Supporting Information

Trifluoroacetate in Precipitation: Deriving a Benchmark Data Set

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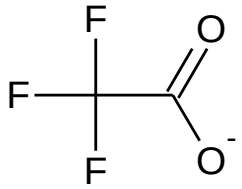
Number of tables: 9

Table S1. Molecular formula, average mass, chemical abstract service (CAS) number, pK_a, log *P*, and chemical structure of trifluroacetate (TFA)

Molecular formula	$C_2F_3O_2$	
Average mass	113.015 Da	
CAS Number (trifluoroacetic acid)	76-05-1	
pK_a	0.60[a]	
log *P*	0.66[b]	

[a]ACD/Labs Consensus log P, [b]ACD/pKa GALAS

Table S2. List of abbreviations

abbreviation	meaning
BR	Brocken (sampling site)
CFC	Chlorofluorocarbon
$C_{P\text{-weigthed}}$	Precipitation-weighted average concentration
ES	Essen (sampling site)
F_{total}	Total deposition fluxes
F_{wet}	Daily wet deposition flux
$F_{wet\ (annual)}$	Annual wet deposition flux
GW	Greifswald (sampling site)
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HFC-134a	1,1,1,2-tetrafluoroethane
HFO	Hydrofluoroolefin
HFO-1234yf	2,3,3,3-tetrafluoropropene
HFP	Hexafluoropropene
IC	Ion exchange liquid chromatography
IS	Internal Standard
$j(O^1D)$	Photolysis frequencies of ozone
LOQ	Limit of quantification
MeOH	Methanol
MO	Munich-Oberschleißheim (sampling site)
MS/MS	Tandem mass spectrometry
$^{\bullet}OH$	Hydroxyl radical
P	Precipitation amount
PD	Potsdam (sampling site)
PFAS	Per- and polyfluoroalkyl substances
PP	Polypropylene
ppt	Parts per trillion
PTFE	Polytetrafluoroethylene
r	Pearson’s correlation coefficient
ROS	Regression on order statistics
SMS	Substance from multiple sources
SU	Stuttgart (sampling site)
SW	Schleswig (sampling site)
t	Sampling duration
TFA	Trifluoroacetate
USA	United States of America
WD	Wet deposition
WK	Wasserkuppe (sampling site)

Text S1

Population density at the sampling sites

To get a comparable estimate of the population density in the vicinity of the sampling sites, a map of the population density at the municipal level was produced using QGIS 3.8.3 based on population and geographic data provided by the German Federal Agency for Cartography and Geodesy.[1] Subsequently, the population density within a 10-km radius of each of the studied sampling sites was calculated (Fig. S1).

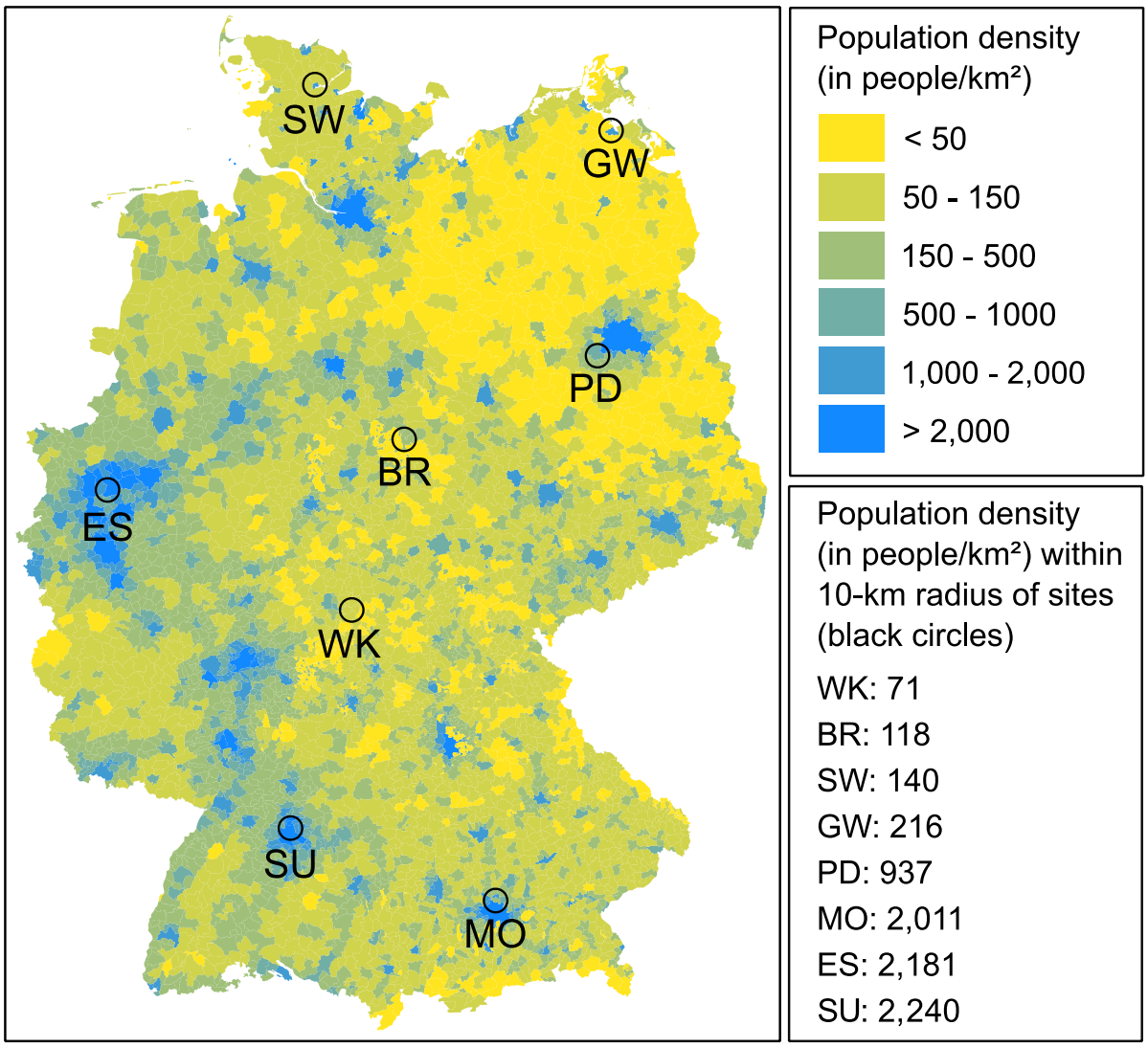


Figure S1. Population densities of the municipalities of Germany. The population density within a 10-km radius of each of the studied sampling sites (geographic extent depicted by black circles) is given in the button right box.

Table S3. MS/MS conditions for TFA and its internal standard in ESI negative mode. General interface parameters: Curtain Gas: 40 psi; Collision Gas: 8 psi; IonSpray Voltage: −3000 V; Temperature: 450 °C; Ion Source Gas 1: 60 psi; Ion Source Gas 2: 75 psi

compound	precursor ion *m/z*	product ion *m/z*	declustering potential in V	entrance potential in V	collision energy in V	cell exit potential in V
TFA	112.9	68.9	−5	−10	−16	−9
TFA-$^{13}C_2$	114.9	69.9	−5	−10	−16	−9

Text S2

Validation of the analytical method for TFA

The precision and accuracy of the analytical method for TFA was determined by analyzing five replicates of a tap and surface water sample, respectively. Prior to analysis, the tap (background concentration: 0.434 µg/L) and surface water samples (background concentration: 0.543 µg/L) were spiked with a TFA concentration of 0.250 µg/L. Method precision was determined as relative standard deviation (RSD) from the recovery experiments. A summary of the method validation results can be found in Table S4.

Table S4. Validation results of the IC-MS/MS method for the analysis of TFA

parameter	matrix	result
Precision (RSD; n=5)	tap water	1%
Precision (RSD; n=5)	surface water	1%
Accuracy (average recovery; n=5)	tap water	102%
Accuracy (average recovery; n=5)	surface water	100%

Text S3

Significant figures

The appropriate number of significant figures when reporting concentrations of TFA was derived from the analysis of split replicates (n = 5) of two precipitation samples. The uncertainty was given by the standard deviation (SD) for the data, in this case concentration of TFA, rounded off to one digit to obtain the number of significant figures.[2] Based on the obtained results, concentrations of TFA < 0.1 µg/L and ≥ 0.1 µg/L were reported with two and three significant figures, respectively (Table S5).

Table S5. Determination of the appropriate number of significant figures when reporting concentrations of TFA

Sample 1	TFA in µg/L	Sample 2	TFA in µg/L
Replicate # 1	0.078174	Replicate # 1	0.539296
Replicate # 2	0.072165	Replicate # 2	0.546809
Replicate # 3	0.076746	Replicate # 3	0.548648
Replicate # 4	0.071675	Replicate # 4	0.546829
Replicate # 5	0.074266	Replicate # 5	0.544399
SD	0.002827	SD	0.003627
SD with 1-digit uncertainty	0.003	SD with 1-digit uncertainty	0.004
average with precision matched to SD	0.075	average with precision matched to SD	0.545
number of significant figures for concentrations of TFA < 0.1 µg/L	**2**	**number of significant figures for concentrations of TFA ≥ 0.1 µg/L**	**3**

Table S6. p-values from Wilcoxon rank sum tests of TFA concentration data (WD samples) of studied sampling site pairs. Bold numbers indicate sampling site pairs with statistically significant ($p < 0.05$; p-value adjustment method: Benjamini & Hochberg[3]) differences. February 2019 was not included because only data for the site SU was available. See Figure 1 for site abbreviations

February 2018						
site	ES	GW	MO	PD	SU	SW
GW	1.00	-	-	-		-
MO	0.63	0.63	-	-		-
PD	0.84	0.80	0.84	-		-
SU						
SW	0.63	0.63	0.63	0.63		-
WK	0.63	0.63	0.63	0.63		1.00
March 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.87	-	-	-	-	-
MO	0.41	0.51	-	-	-	-
PD	0.98	0.87	0.40	-	-	-
SU	0.40	0.50	0.92	0.40	-	-
SW	0.44	0.40	0.13	0.44	0.13	-
WK	0.51	0.44	0.13	0.54	0.13	0.79
April 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.91	-	-	-	-	-
MO	0.66	0.80	-	-	-	-
PD	0.66	0.80	0.86	-	-	-
SU	0.31	0.31	0.80	0.80	-	-
SW	0.80	1.00	0.80	0.80	0.42	-
WK	0.86	0.80	0.66	0.66	0.31	0.80
May 2018						
site	ES	GW	MO	PD	SU	SW
GW	1.00	-	-	-	-	-
MO	0.90	1.00	-	-	-	-
PD	1.00	1.00	1.00	-	-	-
SU	1.00	1.00	1.00	1.00	-	-
SW	1.00	1.00	1.00	1.00	1.00	-
WK	0.73	1.00	1.00	1.00	1.00	1.00
June 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.87	-	-	-	-	-
MO	0.87	1.00	-	-	-	-

PD	0.21	0.36	0.76	-	-	-
SU	0.77	0.87	1.00	0.76	-	-
SW	0.76	0.81	0.88	0.75	1.00	-
WK	0.21	0.74	0.76	0.76	0.82	0.82
July 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.58	-	-	-	-	-
MO	0.45	0.93	-	-	-	-
PD	0.45	0.76	0.74	-	-	-
SU	0.58	0.58	0.67	0.53	-	-
SW	0.67	0.72	0.82	0.67	0.80	-
WK	0.58	0.80	0.82	0.58	0.82	1.00
August 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.117	-	-	-	-	-
MO	0.117	0.568	-	-	-	-
PD	0.117	0.773	0.625	-	-	-
SU	0.065	0.568	0.930	0.625	-	-
SW	0.568	0.069	0.065	0.069	**0.046**	-
WK	0.848	0.366	0.117	0.218	0.065	0.568
September 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.252	-	-	-	-	-
MO	0.252	0.972	-	-	-	-
PD	0.252	0.232	0.167	-	-	-
SU	0.232	0.232	0.167	0.789	-	-
SW	0.074	0.403	0.252	0.074	0.074	-
WK	0.232	0.403	0.403	0.167	0.167	0.789
October 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.674	-	-	-	-	-
MO	0.693	0.664	-	-	-	-
PD	0.292	0.317	0.713	-	-	-
SU	0.229	0.174	0.360	0.316	-	-
SW	0.172	0.364	0.172	0.084	0.084	-
WK	0.172	0.529	0.316	0.084	0.084	0.432
November 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.90	-	-	-	-	-
MO	0.84	0.90	-	-	-	-
PD	0.90	0.58	0.84	-	-	-

SU	0.93	0.90	0.90	0.44	-	-
SW	0.13	0.39	0.90	0.13	0.39	-
WK	0.13	0.39	0.90	0.13	0.21	0.165
			December 2018			
site	ES	GW	MO	PD	SU	SW
GW	0.68	-	-	-	-	-
MO	0.92	1.00	-	-	-	-
PD	1.00	0.60	1.00	-	-	-
SU	1.00	0.72	1.00	1.00	-	-
SW	0.47	0.75	0.72	0.40	0.49	-
WK	0.17	0.40	0.40	0.17	0.17	0.49
			January 2019			
site	ES	GW	MO	PD	SU	SW
GW	0.872	-	-	-	-	-
MO	0.686	0.546	-	-	-	-
PD	0.119	0.063	0.558	-	-	-
SU	0.862	0.984	0.546	0.063	-	-
SW	0.199	0.165	0.984	0.546	0.165	-
WK	0.063	**0.023**	0.184	0.558	**0.023**	0.165

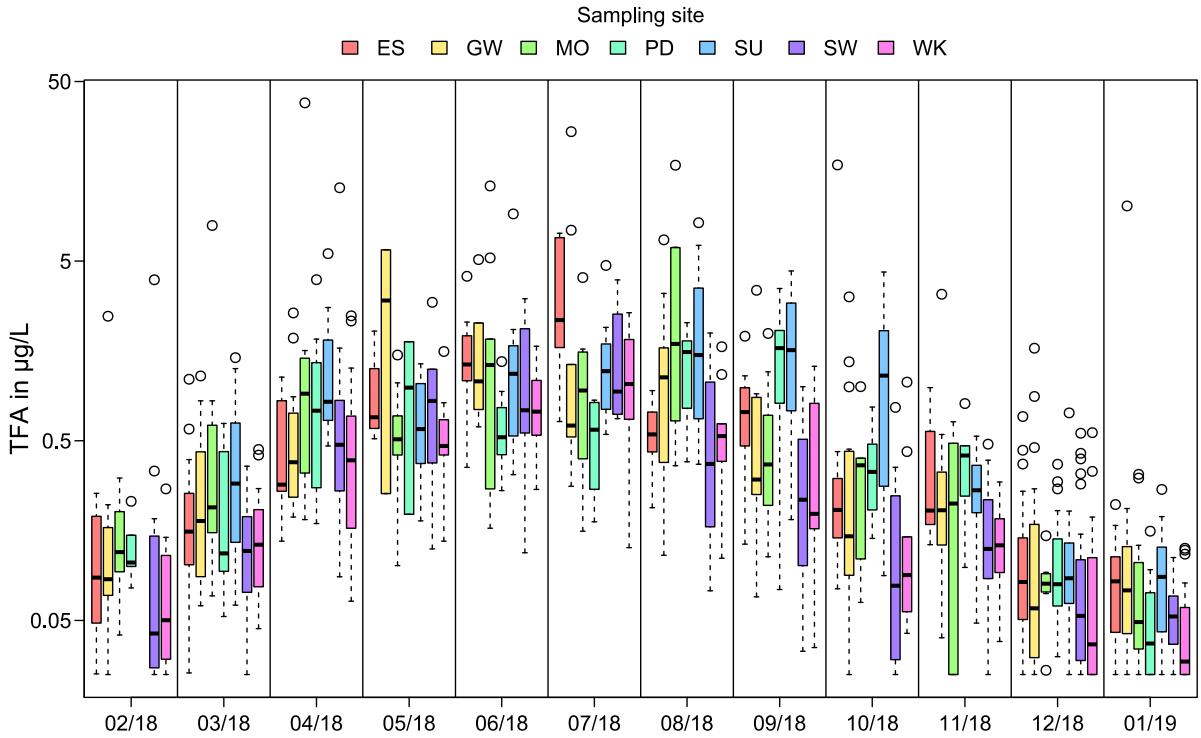


Figure S2. Boxplots of the TFA concentration at the different WD sampling sites within months over the course of the sampling period. February 2018 (02/18) does not include the site SU. February 2019 is excluded as it only contains data from the site SU.

Table S7. Statistical parameters of the TFA concentration in studied precipitation samples (WD samples; BR samples not included) grouped by the sampling month. Note that statistical parameters for February 2018 do not include data from site SU, whereas statistical parameters for February 2019 solely represent data from SU

		TFA concentration			
year/ month	proportion of samples > LOQ	maximum	median	ROS-estimated average	precip.-weighted average
	%	µg/L	µg/L	µg/L	µg/L
2018/2	89.1	3.94	0.085	0.221	0.083
2018/3	99.1	7.90	0.158	0.326	0.166
2018/4	100	38.0	0.489	1.33	0.584
2018/5	100	5.78	0.538	0.846	0.451
2018/6	100	13.1	1.06	1.57	0.782
2018/7	100	26.3	0.901	2.12	0.654
2018/8	100	17.1	0.630	1.49	0.835
2018/9	100	4.41	0.480	0.764	0.349
2018/10	94.6	17.2	0.182	0.627	0.128
2018/11	93.9	3.27	0.198	0.299	0.137
2018/12	83.7	1.64	0.070	0.130	0.063
2019/1	76.3	10.1	0.052	0.146	0.055
2019/2	0	6.27	0.105	1.42	0.121

Table S8. p-values from Wilcoxon rank sum tests of TFA daily wet deposition flux data (WD samples) of studied sampling site pairs. Bold numbers indicate sampling site pairs with statistically significant ($p < 0.05$; p-value adjustment method: Benjamini & Hochberg[3]) differences. No data for the site SU was available for February 2018. February 2019 was not included because only data for the site SU was available. See Figure 1 for site abbreviations

February 2018						
site	ES	GW	MO	PD	SU	SW
GW	1.00	-	-	-		-
MO	0.169	0.195	-	-		-
PD	0.150	0.137	**0.047**	-		-
SU						
SW	0.285	0.304	0.750	**0.027**		-
WK	1.000	1.000	0.304	0.169		0.304
March 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.47	-	-	-	-	-
MO	0.79	0.79	-	-	-	-
PD	0.47	1.00	0.80	-	-	-
SU	0.15	0.72	0.47	0.47	-	-
SW	0.47	0.81	0.79	0.79	0.80	-
WK	0.47	0.80	0.85	0.93	0.47	0.79

April 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.98	-	-	-	-	-
MO	0.98	0.98	-	-	-	-
PD	0.98	0.98	0.98	-	-	-
SU	0.98	0.98	0.98	0.98	-	-
SW	0.98	0.98	0.98	0.98	0.98	-
WK	0.98	0.98	0.98	0.98	0.98	0.98
May 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.78	-	-	-	-	-
MO	0.78	0.78	-	-	-	-
PD	0.78	0.78	0.92	-	-	-
SU	0.78	0.78	0.78	0.92	-	-
SW	0.78	0.78	0.78	0.78	0.78	-
WK	0.78	0.78	0.88	0.78	0.78	0.78
June 2018						
site	ES	GW	MO	PD	SU	SW
GW	1	-	-	-	-	-
MO	1	1	-	-	-	-
PD	1	1	1	-	-	-
SU	1	1	1	1	-	-
SW	1	1	1	1	1	-
WK	1	1	1	1	1	1
July 2018						
site	ES	GW	MO	PD	SU	SW
GW	1	-	-	-	-	-
MO	1	1	-	-	-	-
PD	1	1	1	-	-	-
SU	1	1	1	1	-	-
SW	1	1	1	1	1	-
WK	1	1	1	1	1	1
August 2018						
site	ES	GW	MO	PD	SU	SW
GW	0.9397	-	-	-	-	-
MO	**0.0174**	**0.0174**	-	-	-	-
PD	0.9397	0.9397	**0.0245**	-	-	-
SU	0.7859	0.7859	**0.0174**	0.7859	-	-
SW	0.7859	0.8673	**0.0082**	0.7859	0.5198	-
WK	0.8673	0.8673	**0.0174**	0.8673	0.7859	0.9397
September 2018						
site	ES	GW	MO	PD	SU	SW

GW	0.74	-	-	-	-	-
MO	0.57	0.57	-	-	-	-
PD	0.57	0.57	0.57	-	-	-
SU	0.57	0.57	0.91	0.75	-	-
SW	1.00	0.74	0.57	0.57	0.57	-
WK	0.81	0.98	0.57	0.80	0.57	0.88
	October 2018					
site	ES	GW	MO	PD	SU	SW
GW	0.54	-	-	-	-	-
MO	0.88	0.64	-	-	-	-
PD	0.54	0.54	0.54	-	-	-
SU	0.54	0.54	0.54	0.88	-	-
SW	0.64	0.76	0.76	0.54	0.54	-
WK	0.88	0.54	0.76	0.54	0.54	0.76
	November 2018					
site	ES	GW	MO	PD	SU	SW
GW	0.59	-	-	-	-	-
MO	0.51	0.97	-	-	-	-
PD	0.97	0.48	0.48	-	-	-
SU	0.43	0.85	0.97	0.43	-	-
SW	0.43	0.97	0.97	0.43	0.97	-
WK	0.48	0.97	0.97	0.48	0.97	0.97
	December 2018					
site	ES	GW	MO	PD	SU	SW
GW	0.268	-	-	-	-	-
MO	0.419	0.956	-	-	-	-
PD	0.087	0.419	0.658	-	-	-
SU	0.419	0.956	1.000	0.480	-	-
SW	0.268	0.956	1.000	0.501	0.956	-
WK	0.941	0.419	0.419	0.087	0.419	0.419
	January 2019					
site	ES	GW	MO	PD	SU	SW
GW	0.698	-	-	-	-	-
MO	0.857	0.698	-	-	-	-
PD	0.500	0.535	0.419	-	-	-
SU	0.419	0.500	0.419	0.535	-	-
SW	0.419	0.500	0.419	0.535	0.857	-
WK	0.535	0.327	0.529	**0.036**	**0.036**	**0.036**

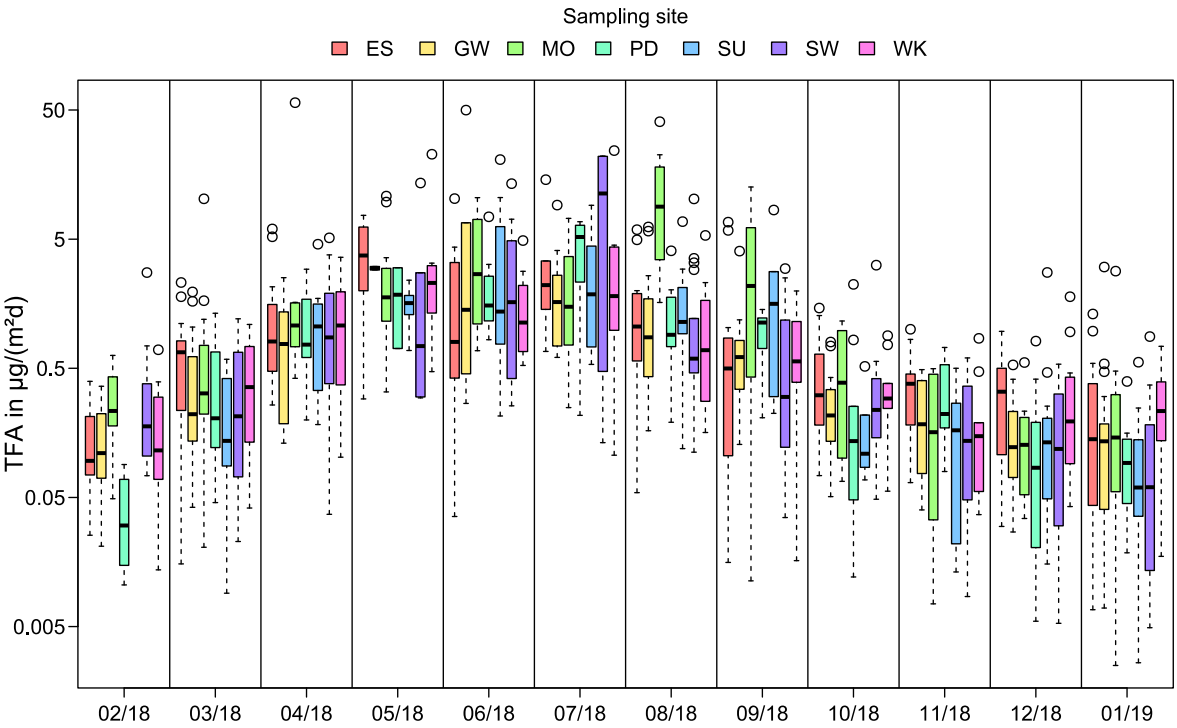


Figure S3. Boxplots of the daily wet deposition fluxes of TFA at the different WD sampling sites within months over the course of the sampling period. Note that the boxplot of February 2018 (02/18) does not include data from site SU. February 2019 is excluded as it only contains data from the site SU.

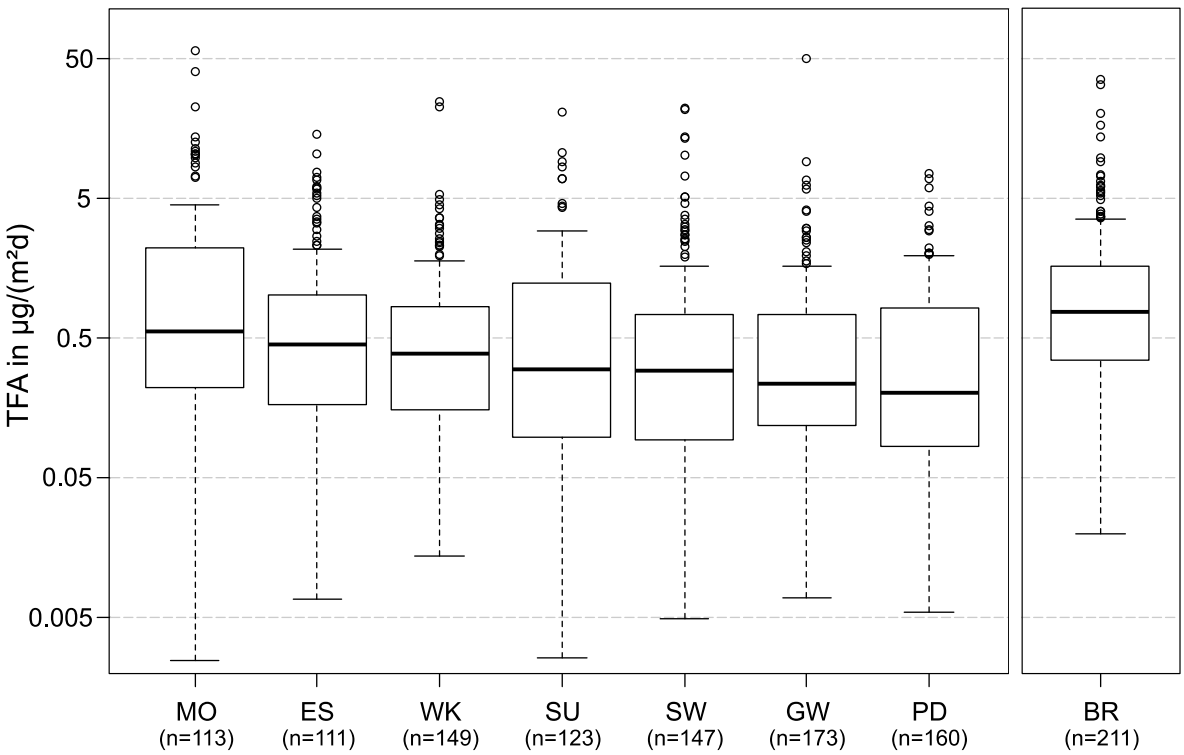


Figure S4: Boxplots of the wet deposition fluxes of TFA in precipitation samples grouped by the sampling site. Sites are plotted in descending median order. Note that the boxplot of site SU includes data from March 2018 to February 2019, whereas boxplots from other sites include data from February 2018 to January 2019. Further note that the boxplot of site BR includes total deposition flux data instead of the wet deposition flux data.

Text S4

Processing of the global radiation data

The global radiation data (10 min temporal resolution) was obtained from the Climate Data Center (CDC; available at: ftp://ftp-cdc.dwd.de/) of the German Meteorological Service. For three of the eight precipitation sampling sites (MO, BR, ES) global radiation data was unavailable and data from meteorological stations located in proximity (< 50 km) of the respective precipitation sampling sites was used instead. Periods of missing data in the time series of each station were filled with the equi-percentile method, using the average radiation data of all eight sampling sites (10 min temporal resolution) as the reference dataset.

Table S9. Monthly precipitation in mm and number of samples at studied sites

site	month	year	precipitation in mm	number of samples	site	month	year	precipitation in mm	number of samples
BR	02	18	45.8	18	ES	02	18	22.5	10
BR	03	18	97.5	20	ES	03	18	69.1	17
BR	04	18	66.6	14	ES	04	18	53.6	14
BR	05	18	59.4	12	ES	05	18	62.7	7
BR	06	18	64.9	18	ES	06	18	35.2	13
BR	07	18	48.6	8	ES	07	18	16.2	6
BR	08	18	35.0	16	ES	08	18	46.5	12
BR	09	18	71.9	15	ES	09	18	46.2	11
BR	10	18	132.1	21	ES	10	18	33.3	11
BR	11	18	62.0	18	ES	11	18	23.2	10
BR	12	18	345.9	28	ES	12	18	133.5	19
BR	01	19	300.1	23	ES	01	19	111.1	19
GW	02	18	22.3	11	MO	02	18	44.5	8
GW	03	18	69.1	16	MO	03	18	33.3	15
GW	04	18	31.7	13	MO	04	18	15.2	8
GW	05	18	12.6	2	MO	05	18	93.2	11
GW	06	18	25.0	6	MO	06	18	87.4	10
GW	07	18	50.8	9	MO	07	18	107.2	8
GW	08	18	35.8	13	MO	08	18	47.3	7
GW	09	18	20.6	9	MO	09	18	143.1	12
GW	10	18	47.0	15	MO	10	18	38.3	6
GW	11	18	11.6	10	MO	11	18	33.3	6
GW	12	18	63.8	23	MO	12	18	42.7	8
GW	01	19	49.5	20	MO	01	19	86.0	12
PD	02	18	1.8	5	SU	03	18	22.4	13
PD	03	18	52.9	19	SU	04	18	24.7	8
PD	04	18	34.8	14	SU	05	18	41.3	8
PD	05	18	15.8	2	SU	06	18	98.5	7
PD	06	18	33.4	7	SU	07	18	52.1	9
PD	07	18	51.9	4	SU	08	18	34.2	11
PD	08	18	10.1	7	SU	09	18	34.0	6

PD	09	18	20.3	7	SU	10	18	18.2	6
PD	10	18	12.43	10	SU	11	18	20.8	9
PD	11	18	14.4	9	SU	12	18	67.4	14
PD	12	18	38.2	20	SU	01	19	65.1	17
PD	01	19	50.9	19	SU	02	19	22.9	5
SW	02	18	47.7	11	WK	02	18	37.5	10
SW	03	18	56.3	14	WK	03	18	90.6	22
SW	04	18	58.6	17	WK	04	18	80.1	15
SW	05	18	42.2	6	WK	05	18	103.4	11
SW	06	18	55.3	11	WK	06	18	20.2	8
SW	07	18	26.0	4	WK	07	18	59.1	8
SW	08	18	81.0	18	WK	08	18	24.2	9
SW	09	18	58.5	17	WK	09	18	56.0	9
SW	10	18	70.2	16	WK	10	18	47.6	10
SW	11	18	29.4	13	WK	11	18	21.3	9
SW	12	18	97.2	27	WK	12	18	148.6	24
SW	01	19	58.2	19	WK	01	19	201.7	25

Text S5

Sea spray as a potential source of TFA in precipitation

Sea water approximately contains 20 g/L of chloride[4] and 0.2 µg/L of TFA.[5] In Germany, the average concentration of chloride in precipitation is around 0.2 mg/L.[6] Consequently, if TFA and chloride are similarly transported from the ocean to the atmosphere, sea spray would only explain around 0.000002 µg/L of the TFA present in precipitation in Germany, which is far lower than the TFA concentrations in precipitation found in this study. Moreover, the deposition of chloride usually decreases strongly with increasing distance from the shore as the droplets and crystals settle by gravitation and are retained by vegetation.[7] In the present study, the two coastal sampling sites (GW, SW) did not show significantly elevated TFA concentrations compared to sites in Southern Germany (MO, SU). Furthermore, the lowest average monthly concentrations of TFA in precipitation (Table S7) were all found in months (December, January, February) with the highest average monthly concentration of chloride in Germany.[6]

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