Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Method for extraction and analysis of per- and poly-fluoroalkyl substances in contaminated asphalt

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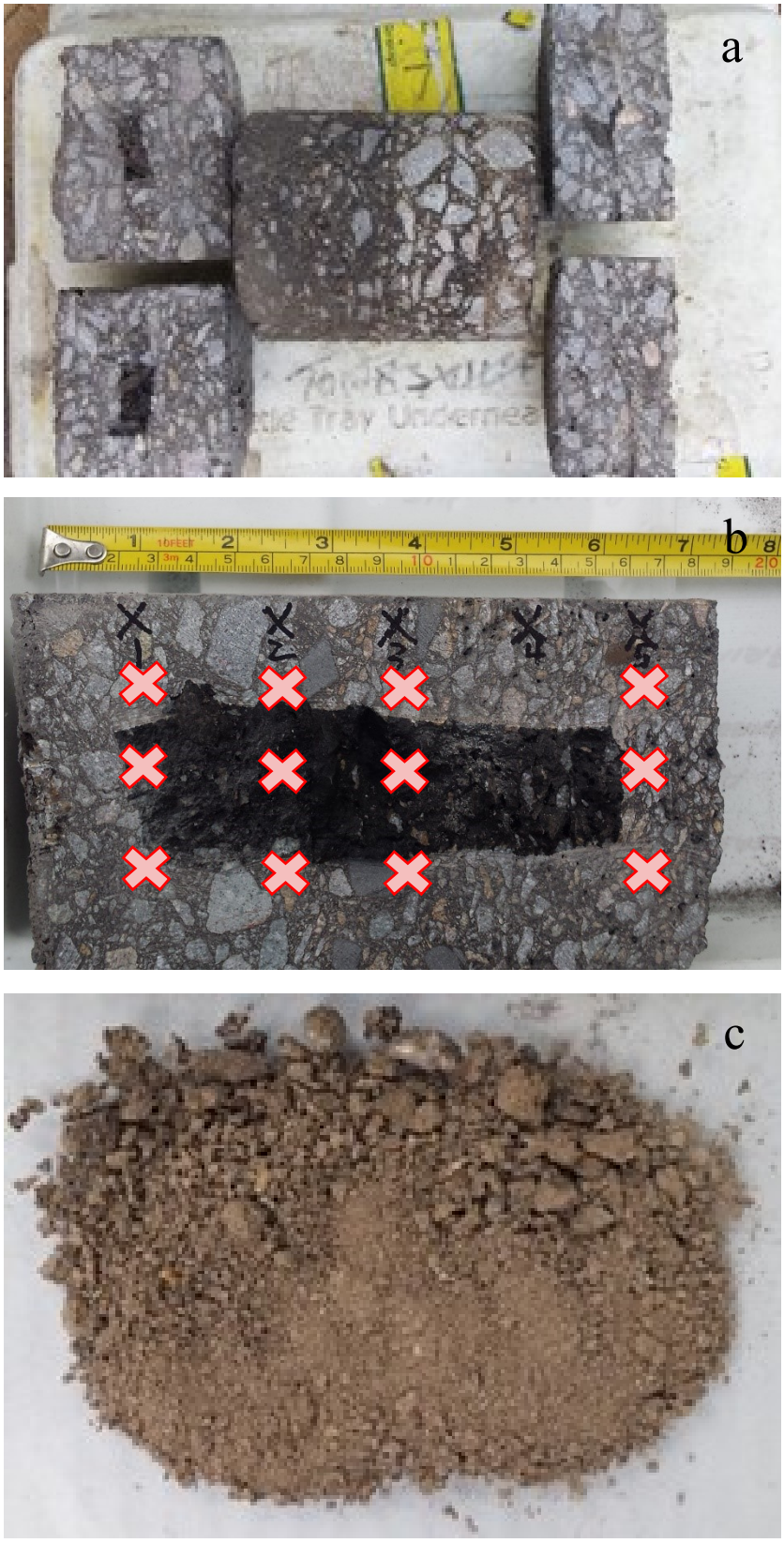

Figure S1. Overview of (a) asphalt core profile, (b) cross-section of asphalt core marked at 50 mm intervals prior to drilling for samples. Red crosses represent an approximate location of triplicate sample for each depth, and (c) asphalt sample collected using a 10 mm drill bit.

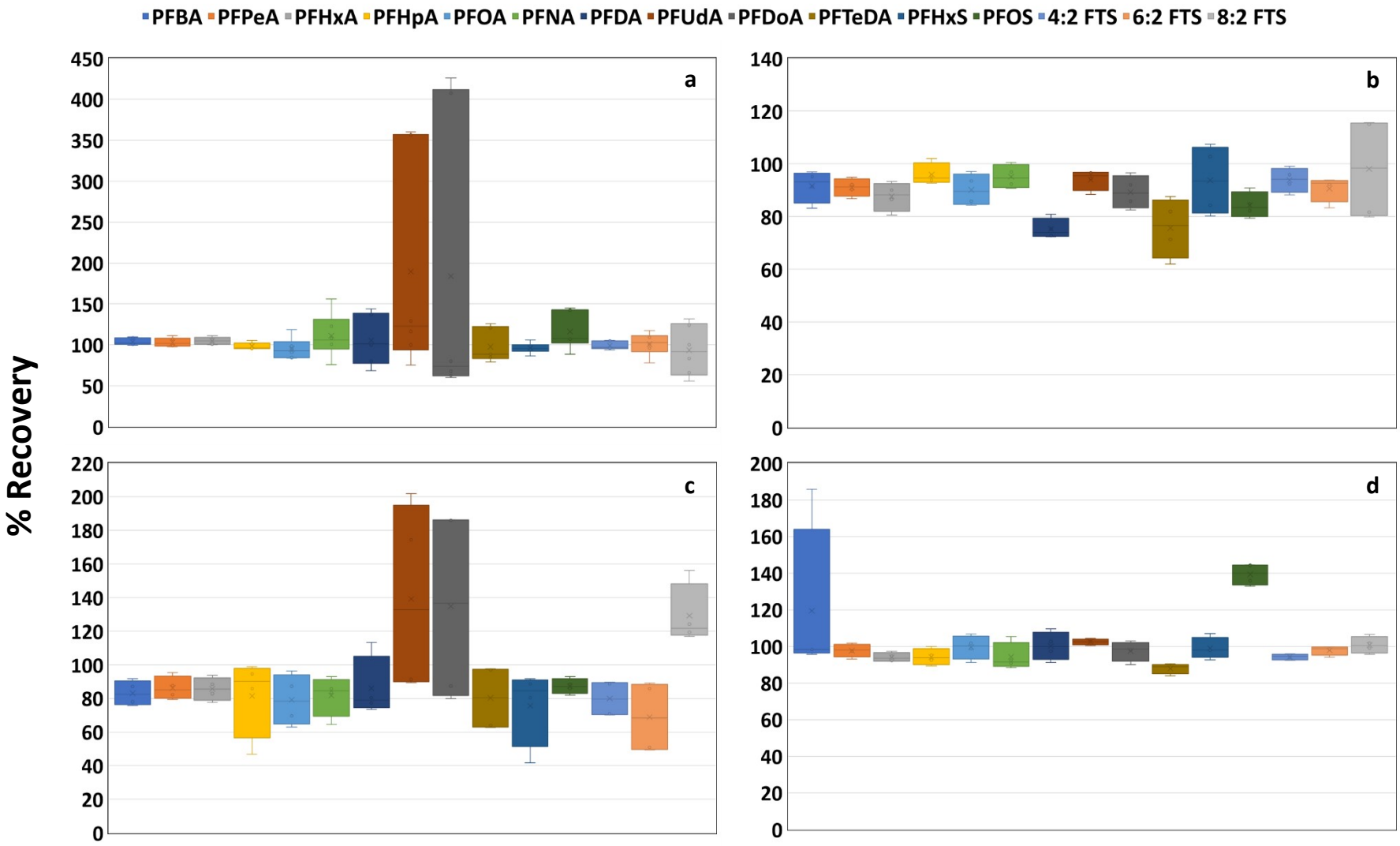

Figure S2. Box plot showing the distribution of recovery of stable isotope-corrected individual PFAS in different cores as a function of (a) stable isotope-labelled internal standard addition timing, (b) sonication temperature, (c) spike level and (d) sample composition (location).

Table S1. Native and stable isotope (SI)-labelled PFAS standards used in this study and their limit of detection (LOD), limit of quantitation (LOQ) and method limit of quantitation (MLOQ) for the chosen method (extractant 2)

Compound	Acronym	Stable isotope	Linear range (ng L^{-1})	LOD (ng L^{-1})	LOQ (ng L^{-1})	MLOQ (µg kg^{-1})
Perfluoroalkane sulfonic acids (PFSAs)						
Perfluorobutane sulfonic acid	PFBS	-	25-10,000	25	83.25	0.70
perfluoropentanesulfonic acid	PFPeS	-	25-10,000	25	83.25	0.90
Perfluorohexane sulfonic acid	PFHxS	$^{18}O_2$PFHxS	25-10,000	25	83.25	1.00
Perfluoroheptanesulfonic Acid	PFHpS	-	25-10,000	25	83.25	1.00
Perfluorooctane sulfonic acid	PFOS	$^{13}C_4$PFOS	250-10,000	250	832.5	0.70
perfluorononanesulfonate	PFNS	-	100-10,000	100	333.0	1.00
Perfluorodecane sulfonic acid	PFDS	-	250-10,000	250	832.5	1.00
Perfluoroalkyl carboxylic acids (PFCAs)						
Perfluorobutanoic acid	PFBA	$^{13}C_4$PFBA	25-100	25	83.25	0.15
Perfluoropentanoic acid	PFPeA	$^{13}C_3$PFPeA	25-100	25	83.25	0.80
Perfluorohexanoic acid	PFHxA	$^{13}C_2$PFHxA	25-100	25	83.25	0.60
Perfluoroheptanoic acid	PFHpA	$^{13}C_4$PFHpA	25-100	25	83.25	0.30
Perfluorooctanoic acid	PFOA	$^{13}C_4$PFOA	25-100	25	83.25	0.60
Perfluorononanoic acid	PFNA	$^{13}C_5$PFNA	25-100	25	83.25	0.80
Perfluorodecanoic acid	PFDA	$^{13}C_2$PFDA	50-100	50	166.50	0.90
Perfluoroundecanoic acid	PFUdA	$^{13}C_2$PFUdA	250-10,000	250	832.50	0.80
Perfluorododecanoic acid	PFDoA	$^{13}C_2$PFDoA	250-10,000	250	832.50	0.60
perfluorotridecanoic acid	PFTrDA	-	250-10,000	250	832.50	0.70
Perfluorotetradecanoic acid	PFTeDA	$^{13}C_2$PFTeDA	250-10,000	250	832.50	0.60
Fluorotelomer sulfonates (FTS)						
4:2 Fluorotelomer sulfonate	4:2 FTS	$^{13}C_2$4:2 FTS	25-100	25	83.25	0.50
6:2 Fluorotelomer sulfonate	6:2 FTS	$^{13}C_2$6:2 FTS	25-100	25	83.25	1.00
8:2 Fluorotelomer sulfonate	8:2 FTS	$^{13}C_2$8:2 FTS	50-100	50	166.50	0.40
10:2 Fluorotelomer sulfonate	10:2 FTS	-	250-10,000	250	832.50	1.00

Table S2. Summary of literature for extraction efficiency of PFAS from various solid matrices

PFAS	Chemical formula	Matrix	% recovery
Perfluorobutanesulfonate (PFBS)	$C_4F_9SO_3$	Soil [2-8] Sediment [5, 6] Wastewater sludge/biosolid [9, 10]	66-81 (M[a]), 62-77 (MO[b]), 71-98 (MN[c]), 62-84 (MA[d]), 74-116 (MB[e]), 61-75 (OS[f]) 75-105 (M), 125 (MA), 371 (MN), 144 (MB), 110-112 (OS) 144 (MB), 110-112 (OS)
Perfluoropentanesulfonate (PFPeS)	$C_5F_{11}SO_3$	Soil [8]	96-100 (MN)
Perfluorohexanesulfonate (PFHxS)	$C_6F_{13}SO_3$	Soil [2-4, 6-8] Sediment [5, 6, 11] Wastewater sludge/biosolid [9-11] Concrete [12]	61-99 (M), 62-80 (MO), 79-100 (MN), 63-90 (MA), 73-116 (MB), 67-80 (OS) 76-85 (M), 56-85 (MA), 102 (MN), 85 (IP[g]) 37-79 (MA), 104 (MB), 110-112 (OS) 108 (M)
Perfluoroheptanesulfonate (PFHpS)	$C_7F_{15}SO_3$	Soil [6-8] Sediment [6] Wastewater sludge/biosolid [10]	82-86 (M), 62-81 (MO), 84-100 (MN), 81-106 (MA), 80-95 (MB), 66-83 (OS) 75 (M), 68 (MA), 90 (MN), 69 (IP) 118 (MB)
Perfluorooctanesulfonate (PFOS)	$C_8F_{17}SO_3$	Soil [2-4, 6-8, 13] Sediment [5, 6, 11] Wastewater sludge/biosolid [9-11] Concrete [12]	70-100 (M), 60-81 (MO), 81-100 (MN), 74-92 (MA), 67-104 (MB), 66-81 (OS) 71-96 (M), 81-87 (MA), 125 (MN), 179 (IP) 79-87 (MA), 95 (MB), 110-112 (OS) 102 (M)
Perfluorononanesulfonate (PFNS)	$C_9F_{19}SO_3$	Soil [8] Wastewater sludge/biosolid [14]	96-100 (MN) 110-112 (OS)
Perfluorodecanesulfonate (PFDS)	$C_{10}F_{21}SO_3$	Soil [2, 3, 6-8] Sediment [5, 6, 11] Wastewater sludge/biosolid [9-11]	53-105 (M), 95-97 (MN), 81 (MA), 70-106 (MB) 75-121 (M), 56-79 (MA), 81 (MN) 63-76 (MA), 153 (MB), 93-109 (OS)
Perfluorododecanesulfonate PFDoS	$C_{12}F_{25}SO_3$	Soil [8]	94-98 (MN)
Fluorotelomer sulphonates (FTS)			
4:2 FTS	$C_6H_4F_9SO_3$	Soil [7]	80-95 (MB)
6:2 FTS	$C_8H_4F_{13}SO_3$	Soil [3, 7-9, 13] Wastewater sludge/biosolid [14]	70 (M), 51-58 (MO), 68-100 (MN), 63-120 (MA), 76-110 (MB), 2-64 (OS) 116-137 (OS)
8:2 FTS	$C_{10}H_4F_{17}SO_3$	Soil [3, 7-9] Wastewater sludge/biosolid [14]	71 (M), 59-60 (MO), 70-100 (MN), 65-100 (MA), 73-121 (MB), 0-96 (OS) 116-127 (OS)
10:2 FTS	$C_{12}H_4F_{21}SO_3$	Soil [8]	103-108 (MN)
Perfluorooctane sulphonamides (FOSA)			
FOSA	$C_8H_2F_9SO_2N$	Soil [3, 7, 8]	97-100 (MN), 95-110 (MB)

MeFOSA	$C_9H_4F_9SO_2N$	Soil [8]	92-98 (MN)
EtFOSA	$C_{10}H_6F_9SO_2N$	Soil [7, 8]	97-101 (MN), 80-95 (MB)
Perfluoroalkyl sulphonamido acetic acids (FOSAA)			
FOSAA	$C_{10}H_3F_9SO_4N$	Soil [7, 8]	91-109 (MN), 60-115 (MB)
MeFOSAA	$C_{11}H_5F_9SO_4N$	Soil [8]	92-103 (MN)
EtFOSAA	$C_{12}H_7F_9SO_4N$	Soil [8]	99-114 (MN)
Perfluoroalkane/fluorotelomer betaines			
PFOSB	$C_{15}H_{15}F_{17}SO_4N_2$	Soil [7]	40 (MB)
6:2 FTAB	$C_{15}H_{19}F_{17}SO_4N_2$	Soil [7, 8]	20 (M), 3 (MO), 46-97 (MN), 19-100 (MA), 17-90 (MB), 0-21 (OS)
12:2 FTAB	$C_{21}H_{19}F_{25}SO_4N_2$	Soil [8]	94-100 (MN)
5:3 FTB	$C_{10}H_{14}F_{11}O_2N$	Soil [8]	21 (M), 4 (MO), 48-97 (MN), 21-100 (MA), 32-82 (MB), 0-22 (OS)
7:3 FTB	$C_{12}H_{14}F_{15}O_2N$	Soil [8]	23 (M), 4-5 (MO), 50-94 (MN), 23-100 (MA), 34-92 (MB), 0-23 (OS)
9:3 FTB	$C_{14}H_{14}F_{19}O_2N$	Soil [8]	26 (M), 5-6(MO), 53-87 (MN), 26-100 (MA), 40-79 (MB), 1-26 (OS)
11:3 FTB	$C_{16}H_{14}F_{23}O_2N$	Soil [8]	25 (M), 5-6 (MO), 50-94 (MN), 25-100 (MA), 35-75 (MB), 0-23 (OS)
5:1:2 FTB	$C_{10}H_{14}F_{12}O_2N$	Soil [8]	23 (M), 4 (MO), 51-75 (MN), 23-100 (MA), 35-97 (MB), 0-2 (OS)
7:1:2 FTB	$C_{12}H_{14}F_{16}O_2N$	Soil [8]	24 (M), 5 (MO), 52-76 (MN), 24-100 (MA), 32-98 (MB), 0-2 (OS)
9:1:2 FTB	$C_{14}H_{14}F_{20}O_2N$	Soil [8]	28 (M), 6 (MO), 55-81 (MN), 28-100 (MA), 42-63 (MB), 0-2 (OS)
11:1:2 FTB	$C_{16}H_{14}F_{20}O_2N$	Soil [8]	28 (M), 6 (MO), 52-76 (MN), 28-100 (MA), 37-102 (MB), 0-2 (OS)
6:2 FTSAB	$C_{12}H_{14}F_{16}O_2N$	Soil [8, 9]	90-99 (MN), 37 (MA)
Fluorotelomer unsaturated acids			
6:2 FTUA	$C_8HF_{12}O_2$	Soil [7, 8]	94-101 (MN), 70 (MB)
8:2 FTUA	$C_{10}HF_{16}O_2$	Soil [7, 8]	96-104 (MN), 70 (MB)

Fluorotelomer carboxylic acids			
4:3 FTCA	$C_7H_4F_9O_2$	Soil [8]	89-96 (MN)
5:3 FTCA	$C_8H_4F_{11}O_2$	Soil [7, 8]	89-95 (MN), 40-60 (MB)
7:3 FTCA	$C_{10}H_4F_{15}O_2$	Soil [7, 8]	92-94 (MN), 60-70(MB)

[a] M=methanol, [b] MO=methanol + other solvent, [c] MN=pH neutral methanol, [d] MA=acidic methanol, [e] MB=basic methanol, [f] OS=other solvent, [g] IP=ion pairing

Table S3. Mass spectrometry multiple reaction monitoring (MRM) parameters for PFAS

Compound	Polarity	Precursor (m/z)	Product (m/z)	Collision Energy (V)	Min Dwell Time (ms)	RF Lens (V)
PFBA	Negative	212.979	168.97	9	25.912	30
$^{13}C_4$PFBA	Negative	216.993	172	9	25.912	30
PFPeA	Negative	262.976	219.042	9	3.384	31
$^{13}C_3$PFPeA	Negative	266	222	9	3.384	32
PFHxA	Negative	312.973	119.042	18.76	3.384	39
PFHxA	Negative	312.973	268.97	9	3.384	39
$^{13}C_2$PFHxA	Negative	315	270	9	3.384	37
PFHpA	Negative	362.97	168.97	15.53	3.384	43
PFHpA	Negative	362.97	319.042	9	3.384	43
$^{13}C_4$PFHpA	Negative	366.983	321.98	9	3.384	43
PFOA	Negative	412.966	169	16.1	3.384	49
PFOA	Negative	412.966	369.042	9	3.384	49
$^{13}C_4$PFOA	Negative	417	372	9	3.384	49
PFNA	Negative	462.963	219.012	15.23	3.384	52
PFNA	Negative	462.963	418.97	9	3.384	52
$^{13}C_5$PFNA	Negative	468	423	9	3.384	52
PFDA	Negative	512.96	269.042	15.8	3.384	56
PFDA	Negative	512.96	469.042	9	3.384	56
$^{13}C_2$PFDA	Negative	515	470	9	3.384	56
PFUdA	Negative	562.957	269.03	16.94	3.384	62
PFUdA	Negative	562.957	518.97	9	3.384	62
$^{13}C_2$PFUdA	Negative	564.964	519.97	9	3.384	62
PFDoA	Negative	612.954	319.042	17.54	3.384	67
PFDoA	Negative	612.954	569	9	3.384	67
$^{13}C_2$PFDoA	Negative	614.96	569.97	9	3.384	67
PFTrDA	Negative	662.95	169	20	3.384	71
PFTrDA	Negative	662.95	618.83	13	3.384	71
PFTeDA	Negative	713	369	18.87	3.384	74
PFTeDA	Negative	713	669	9	3.384	74
$^{13}C_2$PFTeDA	Negative	714.954	669.96	9	3.384	74
PFBS	Negative	298.943	79.957	34	3.384	116
PFBS	Negative	298.943	98.956	29	3.384	116
$^{13}C_3$PFBS	Negative	301.8	80.5	34	3.384	70
PFPeS	Negative	348.94	80.042	33.66	3.384	145
PFPeS	Negative	348.94	99	31	3.384	145
PFHxS	Negative	398.937	79.957	39	3.384	135
PFHxS	Negative	398.937	98.956	35	3.384	135
$^{18}O_2$PFHxS	Negative	403	103	35	3.384	135
PFHpS	Negative	448.933	80.012	37.6	3.384	131
PFHpS	Negative	448.933	98.97	36.2	3.384	131

PFOS	Negative	498.93	79.957	47	3.384	159
PFOS	Negative	498.93	98.956	40	3.384	159
$^{13}C_4$PFOS	Negative	503	99	40	3.384	159
$^{13}C_8$PFOS	Negative	506.8	79.9	47	3.384	70
PFNS	Negative	548.927	80.071	42.34	3.384	148
PFNS	Negative	548.927	98.97	40.67	3.384	148
PFDS	Negative	598.924	80.042	44.92	3.384	169
PFDS	Negative	598.924	98.929	43.48	3.384	169
4:2 FTS	Negative	326.974	81.042	26.07	3.384	115
4:2 FTS	Negative	326.974	307.042	18.11	3.384	115
$^{13}C_2$4:2 FTS	Negative	328.981	308.96	18	3.384	115
6:2 FTS	Negative	426.968	81.042	29.94	3.384	123
6:2 FTS	Negative	426.968	406.988	21.45	3.384	123
$^{13}C_2$6:2 FTS	Negative	428.975	408.96	21	3.384	123
8:2 FTS	Negative	526.962	81.012	34.83	3.384	137
8:2 FTS	Negative	526.962	506.97	24.37	3.384	137
$^{13}C_2$8:2 FTS	Negative	528.968	508.96	24	3.384	137
10:2 FTS	Negative	627.033	81.073	32	3.384	147
10:2 FTS	Negative	627.033	606.975	32	3.384	147

Table S4. Mean recovery (%) of PFAS (without stable isotope-correction) from spiked asphalt using six extractants.

PFAS species		Extractant 1		Extractant 2		Extractant 3		Extractant 4		Extractant 5		Extractant 6	
		Mean	% RSD	Mean	% RSD	Mean	% RSD	Mean	% RSD	Mean	% RSD	Mean	% RSD
Short-chain PFCA	PFBA	121.1	2.6	116.4	5.1	119.0	5.6	52.0*	21.7	135.0	6.0	128.7	2.7
	PFPeA	117.8	7.0	112.1	4.1	109.0	4.1	37.7*	22.3	114.7	8.8	119.1	3.4
	PFHxA	118.1	4.9	115.0	3.9	112.0	4.2	37.4*	18.1	121.7	12.3	120.7	2.3
	PFHpA	112.4	4.5	114.3	3.3	113.3	1.7	45.5*	20.3	116.6	5.1	123.8	5.1
	MEAN	117.4	4.8	114.5	4.1	113.3	3.9	43.2	20.6	122.0	8.0	123.1	3.4
Long-chain PFCA	PFOA	111.0	2.5	111.1	6.8	109.1	2.3	45.6*	28.6	124.2	16.3	136.1	4.8
	PFNA	137.4	16.6	133.3	2.0	142.1	6.3	57.6*	32.2	132.0	10.6	108.5	23.3
	PFDA	162.6	13.6	144.9	32.3	124.0	6.5	40.3*	37.7	152.8	51.3	144.7	21.8
	PFUdA	92.2	22.4	91.9	19.0	131.1	4.8	0.0	0.0	128.0	7.7	202.3	14.7
	PFDoA	90.0	11.7	99.6	13.2	109.8	9.4	0.0	0.0	97.7	16.8	145.5	21.3
	PFTrDA	107.4	3.4	121.8	8.9	114.3	2.0	0.0	0.0	119.2	2.3	211.1	8.8
	PFTeDA	169.1	22.8	149.2	10.8	173.2	3.8	0.0	0.0	178.2	11.1	277.2	1.5
	MEAN	124.2	13.3	121.7	13.3	129.1	5.0	20.5	32.8	133.2	16.6	175.1	13.7
PFCA	MEAN	121.6	10.0	118.9	9.8	123.0	4.6	29.2	26.0	128.9	13.3	155.1	9.7
Short-chain PFSA	PFBS	107.9	2.9	105.5	6.1	103.5	5.9	119.7	8.9	115.5	4.1	116.2	6.4
	PFPeS	109.1	6.8	108.5	6.0	106.2	5.8	120.3	4.6	113.0	3.7	118.9	9.0
	MEAN	108.5	4.9	107.0	6.1	104.8	5.8	120.0	6.7	114.2	3.9	117.6	7.7
Long-chain PFSA	PFHxS	118.8	10.3	114.9	3.4	111.1	7.6	130.2	2.1	127.3	3.6	133.2	3.4
	PFHpS	119.2	4.1	111.3	8.0	111.1	6.5	123.0	5.6	120.8	3.2	116.9	4.1
	PFOS linear	155.4	15.7	150.3	9.4	136.3	15.2	162.7	12.5	164.2	23.6	152.8	12.7
	PFNS	189.8	20.9	174.1	33.3	117.5	10.8	143.8	22.3	157.0	40.6	152.2	21.4
	PFDS	70.4	2.7	85.1	12.0	89.0	1.7	107.2	11.8	96.1	17.9	123.5	18.9
	MEAN	130.7	12.7	127.1	15.0	113.0	9.0	133.4	11.2	133.1	19.3	135.8	12.5
PFSA	MEAN	119.6	9.2	117.1	10.9	108.9	7.5	126.7	9.1	123.6	12.2	126.7	10.3
FTS	4:2 FTS	115.6	2.5	105.9	7.1	116.6	5.2	135.4	4.8	123.1	13.7	136.3	1.0
	6:2 FTS	119.9	9.7	113.5	12.8	116.6	8.0	132.5	15.8	135.4	9.2	152.3	0.2
	8:2 FTS	121.9	11.6	120.4	15.8	85.4	6.8	50.2*	14.4	121.8	48.3	150.8	45.7

10:2 FTS	112.0	3.1	154.1	7.1	161.2	8.6	171.0	23.8	150.1	15.4	209.2	27.9
MEAN	117.4	6.8	123.5	10.5	120.0	7.3	122.3	15.4	132.6	21.0	162.1	19.9

* denotes statistically significant difference in comparison to other extractants.

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