

Supplementary Information

Supplementary Material 1

Table S1 Gradient elution profile for liquid chromatography separation, which was performed using a binary gradient mobile phase consisting of ultra-pure water with 20 mM ammonium acetate buffer (A) and HPLC-MS-grade methanol (B) at a constant flow rate of 0.6 mL/min.

Time (min)	Mobile phase A (%)	Mobile phase B (%)	Flow (mL/min)
0.0	90	10	0.6
1.5	35	65	0.6
8.0	5	95	0.6
8.1	1	99	0.6
12.0	1	99	0.6
12.1	90	10	0.6
16.0	90	10	0.6

Table S2 Limit of Quantification (LOQ) values of different PFAS compounds and matrices directly collected in this study and analyzed by the water chemistry lab at TU Wien. All values are determined by direct injection following DIN 32645 [25] and displayed in nanogram per liter (ng/L). Abbreviations for matrices: River water (RW), Groundwater (GW), Groundwater potentially impacted by landfills (LGW), Wastewater Influent (WWI), Wastewater Effluent (WWE), Landfill Leachate (LF), Surface Runoff (SR).

Substance	CAS Number	RW	GW	LGW	WWI	WWE	LF	SR
PFBA	375-22-4	0.70	0.70	1.71	8.81	1.32	11.33	1.20
PFPeA	2706-90-3	1.18	1.18	0.96	6.61	4.56	22.84	1.66
PFHxA	307-24-4	1.04	1.04	0.84	4.02	3.96	13.58	1.60
PFHpA	375-85-9	0.55	0.55	0.84	2.33	2.28	5.28	0.97
PFOA	335-67-1	1.24	1.24	1.32	0.78	0.84	3.06	0.67
PFNA	375-95-1	0.56	0.56	0.72	1.80	1.80	2.17	0.48
PFDA	335-76-2	1.01	1.01	0.60	0.32	0.32	0.46	0.96
PFUdA	2058-94-8	1.91	1.91	0.81	2.16	2.16	2.04	1.08
PFDoDA	307-55-1	0.83	0.83	1.27	1.56	1.56	1.98	0.72
PFTTrDA	72629-94-8	0.58	0.58	0.94	1.20	1.20	2.18	0.60
PFTeDA	376-06-7	2.03	2.03	1.15	1.56	1.56	2.39	0.78
PFBS	375-73-5	0.31	0.31	0.24	2.52	2.28	6.48	1.32
PFPeS	2706-91-4	0.68	0.68	0.24	1.56	0.72	5.20	0.78
PFHxS	355-46-4	0.18	0.18	0.48	1.32	1.32	12.84	0.66
PFOS	1763-23-1	0.30	0.30	0.48	1.80	1.44	1.69	0.30
PFNS	68259-12-1	0.18	0.18	0.48	0.48	0.48	0.17	0.24
PFDS	335-77-3	0.18	0.18	0.48	0.36	0.36	0.70	0.18
GenX	13252-13-6	0.31	0.31	0.72	1.80	1.80	1.19	0.90
ADONA	919005-14-4	0.25	0.25	0.66	0.30	0.30	0.36	0.31
4:2 FTS	757124-72-4	0.45	0.45	0.60	0.29	0.29	0.53	0.36
6:2 FTS	27619-97-2	0.18	0.18	0.84	0.24	0.24	1.19	0.12
8:2 FTS	39108-34-4	0.34	0.34	0.96	0.48	0.48	0.72	0.24
PFOSA	754-91-6	0.34	0.34	0.90	0.72	0.72	0.86	0.36
N-MeFOSA	31506-32-8	0.22	0.22	0.60	0.20	0.20	0.78	1.14
N-EtFOSA	4151-50-2	0.12	0.12	0.60	0.48	0.48	0.30	0.24
N-MeFOSAA	2355-31-9	0.18	0.18	0.66	1.20	1.20	0.70	0.60
N-EtFOSAA	2991-50-6	0.18	0.18	0.67	0.48	0.48	0.74	0.24
9Cl-PF3ONS	73606-19-6	0.36	0.36	1.86	1.68	1.68	2.52	0.78
11Cl-PF3OUdS	763051-92-9	0.42	0.42	0.96	1.44	1.44	1.56	0.72
N-MeFOSE	24448-09-7	0.18	0.18	0.72	1.44	1.44	1.14	0.72
N-EtFOSE	1691-99-2	0.18	0.18	0.84	1.92	1.92	1.32	0.96

Table S3 Statistical analysis results for surface water samples from the Alz River (Alz), Danube mainstream at Vienna and Budapest (D) and Danube tributaries that categorized by wastewater discharge: <1% (Tri1), 1–3% (Tri2), and >3% (Tri3). Dunn's test is used to assess intra-group differences. Significant results ($p < 0.05$) are reported as z-scores, where higher absolute values indicate greater differences relative to variability. Positive z-scores indicate higher concentrations in the first group compared to the second, while negative z-scores indicate the reverse. NA denotes non-significant differences.

Substance	Alz - Tri1	Alz - Tri2	Alz - Tri3	Alz - D
PFBA	9.6	9.26	8.33	2.21
PFPeA	9.54	9.1	8.63	NA
PFHxA	9.6	9.26	8.19	2.65
PFHpA	11.6	13.1	12.33	2.61
PFOA	10.04	8.8	8.74	2.1
PFBS	5.2	2.35	NA	-2.32
PFHxS	-5.94	-5.36	-6.61	NA
PFOS	4.8	4.29	NA	NA
6:2 FTS	NA	2.57	NA	NA
GenX	5.84	5.86	5.49	NA
ADONA	5.06	4.72	6.51	NA

Table S4 Statistical analysis results for surface water samples from the Danube mainstream (D) and Danube tributaries that categorized by wastewater discharge: <1% (Tri1), 1–3% (Tri2), and >3% (Tri3). Dunn's test is used to assess intra-group differences. Significant results ($p < 0.05$) are reported as z-scores, where higher absolute values indicate greater differences relative to variability. Positive z-scores indicate higher concentrations in the first group compared to the second, while negative z-scores indicate the reverse. NA denotes non-significant differences.

Substance	D - Tri1	D - Tri2	D - Tri3	Tri3 - Tri2	Tri3 - Tri1	Tri2 - Tri1
PFBA	8.01	7.58	6.48	2.99	4	2.34
PFPeA	9.2	8.79	8.24	NA	3.34	2.5
PFHxA	7.41	6.9	5.64	3.47	4.27	2.32
PFHpA	9.75	11.48	10.57	2.49	NA	NA
PFOA	8.65	7.18	7.12	NA	4.15	4.1
PFBS	9.6	6.66	5.97	NA	7.69	6.67
PFHxS	-6.26	-5.71	-7.27	4.46	NA	-2.15
PFOS	7.38	7.19	4.21	8.51	6.55	NA
6:2 FTS	3.31	7.03	4.59	3.35	NA	-2.54
GenX	7.87	8.37	7.64	NA	NA	NA
ADONA	6.63	6.33	9.85	-5.04	-3.13	NA

Table S5 Statistical analysis results for samples from the Danube mainstream (Danube) at Vienna and Budapest, Danube bank-filtration sites at Vienna and Budapest (BF), Groundwater with unknown influences (GW_N), Groundwater potentially impacted by AFFF applications (GW_AFFF) and Groundwater potentially impacted by landfills (GW_LF). Dunn's test is used to assess intra-group differences. Significant results ($p < 0.05$) are reported as z-scores, where higher absolute values indicate greater differences relative to variability. Positive z-scores indicate higher concentrations in the first group compared to the second, while negative z-scores indicate the reverse. NA denotes non-significant differences.

Substance	BF - Danube	BF - GW_N	BF - GW_AFFF	BF - GW_LF
PFBA	-3.62	12.56	-4.66	-4.11
PFPeA	-4.11	15.17	-5.45	-2.56
PFHxA	-5.36	11.92	-6.52	-4.53
PFHpA	NA	15.68	-6.45	-4.43
PFOA	-2.02	11.71	-3.65	-4.13
PFBS	-1.98	9.47	-4.8	-6.4
PFPeS	3.76	-8.38	-16.8	-12.37
PFHxS	3.21	3.36	-12.96	-9.82
PFOS	NA	12.96	-7.02	NA
6:2 FTS	-7.12	-19.05	-21.61	-9.97
GenX	NA	12.94	-2.74	6.95
ADONA	-2.93	20.68	21.24	16.07

Table S6 Statistical analysis results for samples from Groundwater with unknown influences (GW_N), Groundwater potentially impacted by AFFF applications (GW_AFFF) and Groundwater potentially impacted by landfills (GW_LF). Dunn's test is used to assess intra-group differences. Significant results ($p < 0.05$) are reported as z-scores, where higher absolute values indicate greater differences relative to variability. Positive z-scores indicate higher concentrations in the first group compared to the second, while negative z-scores indicate the reverse. NA denotes non-significant differences.

Substance	GW_AFFF - GW_N	GW_LF - GW_N	GW_AFFF - GW_LF
PFBA	18.22	17.29	NA
PFPeA	21.82	17.76	2.79
PFHxA	20.07	17.24	NA
PFHpA	23.59	20.66	1.93
PFOA	16.14	18.16	NA
PFBS	15.44	17.38	NA
PFPeS	14.29	8.39	4.23
PFHxS	20.41	16.12	2.97
PFOS	21.84	12.23	8.25
6:2 FTS	11.47	-4.69	12.16
GenX	13.87	3.05	8.84
ADONA	-9.71	NA	-6.43

Table S7 Statistical analysis results for influent and effluent samples from municipal wastewater treatment plants (WWTPs). Dunn's test is used to assess intra-group differences. Only significant results ($p < 0.05$) are reported as z-scores, where higher absolute values indicate greater differences relative to variability. Positive z-scores indicate higher concentrations in the first group compared to the second, while negative z-scores indicate the reverse. NA denotes non-significant differences.

Substance	Municipal Effluent - Municipal Influent
PFBA	NA
PFPeA	-5.03
PFHxA	3.36
PFHpA	-10.14
PFOA	5.35
PFBS	4.77
PFHxS	-11.31
PFOS	2.67
PFNS	-4.72
ADONA	NA
6:2 FTS	-2.17
8:2 FTS	NA

Table S8 Statistical analysis results for summed PFAS level in influent and effluent samples from municipal wastewater treatment plants (WWTPs). Dunn's test is used to assess intra-group differences. P value indicates the significant of results, while z-score values indicate differences relative to variability. Positive z-scores indicate higher concentrations in the first group compared to the second, while negative z-scores indicate the reverse. NA denotes non-significant differences.

Environmental Standard	Comparison	p	Z
DWD (2020) $\sum$ 20 PFAS	Municipal Effluent - Influent	<0.05	5.82
proposed EQS (2022) $\sum$ 24 PFAS	Municipal Effluent - Influent	<0.05	7.78

Table S9 Statistical analysis results for influent and effluent samples from municipal wastewater treatment plants (WWE), pulp and paper industries (ID_Paper) and other industries (ID_Others). Dunn's test is used to assess intra-group differences. Only significant results ($p < 0.05$) are reported as z-scores, where higher absolute values indicate greater differences relative to variability. Positive z-scores indicate higher concentrations in the first group compared to the second, while negative z-scores indicate the reverse. NA denotes non-significant differences.

Substance	ID_Paper - WWE	ID_Paper - ID_Others	ID_Others - WWE
PFBA	NA	NA	NA
PFPeA	3.25	4.69	-3.60
PFHxA	NA	NA	NA
PFHpA	3.93	2.51	NA
PFOA	NA	3.56	-5.00
PFBS	2.98	2.79	NA
PFHxS	NA	NA	-2.63
PFOS	NA	NA	-2.21
PFNS	NA	NA	NA
ADONA	NA	NA	NA
6:2 FTS	NA	NA	NA
8:2 FTS	-3.25	NA	-2.14

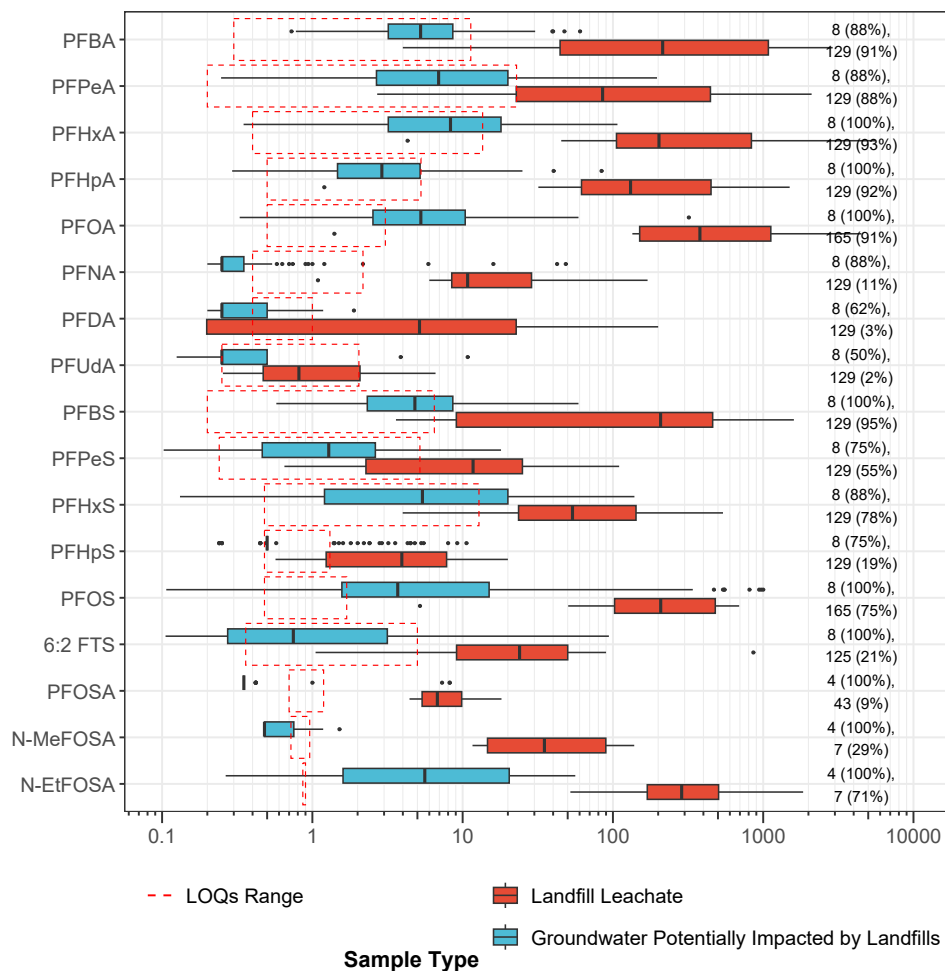


Fig. S1 PFAS concentrations on a logarithmic scale for landfill leachate and groundwater potentially impacted by landfills samples. Box in red dashed outline represents the range of LOQ values among measurements; For different compounds, sample sizes and detection above the LOQ (%) of each type are listed on the right side of the graph, in a sequence of their appearance on the graph. Values below LOQ are semi-quantitative.

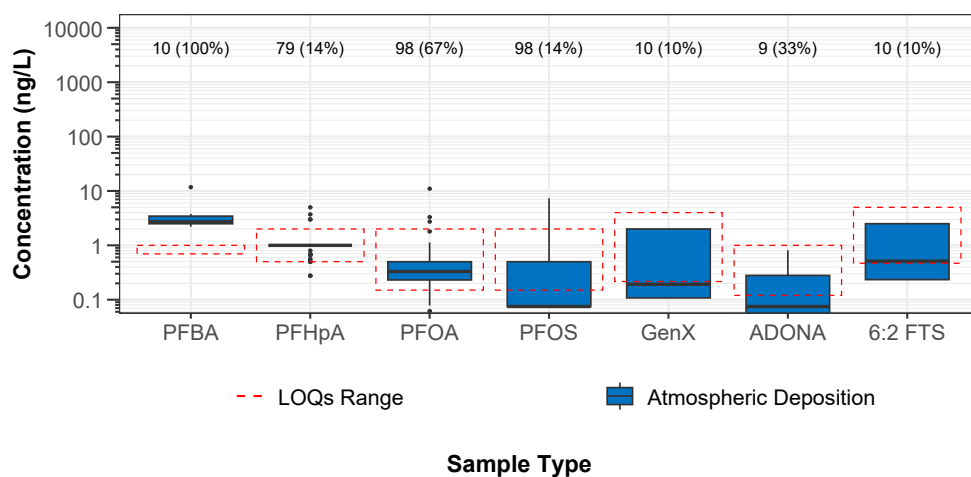


Fig. S2 PFAS concentrations on a logarithmic scale for atmospheric deposition samples. Box in red dashed outline represents the range of limit of quantification (LOQ) values among measurements; For different compounds, sample sizes and detection above the LOQ (%) of each type are listed on top of the graph, in a sequence of their appearance on the graph. Values below LOQ are semi-quantitative.

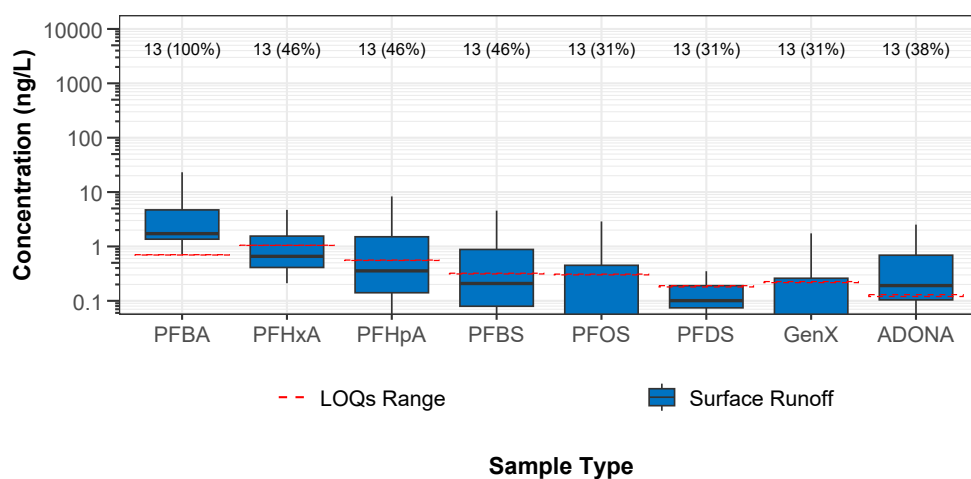


Fig. S3 PFAS concentrations on a logarithmic scale for surface runoff samples. Box in red dashed outline represents the range of limit of quantification (LOQ) values among measurements; For different compounds, sample sizes and detection above the LOQ (%) of each type are listed on top of the graph, in a sequence of their appearance on the graph. Values below LOQ are semi-quantitative.