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Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs

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The partly halogenated C_2-hydro(chloro)fluorocarbons (HFC, HCFC) 1,1,1-trifluoro-2,2-dichloroethane (HCFC-123), 1,1,1,2-tetrafluoro-2-chloroethane (HCFC-124), and 1,1,1,2-tetrafluoroethane (HFC-134a) are CFC substitutes found at increasing levels in the atmosphere. Trifluoroacetate (TFA) is an atmospheric degradation product of these compounds and due to its perstistence its potential accumulation in some aquatic ecosystems is a matter of environmental concern. The present study was undertaken to determine the present-days base level of environmental TFA and whether model calculations are in line with the actual data. Average levels of about 120 ng L^{-1} as predicted for the year 2010 are found in rain in Germany already now, slightly higher than in rain collected in Switzerland or Nevada. In the major rivers in Germany, TFA is present at average concentrations of 140 ng L^{-1}. In air, levels of 45−60 pg m^{-3} have been found in Central Europe. Between March 1995 and September 1996, a period of substantial increase in atmospheric HFC-134a mixing ratio, the TFA concentrations in air and precipitation did not significantly increase. TFA is absent in old groundwater samples, and in river water from remote locations, concentrations are low. These data suggest that the total TFA in both compartments exceeds the formation potential of currently known sources, that TFA in atmosphere and rain is regionally associated with industrial or population density, and that other unresolved sources must contribute to the present concentrations.

Introduction

The role of chlorofluorocarbons in the depletion of stratospheric ozone (*1*, *2*) has led to an international agreement to discontinue their production (*3*). Partially fluorinated ethanes with relatively short atmospheric residence times are now being introduced as alternatives. Atmospheric concentrations of 1,1,1,2-tetrafluoroethane (HFC-134a), the prominent CFC replacement compound for automotive air conditioning and domestic refrigeration which began to be produced in 1990, have been steadily increasing (*4*, *5*). The most significant rise in atmospheric concentrations was from 1994 onward, a result of increased production volumes and subsequent emission. Investigation of the environmental fate of this compound (*6*), especially of its atmospheric lifetime (e.g. ref *7*) and its degradation products (e.g. ref *8*), has revealed trifluoroacetyl fluoride (CF_3COF) as a major end product. Its yield depends on temperature and pressure and amounts to 7−20% averaged over the troposphere (*9*). Trifluoroacetyl fluoride is taken up by clouds, hydrolyzed to TFA within days (*10*), and wet-deposited to land and ocean surfaces. The CFC substitutes HCFC-123 (CF_3CHCl_2) and HCFC-124 (CF_3CHClF) are converted to trifluoroacetyl halides with higher yields (*11*, *12*), but these substances are manufactured in lower quantities.

Laboratory investigations have suggested that TFA could be reductively metabolized under methanogenic conditions in sediments (*13*), but others have failed to detect any microbial or abiotic degradation of TFA under environmental conditions (*14, 15*). Behavior in soils is similar to that of chloride and bromide, i.e., TFA is only slightly retained (*16, 17*). It seems to persist in the hydrosphere and is taken up by higher plants (*17, 18*) and trees with the transpiration water, accumulating in leaves and needles of conifers.

Model calculations predict global mean TFA concentrations in precipitation in Europe of about 14 ng L^{-1} in 1995 (*19*) and of 120 ng L^{-1} in 2010 (*10*). These latter levels are already reached now; TFA analyses in Southern Germany (*20, 21*) show concentrations ranging from 10 to 200 ng L^{-1} in precipitation and from 60 to 600 ng L^{-1} in surface waters. Similar data have been reported recently for the Western United States (*22, 23*). These observations imply that the global environmental inventory of TFA is much higher than the amounts resulting from the degradation of presently known precursors.

The aim of this work was to extend the database of environmental TFA concentrations in order to enable global budget estimations. Air, precipitation, and river water samples have been taken regularly and analyzed for TFA from March 1995 to September 1996 in Bayreuth (Northern Bavaria, Germany). Surface and ocean waters from several other locations and continents have also been analyzed as well as groundwater samples of preindustrial origin.

Experimental Section

Sampling. All glass ware used for sampling and cleanup was thoroughly washed with hot tap water and deionized water. It was stored at 280 °C in an oven and cooled prior to use in a closed glove compartment, both flushed with air purified by passage through cartridges filled with activated charcoal and potassium hydroxide.

Rain samples were collected in the botanical garden of the University of Bayreuth from May 1995 to June 1996 using Pyrex glass funnels (diameter 40 cm) and 500-mL brown glass bottles. From May 1996 to September 1996, samples of canopy runoff were collected from a conifer forest and from a clearing nearby.

Surface water samples were collected in 250-mL brown glass bottles with screw-caps lined with Teflon-laminated butyl-rubber disks. After rinsing five times with the water of the location, the bottle was filled by immersion leaving about 1 mL of air space under the lid.

Air samples were collected using glass denuder tubes (2.5 m × 1 cm id) consisting of five segments of 0.5 m length connected with ground-joints and Teflon sleeves on both ends. The denuders were coated with aqueous saturated solution of sodium carbonate in glycerol (*20*) which was always done at the sampling site to avoid contamination from laboratory air. Three denuders were run in parallel, each one connected to a membrane pump (N 035.1.2 AN 18, KNF Neuberger, Freiburg, Germany) followed downstream by a gas-volume counter (NBG, Kromschröder, Osnabrück, Germany). In most cases, air volumes of 50−60 m^3 per

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denuder were sampled in the course of 5 days at flow rates of 7−8 L min^{-1} through each tube. The glycerol film containing the entrapped acids was then eluted with five portions of 2 mL deionized water into a 20-mL test tube with its ground-joint directly connected to the front end of the denuder.

Sample Preparation. For analysis, an aliquot of 10 mL of aqueous samples or denuder eluate was taken in the clean-air glove compartment and transferred with a volumetric pipet to a 20-mL test tube with ground-joint stopper. The actual sample volume was determined by weight. Analyses were always performed in triplicate within 1 day of sample collection, except for those samples collected at remote sites. Sets of 15−20 actual samples, three blank samples (10 mL deionized water), and seven calibration samples were always processed in parallel. A volume of 100 μL of a solution of 100 ng mL^{-1} pentafluoropropionic acid (PFP) in deionized water was added to each sample as internal standard. Sodium chloride (2 g) and concentrated sulfuric acid (350 μL) were added, and trifluoroacetic acid was extracted with 1 mL of *tert*-butyl methyl ether by agitation with a test tube mixer for 60 s. After standing for 10 min, 0.9 mL of the supernatant ethereal extract was placed in a silanized 1-mL crimp-cap vial containing 10 μL of a solution of 200 μmol mL^{-1} 1-(pentafluorophenyl)diazoethane (*24*) in *tert*-butyl methyl ether. Derivatization was complete within 1 h at room temperature.

The extraction efficiency was determined as 92 ± 3% by spiking river and North Seawater in the concentration range of 20−3500 ng L^{-1}. Further details of the analytical method have been desribed elsewhere (*25*).

GC-MS Determinations. GC-MS analyses were performed on a gas chromatograph interfaced to a quadrupole mass spectrometer equipped with chemical-ionization source (Model 5989 A, Hewlett-Packard, Walnut Creek, U.S.A.). Aliquots of 3 μL of the derivatized sample were injected onto a deactivated fused-silica retention gap (50 cm × 0.53 mm). Gas chromatographic separation was carried out on a fused-silica column coated with methyl-phenyl-(5%)-silicone (CP-Sil 8 CB-MS, 25 m × 0.25 mm, film thickness 0.25 μm; Chrompack, Middelburg, The Netherlands).

Helium was used as carrier gas at an inlet pressure of 80 kPa. The initial oven temperature was 65 °C for 1 min, followed by a temperature program of 25° min^{-1} to 159 °C, 1° min^{-1} to 161 °C, 25° min^{-1} to 240 °C, 2 min isothermal. The ion source temperature was 200 °C; methane (purity 99.95%) was the reactand gas. TFA and the internal standard were detected in the selected-ion monitoring mode as carboxylate anions (TFA: $m/z = 113$; PFP: $m/z = 163$).

Calibration. Each calibration series included seven TFA standard samples ranging from 20 to 4000 ng L^{-1}. Relative response factors are known to be variable in the negative chemical-ionization mode; therefore, after each series of 20 samples, a calibration run was included, and response factors were determined by interpolation.

Results

Air, precipitation, and river water samples were collected in Bayreuth from March 1995 to September 1996. The results are given in Figures 1−4.

TFA in Air. Air levels ranged from 10 to 125 pg m^{-3}, with an average value of 44 pg m^{-3} (Figure 1). Similar levels have been determined in air sampled on the Vista-University campus in Mamelodi (40 pg m^{-3}) near Pretoria, South Africa, in August 1996; in Zuerich, Switzerland (65 pg m^{-3}), in September 1995; and at Waldstein, Northern Bavaria, Germany (20−40 pg m^{-3}), in June 1995 (*21*).

TFA in precipitation. TFA concentrations in precipitation collected at the Botanical Garden of the University of Bayreuth and on a forest clearing about 0.5 km to the south ranged from 10 to 410 ng L^{-1} with an average of 110 ng L^{-1}, one sample having a concentration below determination limit (10 ng L^{-1}) (Figure 2). Comparison of TFA levels in rain samples collected in summer 1995 and in summer 1996 seem to suggest an upward trend, although statistically not significant. TFA levels in rain samples from Switzerland (50−

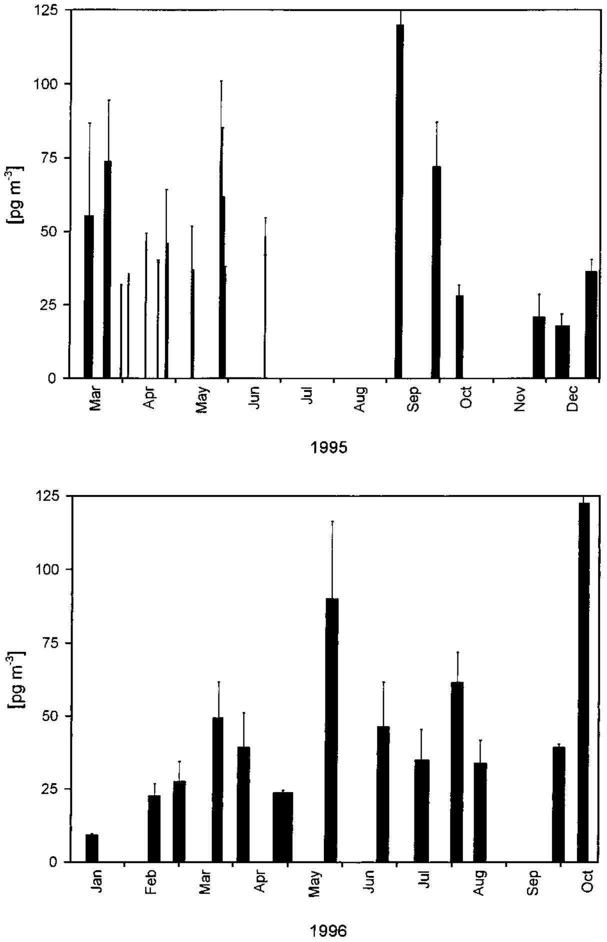

FIGURE 1. Trifluoroacetate in ambient air near Bayreuth, Germany in 1995 (a) and 1996 (b). The height of each sample bar represents the average of three replicate analyses; when no standard deviations are indicated, only one analysis was performed. The width of each bar corresponds to the length of the sampling period.

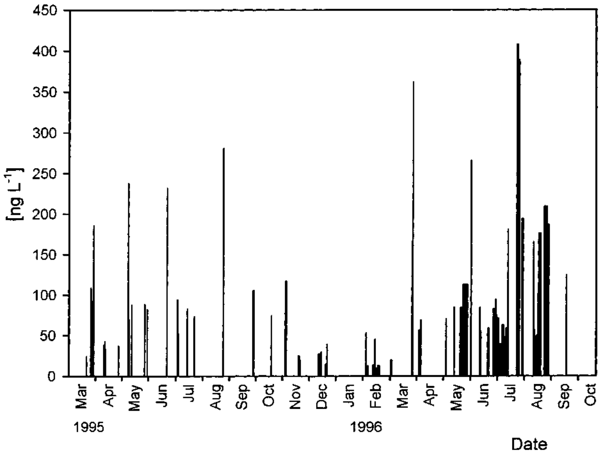

FIGURE 2. Trifluoroacetate in precipitation near Bayreuth in 1995 and 1996. The width of each bar corresponds to the length of the respective rain/snowing period; The values represent the means of three replicate analyses (relative standard deviations about ±15%).

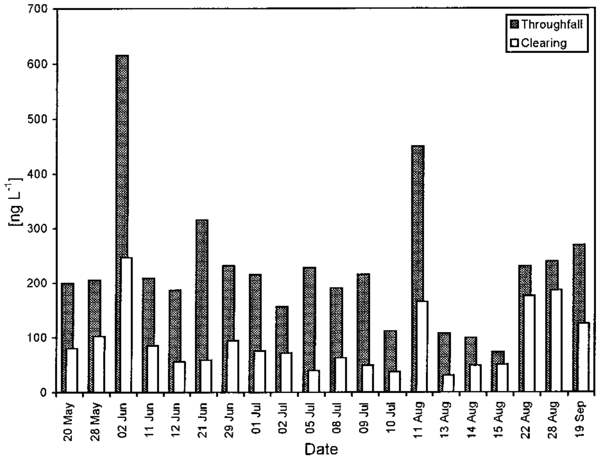

FIGURE 3. Trifluoroacetate in free-falling precipitation and canopy throughfall collected on a forest clearing and in a spruce forest near Bayreuth.

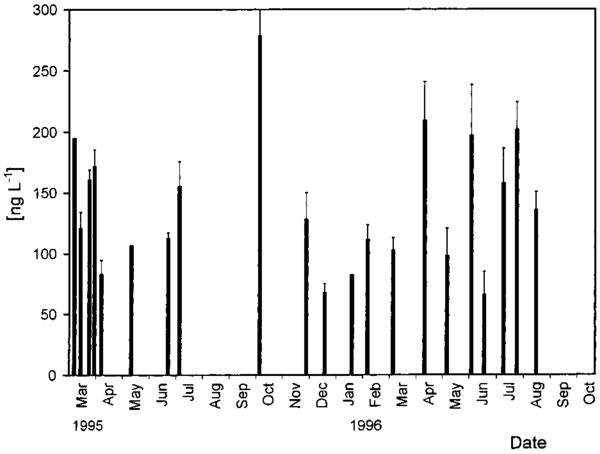

FIGURE 4. Trifluoroacetate in the River Roter Main at Bayreuth; the errors bars indicate the standard deviations of the average of three independent samples.

80 ng L^{-1}) (*21)* and Nevada (30−90 ng L^{-1}) (*22, 23*) have been in a similar range. TFA was below determination limit in four rainwater samples collected at Mace Head, Ireland, in October 1995 and in surface runoff water collected after heavy rainfall near Oudtshoorn, South Africa, in October 1996.

Canopy throughfall of a conifer forest was generally higher in TFA by a factor of 2.6 than rain samples collected in parallel on a nearby clearing (Figure 3). This is indicative of evaporative concentration of rain on leaves and needles before collection as canopy throughfall; dry deposition on plant surfaces and subsequent rinse-off or leaching of TFA from needles may also contribute. However, further studies are necessary of the effects of the intensity and duration of precipitation on TFA levels in canopy throughfall as well as studies on dry deposition fluxes.

TFA in River Water. Water collected in Bayreuth from the Roter Main River contained TFA ranging from 60 to 280 ng L^{-1} (average 140 ng L^{-1}) (Figure 4). This is similar to concentrations previously reported for eight other German rivers (*21)* (Table 1). The average concentration in river water is 1.3-fold higher than that in precipitation; since evaporation of hydrometeors should entail a concentration increase slightly higher than 2-fold for Germany, this suggests a sink for TFA either in the form of a so far unaccountable depot or an unknown removal process.

TFA concentrations in the Kemijoki River (Rovaniemi, Finland) near the polar circle were 210 ng L^{-1}, suggesting a significant contribution of Central European air masses to subarctic TFA-deposition due to prevailing southwesterly winds. In contrast, the Jennessej River (Krasnojarsk, Siberia) contained only 40 ng L^{-1} in July 1996.

Surface waters were collected on the southern hemisphere in Brazil and South Africa in August 1996. TFA was not detected in water samples from the Rio Tocantins (Cotijuba, Brazil) or from a small river near Tweede Tol (Hottentot-Mountains, South Africa) but was present in the Apies River (15 km north of Pretoria, South Africa) at 500 ng L^{-1} and in the Vaal River (Christiana near Kimberley) at 100 ng L^{-1}. An intermediate level of 40 ng L^{-1} was found in a freshwater pond in the Golden Gate Nationalpark about 300 km south of Johannesburg South Africa (Table 1).

TFA in Ocean Water. TFA levels of 70 and 250 ng L^{-1} respectively were determined in Atlantic Ocean water collected directly from the shore at Mace Head (Ireland) and of the Ile d'Yeu (France) in 1995. South Atlantic Ocean water taken at Cape Point (Cape of Good Hope, South Africa) contained 160 ng L^{-1}, Pacific Ocean water at Noosa Heads 200 ng L^{-1} (50 km north of Brisbane, Australia).

TFA in Spring and Well Water. TFA levels in spring waters of young age have been found in the same range as surface waters. In groundwater of known old age as determined by radioisotope analysis, TFA was very low (Table 2). Two samples with negligible freshwater contents ($<$1%) ("Antonien Quelle" and "Thüringer Wald Quelle") had TFA at blank levels. The "Bayern Quelle" and the "Rennsteig Quelle" with young water contents of 10% and 15%, respectively, had levels of 13 and 25 ng L^{-1}.

Discussion

TFA as Degradation Product of HFC-134a, HCFC-123, and HCFC-124. The tropospheric lifetime of HFC-134a is about 14 years leading to global distribution of the compound. Currently an interhemispheric gradient in HFC-134a concentrations of about 2 is observed due to rapidly increasing emissions on the northern hemisphere (NH). Abundances of 3 pptv (NH) in the end of 1995 have been reported (*5*) resulting in an inventory of 22 000 t HFC-134a in the northern hemispheric troposphere (NH tropospheric mass: 7.2 10^{19} mol) when assuming uniform distribution. At an average tropospheric temperature of 277 K, 8% degradation per year is calculated ($k_{OH} = 3.3 \times 10^{-15}$ cm^3 molec^{-1} s (*7*); $c_{OH^{\bullet}} = 8.5 \times 10^5$ molec cm^{-3}). Rainfall on the northern hemisphere amounts to 2.5 × 10^{17} L per year (*26*) resulting in an average TFA concentration of 7 ng L^{-1}. Rain samples collected in Bayreuth, Germany, near Zurich, Switzerland, and near Reno, Nevada, U.S.A., all contain TFA at higher levels, suggesting that HFC-134a is not the sole source of TFA.

Kotamarthi et al. (*19*) expect HCFC-123 and HCFC-124 to be the dominant source of TFA in 1995 due to their short atmospheric lifetimes. They calculated a western European average of 14 ng L^{-1} TFA in rain for 1995, based on NH mixing ratios of 3.4 pptv HFC-134a, 2.0 pptv HCFC-124, and 0.2 pptv HCFC-123; the latter two mixing ratios were derived from estimated emission scenarios. In mid 1995, the actually determined mixing ratio of HFC-134a on the NH (*4, 5*) has been 2.2 pptv. For HCFC-123 and HCFC-124, no actual atmospheric levels have been determined but a NH mean of 2.0 pptv (HCFC-124) would yield an inventory of 19 000 t, whereas reported cumulative production figures up to 1995 are only 4650 t (*27*). Recently estimated cumulative HCFC-124 emissions of 2600 t (1995) would entail a mixing ratio of 0.2 pptv. On the basis of these latter values, the annual average TFA concentration in background precipitation should be well below 10 ng L^{-1}; this is in line with the TFA levels found in rain collected at Mace Head. In view of the high levels in rain in Nevada, Wujcik et al. (*23*) have suggested that the reaction velocities of H(C)FCs with hydroxyl radicals have

TABLE 1. Trifluoroacetate Concentrations [ng/L] in Fresh and Marine Surface Waters

identity	location	date	concn ± std dev	*n*
		Rivers		
Elbe	Wittenberg; Germany	24.02.1995	200 ± 20	3[a]
Danube	Regensburg; Germany	25.03.1995	200 ± 3	3[a]
Main	Mainleus; Germany	03.04.1995	10 ± 6	3[a]
Neckar	Tübingen; Germany	23.04.1995	260 ± 13	3[a]
Elbe	Hamburg-Altona; Germany	07.07.1995	100 ± 14	5[a]
Weser	Bremerhaven; Germany	06.07.1995	100 ± 7	4[a]
Rhine	Duisburg-Ruhrort; Germany	06.07.1995	630 ± 100	4[a]
Rhine	Bregenz; Austria	14.09.1995	55 ± 5	3[a]
Warnow	Rostock; Germany	09.07.1995	60 ± 15	4[a]
Naab	Schwandorf; Germany	29.10.1996	130 ± 18	3
Jordan	below Lake Kinneret; Israel	11.11.1995	250 ± 20	3[a]
Jennessej	Krasnojarsk; Russia	28.07.1996	35 ± 9	3
Rio Tocantins	Cotijuba; Brasil	31.08.1996	<15	3
Kemijokj	Rovaniemi; Finland	13.07.1996	210 ± 40	4
Apies River	North of Pretoria; RSA	31.05.1996	500 ± 35	3
Vaal River	Christiana; RSA	30.08.1996	100 ± 10	6
Tweede Tol	Hottentot Mts.; RSA	22.10.1996	<15	3
		Lakes		
Lake Fichtel	Fichtelberg; Germany	17.05.1995	70 ± 18	3[a]
Lake Weissenstadt	Weissenstadt; Germany	17.05.1995	115; 100	2[a]
Lake Constance	Constance; Germany	14.09.1995	60 ± 5	3[a]
Lough Ahalia	Connemara; Ireland	01.11.1995	<10	3
Lough Skannive	Connemara; Ireland	01.11.1995	20 ± 4	3[a]
Lake Kinneret	Capernaum; Israel	11.11.1995	200 ± 8	3[a]
Dead Sea	En Bokek; Israel	10.11.1995	6400 ± 600	3[a]
Borehole	Waterval District; RSA	26.08.1996	45 ± 2	3
Pond	Fourriesburg; RSA	26.10.1996	40 ± 6	3
		Marine Waters		
North Sea	Husum; Germany	07.07.1995	90 ± 15	4[a]
Baltic Sea	Warnemünde; Germany	08.07.1995	40 ± 10	3[a]
Atlantic	Ile d'Yeu; France	07.09.1995	250 ± 25	3[a]
Atlantic	Marce Head; Ireland	31.10.1995	70 ± 18	4[a]
Atlantic	Cape Point; RSA	18.10.1996	160 ± 5	3
Pacific	Noosa Heads; Australia	22.04.1996	200 ± 50	3

[a] Analyzed earlier and listed in ref 20.

TABLE 2. Trifluoroacetate Concentrations [ng/L] in Springs and Mineral Water Wells, Some of Known Age

identity	location	date	concn ± std dev	*n*	age [yr]
		Spring Waters			
Saale Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	130 ± 20	3	ca. 4
Eger Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	110 ± 25	3	ca. 4
Naab Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	80 ± 6	3	ca. 4
White Main Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	70 ± 8	3	ca. 4
Friesen Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	320 ± 20	3	ca. 4
		Well Waters			
Antonien Source	Kondrau (Bavaria; Germany)	28 Oct 1996	<10	3	>700
Dippold Source	Kondrau (Bavaria; Germany)	28 Oct 1996	<10	3	unknown
Bayern Source	Kondrau (Bavaria; Germany)	28 Oct 1996	23 ± 3	5	ca. 200
Gerwig Source	Kondrau (Bavaria; Germany)	28 Oct 1996	10 ± 3[a]	3	unknown
Thüringer Wald Source	Schmalkalden (Thuringia; Germany)	04 Nov 1996	<9	3	400 ± 60
Rennsteig Source	Schmalkalden (Thuringia; Germany)	04 Nov 1996	13 ± 3	3	185

[a] Detection limit = 10 ng/L.

been underestimated. This is unlikely as the commonly accepted rate constant is based upon the findings of several studies (*28*−*33*).

The concentrations determined in water samples collected from the major rivers of Germany near their mouths multiplied by the annual runoff volume from the area of Germany suggests a total removal of about 50 t TFA per year which would correspond to a concentration of about 200 ng L^{-1} in rain, under the assumption that there is no deposition pathway other than rain and that there no significant removal mechanisms.

High environmental TFA levels call for sources other than the CFC-alternatives. The regional pattern of high TFA levels in river waters in industrialized zones versus low levels rivers at sparsely industrialized regions (Rio Tocantins, Tweede Tol, Jennessej) suggest other significant industrial contributions. Further evidence is provided by the fact that air and rain levels in Germany do not exhibit significant upward trends (Figures 1 and 2) during a period of a rapid growth of the atmospheric abundance of HFC-134a (*4*, *5*). The presence of TFA in spring waters at similar concentrations as in rain and surface waters indicate that TFA is persistent (*14*, *15*), and the absence of TFA in old groundwaters suggest that most of the environmental TFA burden is of modern origin. The fact that TFA is also found in all ocean surface water samples even on the southern hemisphere suggest that there is potentially a large global budget; however, before further conclusions can be drawn, the database on oceanic TFA concentrations must be enlarged and depth profiles be determined.

Other Potential TFA Sources. The fluorinated inhalation anaesthetics halothane ($CF_3CHClBr$), desflurane ($CF_3CHFOCHF_2$), and isoflurane ($CF_3CHClOCHF_2$) are oxidized in the atmosphere to TFA. The amount of these compounds released globally has not yet been firmly assessed. For halothane, a global annual emission of 1500 t (*34*) has been estimated, but its share may have decreased to less than 30% since 1988 (*35*). To estimate an upper limit for TFA from narcotic gases, it is assumed that the other 70−80% (i.e. $\approx$ 6000 t) of halogenated inhalation anaesthetics are mainly TFA-producing isoflurane. With an atmospheric lifetime of about two years (*36*) this should yield an average rain concentration of less than 5 ng L^{-1}.

Several pesticides have a trifluoromethyl-substituted aromatic ring system, with trifluralin being the compound with greatest production volume, i.e., about 50 000 t in 1986 (*37*). A fraction of the applied pesticide may volatilize (*38, 39*), undergo photooxidation (*40, 41*), and will be wet deposited. Ring-cleavage has not been observed to date and is not to be expected as the electronegative CF_3-group decreases the OH-reactivity of the aromatic ring. Although metabolism of trifluoromethylated aromatics in soils has been suggested to produce TFA (*42*), studies with [^{14}C-]trifluralin showed slow degradation (*43, 44*). Even if TFA was formed in soil, it is not conceivable that it is a relevant source of atmospheric TFA.

Electrolytic aluminum production is known to entail emissions of CF_4 and C_2F_6 (*45*). Formation of TFA or trifluoroacetyl fluoride was also considered possible, but analysis of a stackgas sample of an aluminum production site did not reveal any TFA. An upper limit of 0.25 g of TFA emitted per ton aluminum as derived from the limit of determination would result in a maximum annual global release of 5 t a^{-1} from this source, assuming a global annual aluminum production of 20 million tons. However, these are preliminary results which warrant more detailed investigations.

Perfluorinated polymers are widely used as plastics, elastomers, and water repellents with a global annual production of 40 000 t in 1988 (*46*). The annual consumption of fluoropolymers in Western Europe at the same time was about 16 000 t (*47*). As they are mostly used in long-term applications with product lifetimes of 20 years and more, it may be expected that TFA from this source will slowly increase in the coming years. The fraction of waste currently being incinerated in Europe is 50%; for nonfluorinated plastics a share of 17% has been stated. Several studies have shown that hexafluoropropene and trifluoroacetylfluoride (TFAF) are pyrolysis products of perfluoroalkyl ethers (*48, 49*), polytetrafluoroethene (PTFE) (*50−54*), and polyperfluoroethenepropene (*50, 55*). Atmospheric reaction of hexafluoropropene with hydroxyl radicals leads to TFAF (*56, 57*) within about 6 days (*58, 59*) followed by hydrolysis to TFA within days (*10, 60*). Due to its hydrophilicity, TFA should predominantly be deposited close to the source regions. On the assumption that 2500 t fluoropolymer waste are presently incinerated in Europe and 10% hexafluoropropene are formed, about 200 t TFA may be released annually. This is on a similar scale as the amount of annual wet deposition upon Europe of about 500 t (average concentration = 100 ng L^{-1}; annual precipitation rate = 500 L m^{-2}). Thus, thermolysis of fluoropolymers may be an important source of the current environmental TFA burden.

TFA seems to be predominantly if not exclusively of anthropogenic/industrial origin. As a fully persistent and strongly hydrophilic compound it accumulates in the hydrosphere, particularly in the oceans. Since there are no insoluble salts or stable derivatives known, TFA must be expected to eventually remain and accumulate in the oceans. TFA has been shown not to be acutely toxic at present environmental levels in aquatic and short-term terrestrial ecotoxicological tests. Nevertheless, for higher terrestrial plants such as trees and in particular conifers, enrichment in leaf or needle tissue by a factor of 10^3 within a year relative to rain and surface waters has been observed, calling for detailed studies of potential long-term effects. Investigations about the sources, their respective strengths, and the fate and long-term effects of trifluoroacetate upon the global hydrosphere are needed to be able to assess future trends and to answer the question whether and when critical levels in the various ecosystems may be reached.

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