Supplementary material

Robust LC-MS/MS Methodology for Low-Level PFAS in Sludge Matrices

Luoana Florentina Pascu, Valentina Andreea Petre *, Vasile Ion Iancu, Ioana Antonia Cimpean and Florentina Laura Chiriac *

National Research and Development Institute for Industrial Ecology—ECOIND, Drumul Podu Dambovitei Street 57–73, Sector 6, 060652 Bucharest, Romania; ecoind@incdecoind.ro (L.F.P.); vasile.iancu@incdecoind.ro (V.I.I.);
antonia.cimpean@ecoind.ro (I.A.C.)
* Correspondence: andreea.petre@ecoind.ro (V.A.P.); laura.chiriac@incdecoind.ro (F.L.C.)

Table S1. Physicochemical properties of PFAS compounds.

No.	Abbreviation	Analytes	Molecular formula	Molecular mass	Log Kow (LogP)	Log Koc	LogD (pH 5.5)	LogD (pH 7.4)
1	PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$	214	2.43	1.00	-1.11	-1.13
2	PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$	264	3.4	1.00	-0.32	-0.34
3	PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$	314	4.37	1.00	0.17	0.15
4	PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$	364	5.33	1.97	1.14	1.11
5	PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$	414	6.3	4.81	1.85	1.82
6	PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$	464	7.27	17.2	2.86	2.84
7	PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	514	9.53	45.8	3.64	3.62
8	PFUnA	Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$	564	10.42	92.7	4.25	4.23
9	PFDoA	Perfluorododecanoic acid	$C_{12}HF_{23}O_2$	614	11.3	151	4.60	4.58
10	PFBS	Perfluorobutanesulfonic acid	$C_4HF_9O_3S$	300	1.82	1.93	-1.56	-1.56
11	PFPeS	Perfluoropentanesulfonic acid, potassium salt	$C_5F_{11}KO_3S$	372	-	1.00	-3.20	-
12	PFHxS	Perfluorohexane sulfonic acid	$C_6HF_{13}O_3S$	399	5.25	1.00	-0.54	-0.54
13	PFHpS	Perfluoroheptane sulfonic acid	$C_7HF_{15}O_3S$	450	6.14	1.00	0.10	0.10
14	PFOS	perfluorooctanesulfonic acid	$C_8HF_{17}O_3S$	499	7.03	1.39	0.66	0.66
15	4:2 FTS	1H,1H,2H,2H-Perfluorohexanesulfonate	$C_6H_5F_9O_3S$	328	1.70	1.00	-2.27	-2.27
16	6:2 FTS	1H,1H,2H,2H-Perfluorooctanesulfonate	$C_8H_5F_{13}O_3S$	428	3.47	1.00	-0.92	-1.00
17	8:2 FTS	1H,1H,2H,2H-Perfluorodecanesulfonate	$C_{10}H_5F_{17}O_3S$	528	5.25	1.00	0.23	0.15
18	HFPO-DA (GenX)	Tetrafluoro-2-(heptafluoropropoxy)propanoic acid	$C_6HF_{11}O_3$	330	8.12	2.48	1.34	1.34
19	DONA	Dodecafluoro-3H-4,8-dioxanonanoic acid	$C_7H_2F_{12}O_4$	378	8.65	6.33	2.06	2.04
20	9Cl-PF3ONS	9-Chlorohexadecafluoro-3-oxanone-1-sulfonic acid, potassium salt	$C_8ClF_{16}KO_4S$	570	-	-	-	-
21	11Cl-PF3OUdS	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid, potassium salt	$C_{10}ClF_{20}KO_4S$	670	-	-	-	-
22	PFMPA	Perfluoro-3-methoxypropanoic acid	$C_4HF_7O_3$	230	5.41	1.00	-0.55	-0.58
23	PFMBA	Perfluoro-4-methoxybutanoic acid	$C_5HF_9O_3$	280	6.42	1.00	0.27	0.24
24	PFDHA	Perfluoro-3,6-dioxaheptanoic acid	$C_5HF_9O_4$	296	7.69	2.74	1.41	1.40
25	PFEESA	Perfluoro(2-ethoxyethane)sulfonic acid	$C_4HF_9O_4S$	316	5.09	1.00	-0.92	-0.92
26	PFNS	Perfluorononane sulfonic acid	$C_9HF_{19}O_3S$	550	7.92	3.28	1.35	1.35
27	PFDS	Perfluorodecane sulfonic acid	$C_{10}HF_{21}O_3S$	600	8.81	8.65	2.13	2.13
28	PFOSA	Perfluorooctanesulfonamide	$C_8H_2F_{17}NO_2S$	499	7.64	23507	5.51	5.00
29	[2,3,4-$^{13}C_3$]PFBA	2,3,4-$^{13}C_3$-sodium perfluoro-*n*-butyrate	$C_1{*}C_3F_7O_2{\cdot}Na$	239	-	-	-	-
30	$^{13}C_8$-PFOA	$^{13}C_8$-perfluorooctanoic acid	$*CF_3(*CF_2)_6*COOH$	422	-	-	-	-

log Kow (octanol–water partition coefficient), LogD (distribution coefficient), and log Koc (soil organic carbon–water partitioning coefficient) were obtained by the Estimation Programs Interface (EPI) Suite developed by the US EPA and Syracuse Research Corp.

Table S2. The gradient program used to separate the 28 compounds, where the mobile phase consisted of 2 mM ammonium acetate in both water (A) and methanol (B)

	Time	A	B	Flow
1	0.00 min	95.0 %	5.0 %	0.400 mL/min
2	1.00 min	75.0 %	25.0 %	0.400 mL/min
3	1.50 min	45.0 %	55.0 %	0.400 mL/min
4	5.50 min	30.0 %	70.0 %	0.400 mL/min
5	7.00 min	20.0 %	80.0 %	0.400 mL/min
6	8.50 min	20.0 %	80.0 %	0.400 mL/min
7	8.51 min	95.0 %	5.0 %	0.400 mL/min

Table S3. Acquisition windows set for the most sensitive detection of the investigated analytes

Index	Start Time (min)	Scan Type	Ion Mode	Div Valve	Store
1	0	MRM	ESI	To Waste	No
2	3.2	MRM	ESI	To MS	Yes
3	4.4	MRM	ESI	To MS	Yes
4	4.9	MRM	ESI	To MS	Yes
5	6.3	MRM	ESI	To MS	Yes
6	7.1	MRM	ESI	To MS	Yes
7	7.9	MRM	ESI	To MS	Yes
8	8.5	MRM	ESI	To MS	Yes
9	8.85	MRM	ESI	To MS	Yes
10	9.3	MRM	ESI	To MS	Yes
11	10.6	MRM	ESI	To Waste	No

Tabel S4. Calibration curve parameters for the 28 PFAS compounds (slope, intercept, R^2).

Compounds	Calibration domain (µg/g)	a	b	R2
PFBA		0.00984	0.01112	0.9996
PFMPA		0.00641	0.04302	0.9998
4:2 FTSA		0.00058	0.00146	0.9999
HFPO-DA		0.00361	0.01659	0.9998
NFDHA		0.00019	0.00294	0.999
PFBS		0.00303	0.03217	0.9995
PFEESA		0.02115	0.18796	0.9997
PFHxA		0.01038	0.08786	0.9997
PFMBA		0.00691	0.05283	0.9997
PFPeA		0.01219	0.10333	0.9996
DONA		0.03314	0.24580	0.9998
PFHpA		0.01999	0.17830	0.9996
PFHxS		0.00299	0.03270	0.9993
6:2 FTSA	0.02-0.6	0.00014	0.00068	0.9999
PFHpS		0.00351	0.03206	0.9997
PFOA		0.00339	0.06652	0.9999
PFNA		0.00371	0.03187	0.9996
PFOS		0.00009	0.00058	0.9999
9Cl-PF3ONS		0.00021	0.00084	0.9999
8:2 FTSA		0.00006	0.00063	0.9991
PFDA		0.00407	0.03965	0.9992
PFNS		0.00055	0.00223	0.9996
11Cl-PF3OUdS		0.00118	0.00311	0.9999
PFDoDA		0.00465	0.03799	0.9996
PFDS		0.00072	0.00391	0.9996
PFOSA		0.00193	0.00334	0.9999
PFUnDA		0.00633	0.13581	0.9984