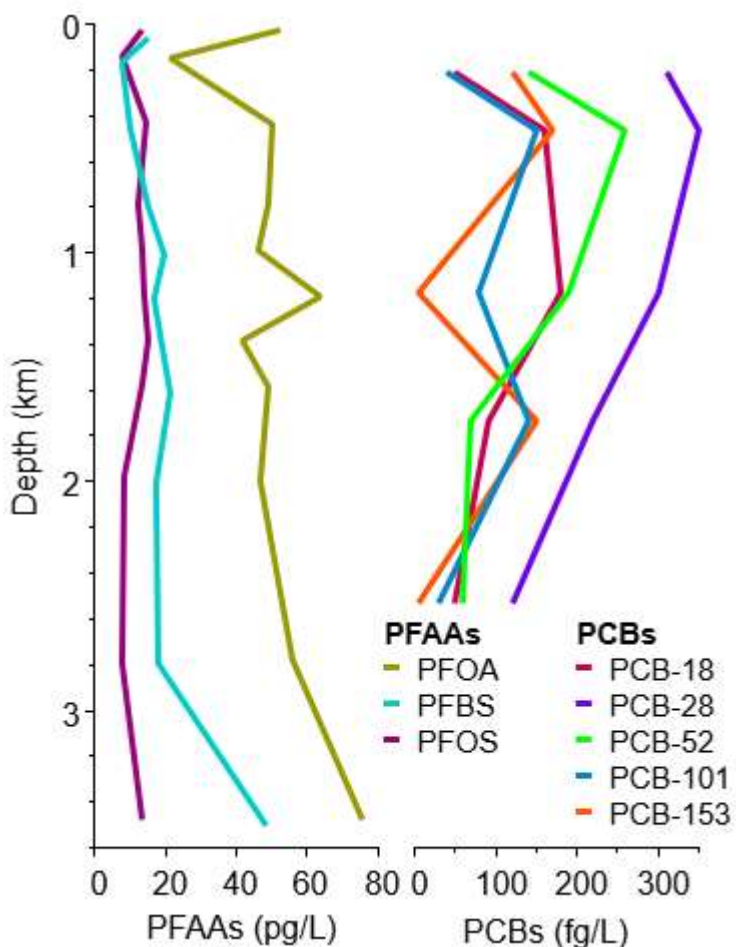
Figure 3. North Atlantic Ocean depth profiles of persistent compound concentrations. PFAAs (perfluorobutane sulfonate (PFBS), perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA)) measured at 56.6 N, 52.8 W in 2004 and reported in Yamashita et al.[54] PCBs (PCB-18, -28, -52, -101, -153) measured at 79 N, 4 E for ~1 year from July 2012 - 2013 and reported in Sun et al.[49]

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 and an ocean volume of 1.34×10^{21} L, resulting in a total of 268×10^6 tonnes of TFA in oceans.[29] 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

268 Arctic Ocean.[30] The authors calculated the total TFA burden using high and low values for
269 Atlantic and Pacific deep water, ultimately reporting a lower total oceanic TFA burden than
270 Frank et al. of $(61 - 205)$ x 10^6 tonnes. Such estimates are speculative as the calculated TFA
271 burdens are based on extrapolation of uncertain concentrations using unrealistic assumptions of
272 spatial homogeneity throughout the ocean, and that their limited measurements are the most
273 representative. The propagation of error in this workflow results in a highly uncertain burden.

274   Poor source apportionment of TFA does not specifically support or refute the presence of
275 a natural source. Most anthropogenic contaminants do not have comprehensively characterized
276 budgets, including those with more widespread and simpler measurements. From a wider
277 perspective, the global biogeochemical cycle of elemental fluorine was only first published in
278 2020.[61] TFA is released both directly into the environment and indirectly via reactive
279 precursors.[24,62] Some reactive precursors are emitted into the gas phase, where they are oxidized
280 predominantly by hydroxyl radicals to form TFA.[63] Like other strong acids, TFA is primarily
281 removed by wet and dry deposition.[14,25] Other precursors are emitted into surface waters, where
282 they are oxidized via hydrolysis or via biological processes.[62] The long-range transport potential
283 and reactivity of different precursors impact the quantity and location of TFA production, in
284 addition to TFA being transported itself.[22,63,64] Among the most important atmospheric
285 precursors to TFA are heat transfer fluids, such as hydrochlorofluorocarbons (HCFCs) and
286 hydrofluorocarbons (HFCs), that have been introduced as replacements for CFCs through the
287 Montreal Protocol and subsequent amendments.[23,65] The atmospheric formation of TFA from
288 these chemicals has been the subject of many studies and the resulting environmental burden is
289 reasonably well constrained.[16,63]

290   However, more sources are being identified, such as recently, when a surprising amount
291 of HCFC-133a (CH_2ClCF_3) was found in East Asia, likely as a byproduct of chemical production
292 processes, updating the global emissions of this TFA precursor to 2300 tonnes/year from 2016-
293 2019.[66] A 2021 paper used a global three-dimensional chemical transport model to investigate
294 the changes in global TFA from the transition of HFC-134a (CF_3CH_2F) to a hydrofluoroolefin,
295 HFO-1234yf (CF_3CFCH_2), and found that this change resulted in a 33-fold increase in the global
296 burden of TFA when the 2015 emissions were used (i.e. 65 tons/year for HFC-134a vs 2200
297 tons/year for HFO-1234yf).[22] Fast reaction of HFO-1234yf to TFA was observed to result in a
298 250-fold increase of urban surface level TFA concentrations across Europe.[22] Zhai et al. reported
299 a 17-fold increase of TFA in Beijing's landscape waters over recent years,[67] and Wu et al.
300 suggested there are additional sources of TFA that are not well constrained.[50] The increase
301 observed in Beijing from 2002 to 2012[67] was much larger than the increase observed by Pickard
302 et al. in remote Arctic ice cores,[23] suggesting local sources and short-lived TFA precursors play
303 an important role. The authors suggested the rapid increase in Beijing was caused by increased
304 usage of the TFA precursor HFC-134a in local automobile air conditioners.[67]

305   Many other chemicals form TFA in small quantities as byproducts of their synthesis or as
306 degradation products. Fluorotelomer-based chemicals can form small yields of TFA depending
307 on their perfluoroalkyl chain length,[68] and directly fluorinated high density polyethylene plastic
308 can leach TFA as well as other fluorinated chemicals.[69] High concentrations of TFA have been

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309 reported in Sweden near firefighter training sites, landfills and hazardous waste management
310 facilities, which show the impact of point sources into waterways.[2] In that study, Björnsdotter et
311 al. reported the highest concentration of 14,000 ng/L TFA near a fire fighter training facility,
312 where aqueous film forming foams were used.[2] Although TFA is not an active ingredient in
313 aqueous film forming foams, and to the best of our knowledge, has not been identified in a
314 commercial foam product, this work shows that TFA is coming from aqueous film forming foam
315 contamination either from its presence as a synthetic byproduct and/or the presence of TFA-
316 precursors. Another source of TFA to the environment is the thermolysis of plastics including
317 polytetrafluoroethylene (PTFE).[70,71] Additionally, many common pesticides and pharmaceuticals
318 contain CF_3-substituted aromatic groups, which can be precursors to TFA. As of 2020, 18% of
319 pharmaceuticals on the market contain organofluorine for a total of 340 molecules, and 54 of
320 them contain a CF_3-substituted aromatic group.[72] Also as of 2020, 16% of agrochemicals that
321 have ever been on the market contain organofluorine, for a total of 424 molecules, and 117 of
322 them contain an aCF_3-substituted aromatic group.[73] Environmental transformation reactions
323 often result in defluorination of the CF_3 group (i.e. F^- is observed), but sometimes TFA forms
324 instead – these two products occur via two different reaction mechanism, that are impacted by
325 pH and other conditions.[74] Scheurer et al. tested the biotransformation of a few suspected TFA-
326 precursors and reported 30-40% conversion to TFA after 60 minutes from three drugs containing
327 CF_3-substituted aromatic groups: fluoxetine, flurtamone, fluopyram.[20] They also reported TFA
328 formation of these three molecules upon ozonation, whereas other pesticides and
329 pharmaceuticals tested whose CF_3 moiety was not on a benzene ring either produced no TFA or
330 small amounts of TFA.[20] Another way TFA-precursors have been identified in landfill leachate is
331 by using the total oxidizable precursor (TOP) assay, which identifies TFA-precursors using
332 extreme oxidative conditions in the laboratory.[75]

333   A mass balance approach to estimate the fraction of TFA in environmental samples that
334 can be traced to anthropogenic sources is not reasonable given the wide range of TFA precursors.
335 Much more work is necessary to fully understand the sources of TFA, which is more possible
336 now with improved analytical techniques. The budgets determined in the late 1990s and early
337 2000s must be revisited in light of the recent experimental and observational evidence of
338 additional TFA precursors.

339

Conclusions

341   Here, we have summarized the ubiquity of TFA throughout the environment, a lack of
342 rigour in TFA measurements highlighting uncertainty on absolute concentrations in older studies,
343 and have proposed plausible mechanisms that can transport TFA into "old" samples. Irrespective
344 of analytical data quality, the presence of TFA in the deep ocean cannot itself be considered
345 evidence of a naturally derived source. There is no data to support a natural geological source of
346 TFA. Recent reports suggest we will continue to find additional novel TFA sources, and we must
347 better constrain known sources to effectively understand its global burden. As scientists, it is our
348 responsibility to ensure the foundation for scientific discussion is supported by sound science.
349 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.

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