

**The Analysis of Per- and Polyfluoroalkyl Substances in
Wastewater Sludges and Biosolids: Which Adsorbents
Should be Used for
the Cleanup of Extracts?**

(Supporting Information)

Table S1. LC/MS/MS operating condition and other information.

Instrument	Shimadzu LCMS-8030 Triple Quadrupole Mass Spectrometer				
Ionization	Negative electrospray				
Precolumn	Guard Column Thermo Scientific™ Acclaim 120 Å C18, 4.6 x 10 mm, 5 µm				
Column	Agilent Infinity Lab Poroshell 120 Å EC-C18, 3.0 x 50 mm, 2.7 µm				
Column oven temperature	30°C				
Injection volume	30 µL				
Mobile phases	A: 10 mM ammonium acetate in LCMS grade water B: 10 mM ammonium acetate in LCMS grade Methanol				
Flow rate	0.5 mL/min				
Gradient profile	Time (min)	Eluent A Conc. (%)		Eluent B Conc. (%)	
	0	60		40	
	0.5	60		40	
	4.5	20		80	
	10	20		80	
	10.5	60		40	
	13.5	Stop			
Monitored ion transitions	Analytes	Ion transitions	Internal standards	Ion transitions	Calibration range (µg/L)
	PFBA	213 > 169	[¹³ C ₄] MPFBA	217 > 172	1 - 20
	PFPeA	263 > 219	[¹³ C ₅] MPFPeA	268 > 223	1 - 20
	PFHxA	313 > 269	[¹³ C ₅] MPFHxA	318 > 273	0.05 - 20
	PFHpA	463 > 319	[¹³ C ₄] MPFHpA	367 > 322	0.05 - 20
	PFOA	413 > 369	[¹³ C ₈] MPFOA	421 > 376	0.05 - 20
	PFNA	463 > 419	[¹³ C ₉] MPFNA	472 > 427	0.05 - 20
	PFDA	513 > 469	[¹³ C ₆] MPFDA	519 > 474	0.05 - 20

Monitored ion transitions	PFUdA	563 > 519	[¹³ C ₇]	MPFUdA	570 > 525	0.05 - 20
	PFDoA	613 > 569	[¹³ C ₂]	MPFDoA	615 > 570	0.05 - 20
	PFTTrDA	663 > 619	[¹³ C ₂]	MPFTTeDA	715 > 670	0.05 - 20
	PFTeDA	713 > 669	[¹³ C ₂]	MPFTeDA	715 > 670	0.05 - 20
	PFBS	299 > 80	[¹³ C ₃]	MPFBS	302 > 99	0.05 - 20
	PFPeS	349 > 80	[¹³ C ₃]	MPFBS	302 > 99	0.1 - 20
	PFHxS	399 > 80	[¹³ C ₃]	MPHxS	402 > 99	0.05 - 20
	PFHpS	449 > 80	[¹³ C ₃]	MPHxS	402 > 99	0.05 - 20
	PFOS	499 > 80	[¹³ C ₈]	MPFOS	507 > 99	0.05 - 20
	PFNS	549 > 80	[¹³ C ₈]	MPFOS	507 > 99	0.05 - 20
	PFDS	599 > 80	[¹³ C ₈]	MPFOS	507 > 99	0.05 - 20
	4:2FTS	327 > 307	[¹³ C ₂]	M4:2FTS	329 > 81	0.05 - 20
	6:2FTS	427 > 407	[¹³ C ₂]	M6:2FTS	429 > 81	0.05 - 20
	8:2FTS	527 > 507	[¹³ C ₂]	M8:2FTS	529 > 81	0.05 - 20
	FOSA	498 > 78	[¹³ C ₈]	MFOSA	506 > 78	0.05 - 20
	MeFOSAA	570 > 419	[² d ₂]	MMeFOSAA	573 > 419	0.05 - 20
	EtFOSAA	584 > 419	[² d ₂]	MEtFOSAA	589 > 419	0.05 - 20

Table S2. Limit of Quantitation (LOQ). Seven Ottawa sand samples (0.5 g/sample) were spiked with native PFAS (2 ng each) and isotopically labeled PFAS (1 ng each), and the spiked samples were extracted and analyzed. The standard deviation (SD) of the analyzed PFAS concentrations was calculated based on these 7 samples, and the limit of quantitation (LOQ) for each PFAS was calculated as $LOQ = 10 \times SD$. The values should be considered as the “best-case-scenario” LOQ. Since the background organics eluted in the extraction step could affect chromatogram quality, LOQ would vary among biosolid samples. The LOQ of 6:2 FTS is not reported due to cross contamination in some samples.

	LOQ (ng/g dry weight)
PFBA	0.5
PFPeA	1.5
PFHxA	0.1
PFHpA	0.1
PFOA	0.1
PFNA	0.1
PFDA	0.1
PFUdA	0.5
PFDoA	0.5
PFTrDA	1.0
PFTeDA	1.0
PFBS	0.5
PFPeS	0.5
PFHxS	0.1
PFHpS	0.1
PFOS	0.1
PFNS	0.5
PFDS	0.5
4:2 FTS	0.5
6:2 FTS	-
8:2 FTS	0.5
FOSA	0.5
MeFOSAA	1.0
EtFOSAA	1.0

Table S3. Recovery values for native and isotopically labeled PFAS. Biosolid 1 and Biosolid 4 were spiked with both native PFAS (5 ng/compound) and isotopically labeled PFAS (2 ng/compound), and the spiked samples were extracted and analyzed.

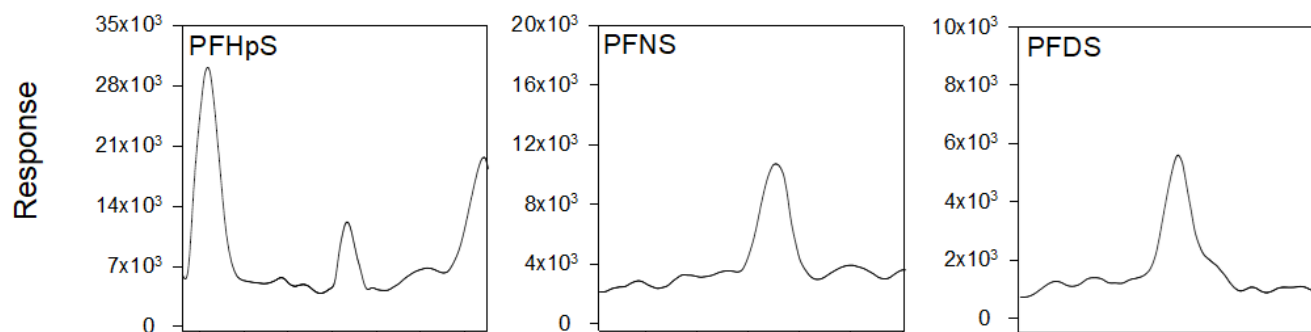
Biosolid 1

Analytes	Recovery	Internal standards	Recovery	p
PFBA	95 ± 4	[¹³ C ₄] MPFBA	87 ± 4	0.07
PFPeA	95 ± 6	[¹³ C ₅] MPFPeA	92 ± 5	0.50
PFHxA	97 ± 7	[¹³ C ₅] MPFHxA	101 ± 4	0.29
PFHpA	108 ± 5	[¹³ C ₄] MPFHpA	112 ± 2	0.30
PFOA	102 ± 3	[¹³ C ₈] MPFOA	108 ± 3	0.10
PFNA	137 ± 6	[¹³ C ₉] MPFNA	130 ± 8	0.28
PFDA	160 ± 11	[¹³ C ₆] MPFDA	156 ± 10	0.62
PFUdA	109 ± 6	[¹³ C ₇] MPFUdA	117 ± 7	0.09
PFDoA	95 ± 4	[¹³ C ₂] MPFDoA	85 ± 5	0.08
PFTrDA	85 ± 5	[¹³ C ₂] MPFTrDA	74 ± 4	0.05
PFTeDA	80 ± 5	[¹³ C ₂] MPFTeDA	74 ± 4	0.14
PFBS	78 ± 5	[¹³ C ₃] MPFBS	84 ± 3	0.17
PFPeS	90 ± 4	[¹³ C ₃] MPFBS	84 ± 3	0.17
PFHxS	96 ± 6	[¹³ C ₃] MPHxS	91 ± 3	0.21
PFHpS	94 ± 4	[¹³ C ₃] MPHxS	91 ± 3	0.25
PFOS	93 ± 3	[¹³ C ₈] MPFOS	93 ± 2	1.00
PFNS	98 ± 5	[¹³ C ₈] MPFOS	93 ± 2	0.22
PFDS	100 ± 9	[¹³ C ₈] MPFOS	93 ± 2	0.38
4:2FTS	215 ± 12	[¹³ C ₂] M4:2FTS	190 ± 10	0.05
6:2FTS		[¹³ C ₂] M6:2FTS	410 ± 20	
8:2FTS	325 ± 13	[¹³ C ₂] M8:2FTS	298 ± 13	0.05
FOSA	100 ± 5	[¹³ C ₈] MFOSA	107 ± 4	0.11
MeFOSAA	137 ± 6	[² d ₂]MMeFOSAA	134 ± 3	0.58
EtFOSAA	138 ± 7	[² d ₂]MEtFOSAA	144 ± 3	0.14

Biosolid 4

Analytes	Recovery	Internal standards	Recovery	p
PFBA	86 ± 6	[¹³ C ₄] MPFBA	81 ± 5	0.28
PFPeA	89 ± 4	[¹³ C ₅] MPFPeA	93 ± 2	0.25
PFHxA	109 ± 4	[¹³ C ₅] MPFHxA	111 ± 3	0.41
PFHpA	125 ± 5	[¹³ C ₄] MPFHpA	128 ± 3	0.49
PFOA	134 ± 4	[¹³ C ₈] MPFOA	133 ± 2	0.70
PFNA	156 ± 7	[¹³ C ₉] MPFNA	152 ± 3	0.37
PFDA	181 ± 6	[¹³ C ₆] MPFDA	175 ± 3	0.23
PFUdA	158 ± 7	[¹³ C ₇] MPFUdA	164 ± 5	0.25
PFDoA	141 ± 5	[¹³ C ₂] MPFDoA	142 ± 3	0.85
PFTeDA	66 ± 4	[¹³ C ₂] MPFTeDA	68 ± 6	0.60
PFTeDA	74 ± 3	[¹³ C ₂] MPFTeDA	68 ± 6	0.26
PFBS	116 ± 7	[¹³ C ₃] MPFBS	115 ± 4	0.78
PFPeS	111 ± 7	[¹³ C ₃] MPFBS	115 ± 4	0.43
PFHxS	109 ± 6	[¹³ C ₃] MPHxS	114 ± 5	0.27
PFHpS	119 ± 4	[¹³ C ₃] MPHxS	114 ± 5	0.29
PFOS	105 ± 5	[¹³ C ₈] MPFOS	110 ± 4	0.21
PFNS	101 ± 6	[¹³ C ₈] MPFOS	110 ± 4	0.10
PFDS	104 ± 5	[¹³ C ₈] MPFOS	110 ± 4	0.16
4:2FTS	232 ± 14	[¹³ C ₂] M4:2FTS	210 ± 10	0.06
6:2FTS		[¹³ C ₂] M6:2FTS	399 ± 10	
8:2FTS	369 ± 13	[¹³ C ₂] M8:2FTS	400 ± 20	0.05
FOSA	97 ± 3	[¹³ C ₈] MFOSA	100 ± 3	0.26
MeFOSAA	121 ± 5	[² d ₂]MMeFOSAA	129 ± 3	0.11
EtFOSAA	156 ± 6	[² d ₂]MEtFOSAA	170 ± 10	0.13

Extract of Biosolid 1 cleaned with ENVI-Carb + WAX and subsequently spiked with a mixture of 24 native PFAS (2.5 ng/mL)



Extract of Biosolid 1 cleaned with ENVI-Carb + PSA + C18 and subsequently spiked with a mixture of 24 native PFAS (2.5 ng/mL)

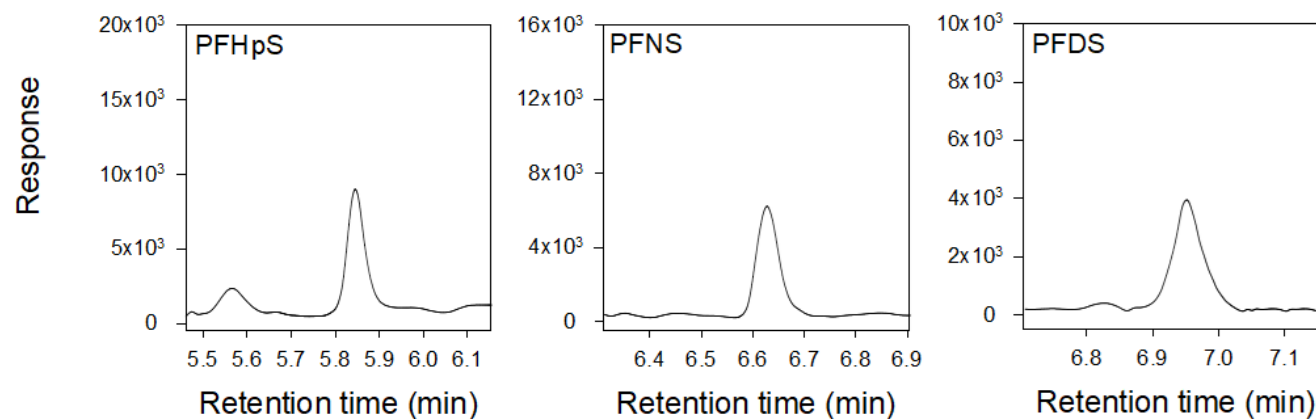


Figure S1-A. Chromatograms of perfluoro sulfonates in the Biosolid 1 extract cleaned with ENVI-Carb and WAX (top panels) and with a blend of ENVI-Carb, PSA, and C18 (bottom panels). These compounds were not present in Biosolid 1. Thus, the compounds were added to the cleaned-up extract prior to LC/MS/MS analysis.

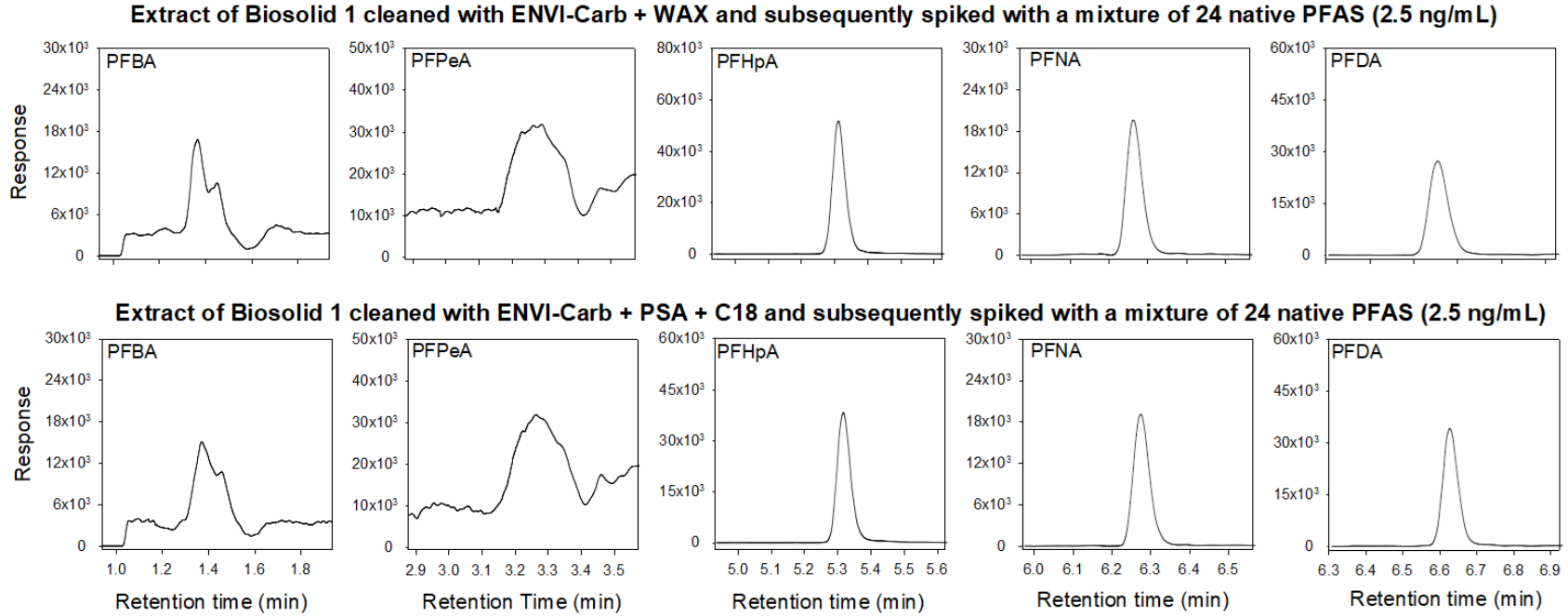


Figure S1-B. Chromatograms of other PFCAs in the Biosolid 1 extract cleaned with ENVI-Carb and WAX (top panels) and with a blend of ENVI-Carb, PSA, and C18 (bottom panels). The cleaned-up extracts were spiked prior to LC/MS/MS analysis.

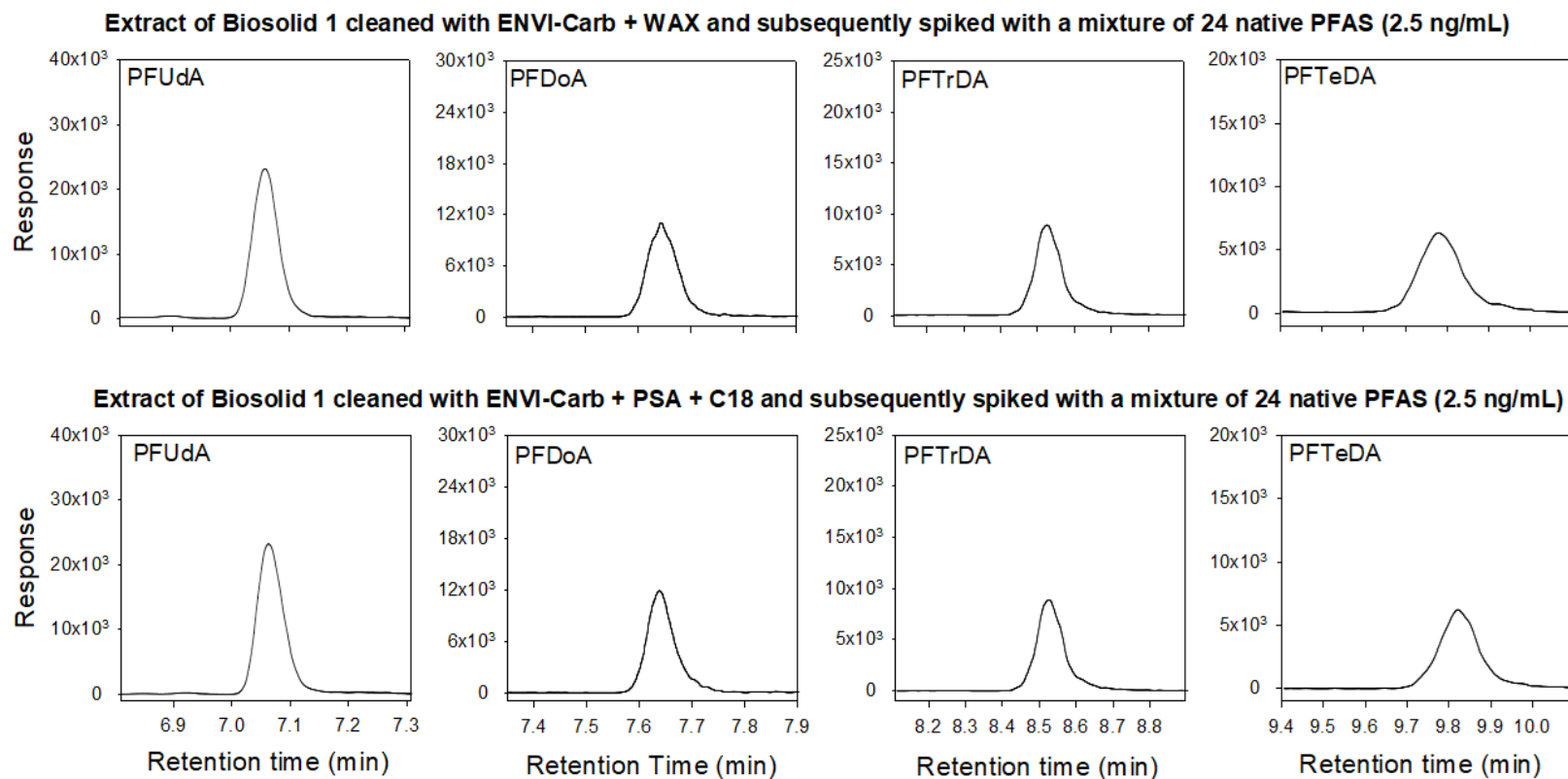
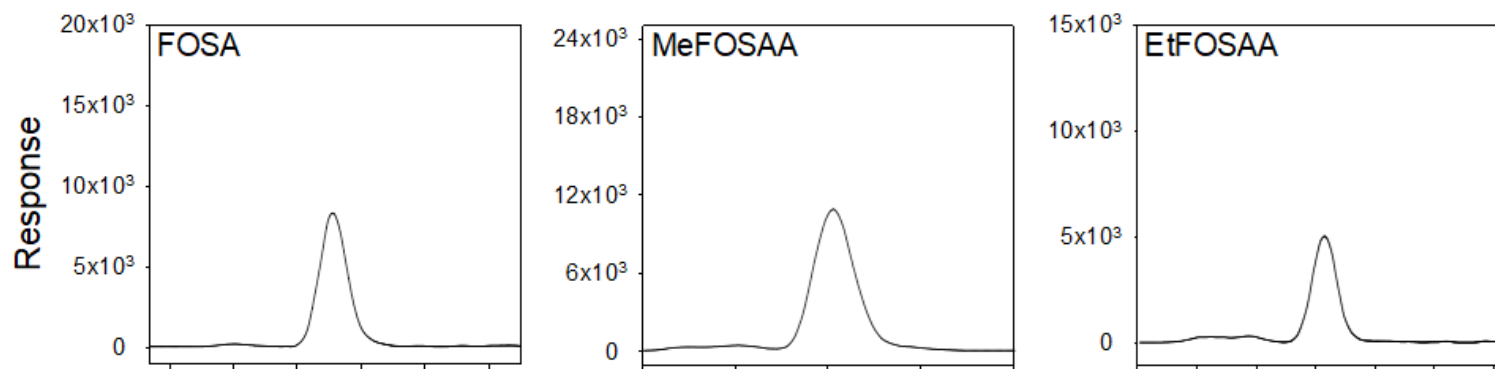


Figure S1-B cont'd. Chromatograms of other PFCAs in the Biosolid 1 extract cleaned with ENVI-Carb and WAX (top panels) and with a blend of ENVI-Carb, PSA, and C18 (bottom panels). The cleaned-up extracts were spiked prior to LC/MS/MS analysis.

Extract of Biosolid 1 cleaned with ENVI-Carb + WAX and subsequently spiked with a mixture of 24 native PFAS (2.5 ng/mL)



Extract of Biosolid 1 cleaned with ENVI-Carb + PSA + C18 and subsequently spiked with a mixture of 24 native PFAS (2.5 ng/mL)

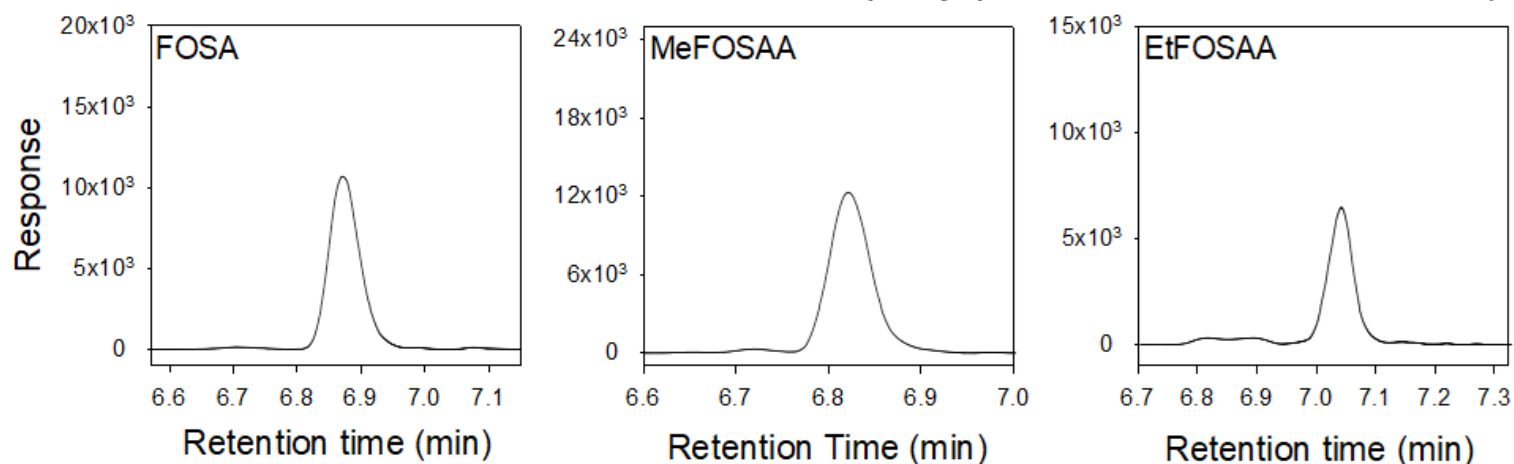


Figure S1-C. Chromatograms of precursors in the Biosolid 1 extract cleaned with ENVI-Carb and WAX (top panels) and with a blend of ENVI-Carb, PSA, and C18 (bottom panels). The cleaned-up extracts were spiked prior to LC/MS/MS analysis.

Photo A



**Biosolid 1
1g PSA**

Photo B



**Biosolid 1
1g C18**

Photo C



**Biosolid 1
1g ENVI-Carb**

Photo D



**Biosolid 1
1g PSA
1g C18**

Photo E



**Biosolid 1
1g ENVI-Carb
1g PSA**

Photo F



**Biosolid 1
1g ENVI-Carb
1g C18**

Photo G



**Biosolid 1
1g ENVI-Carb
1g PSA
1g C18**

Figure S2. Photos A, B, C, D, E, F and G present the physical appearance of the Biosolid 1 extract cleaned with various adsorbents specified below each photo.

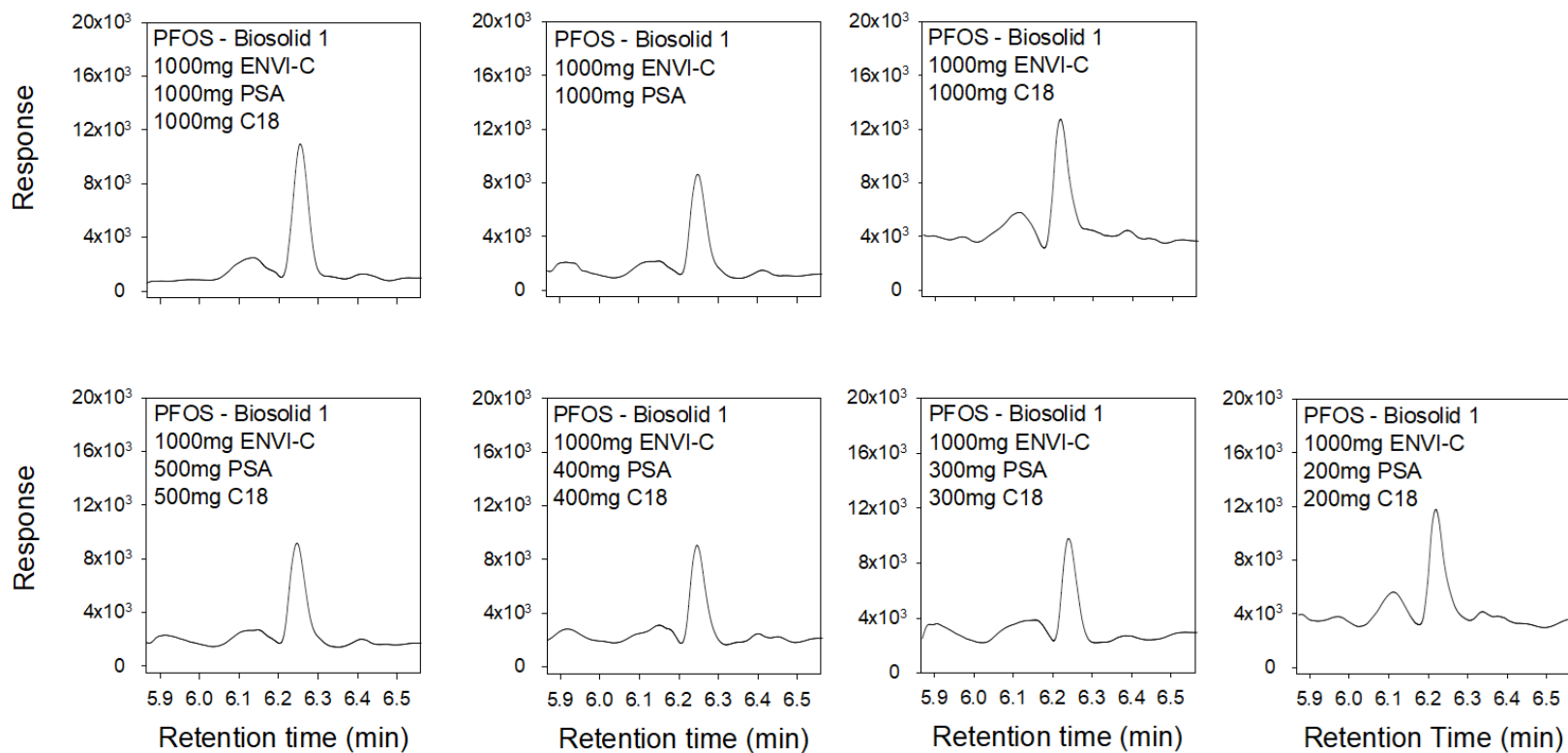


Figure S3. Chromatograms of PFOS in the Biosolid 1 extract cleaned with blends of ENVI-Carb, PSA, and C18.

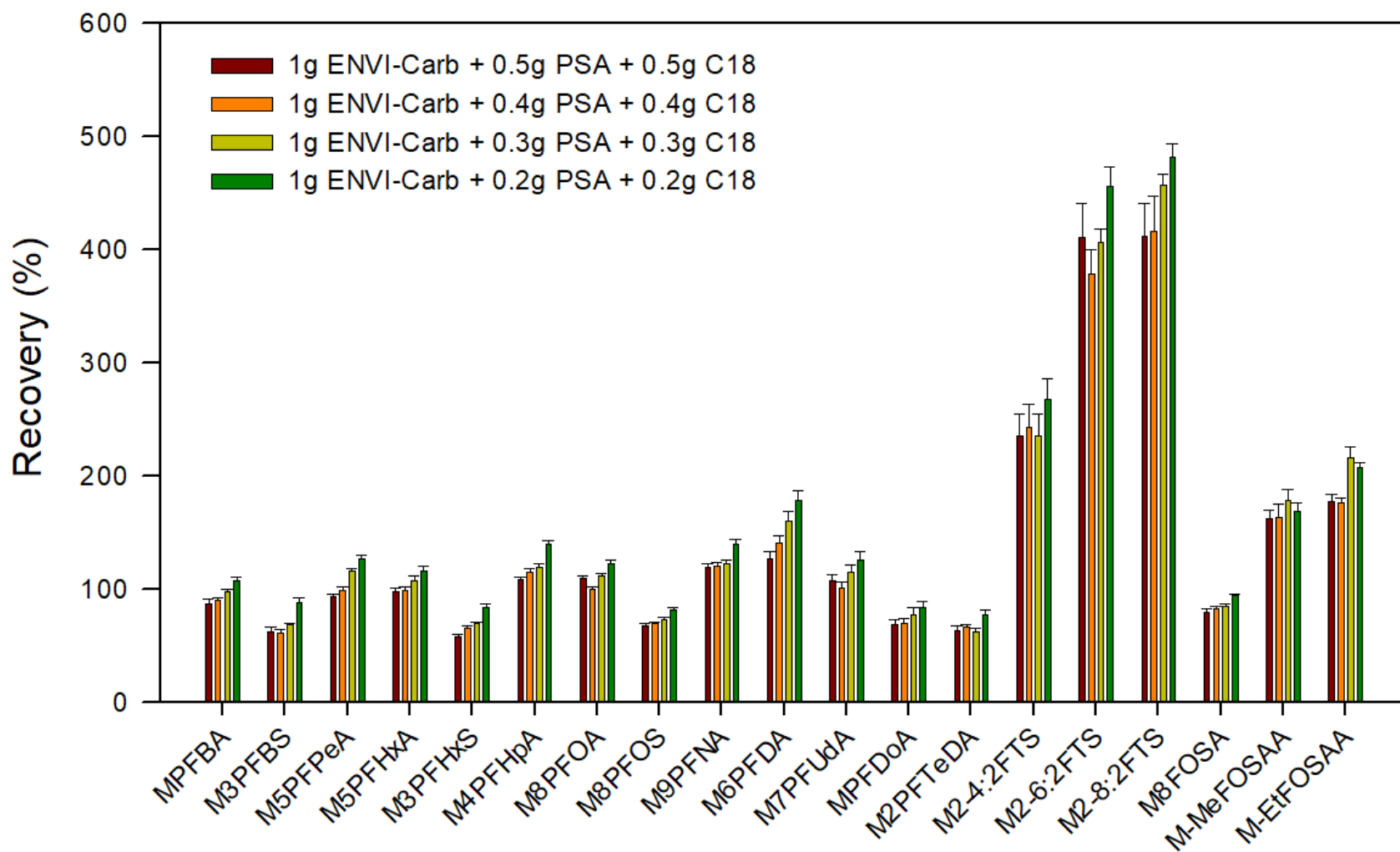


Figure S4. Mean Recovery Values (n=3) of mass-labelled PFAS of Biosolid 1 cleaned with 1g ENVI-Carb and various amounts of PSA and C18.

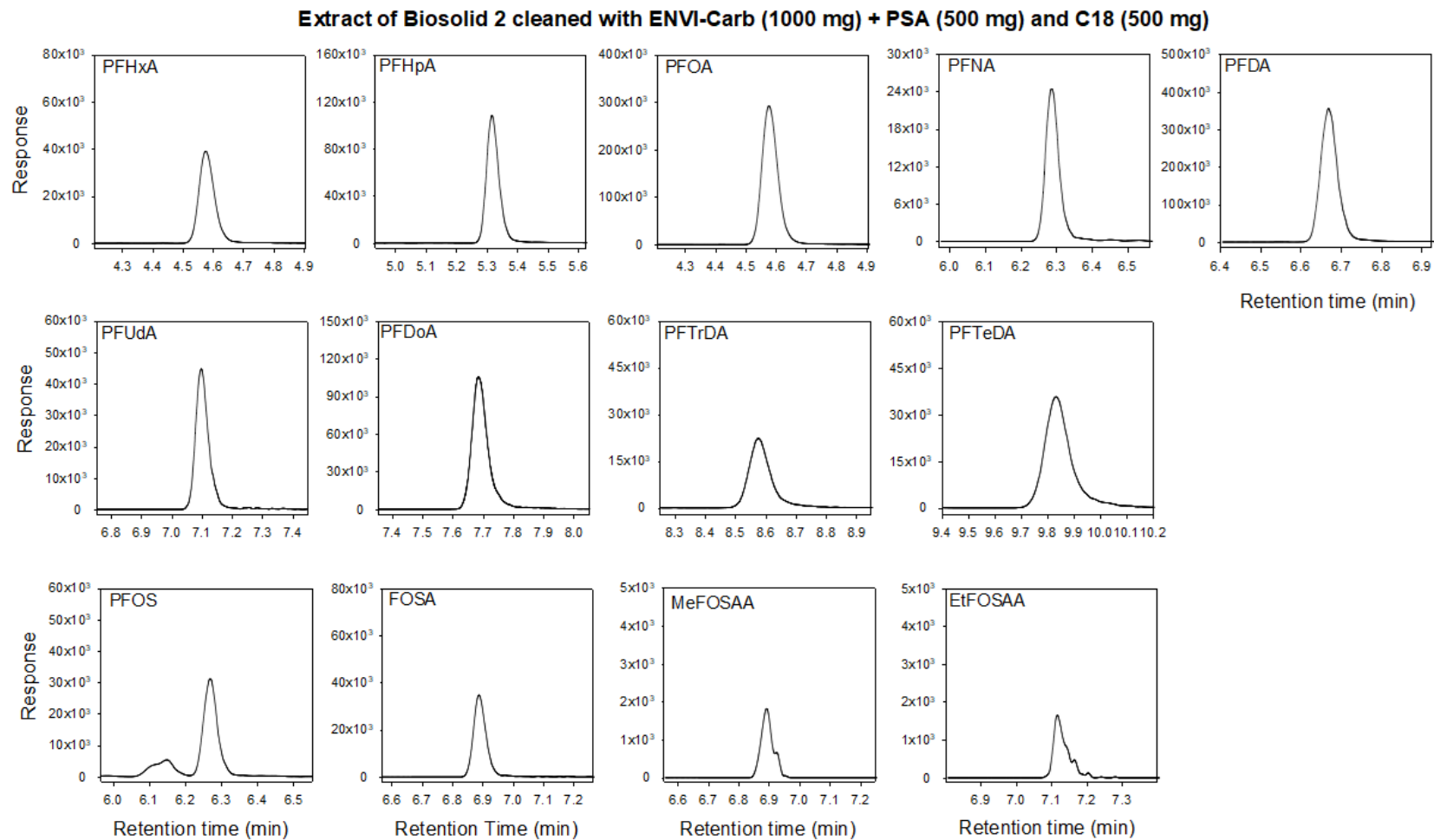


Figure S5-A. Chromatograms of all PFASs in the Biosolid 2 extract cleaned with ENVI-Carb (1000 mg), PSA (500 mg) and C18 (500 mg)

Extract of Biosolid 3 cleaned with ENVI-Carb (1000 mg) + PSA (500 mg) and C18 (500 mg)

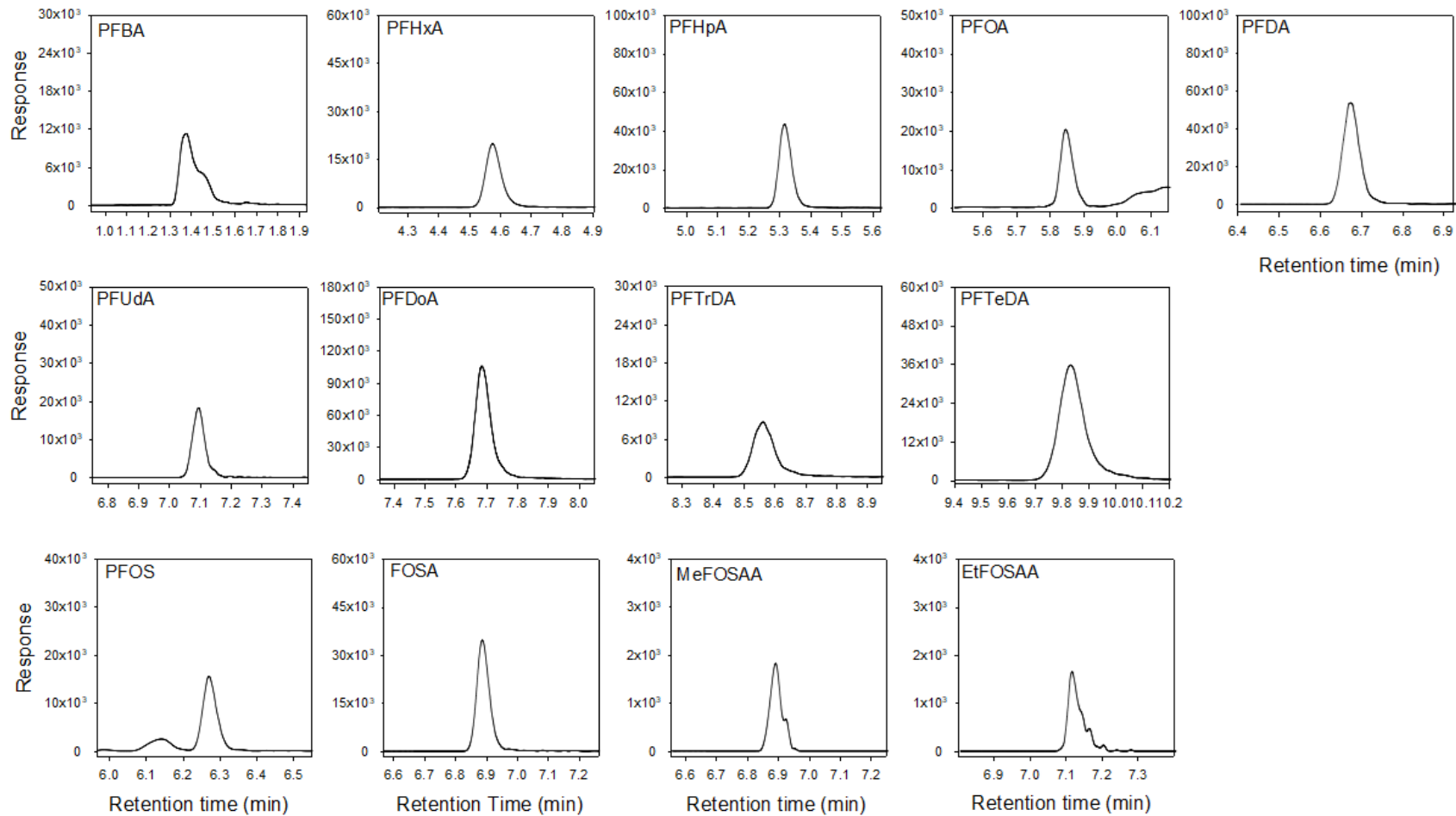


Figure S5-B. Chromatograms of all PFASs in the Biosolid 3 extract cleaned with ENVI-Carb (1000 mg), PSA (500 mg) and C18 (500 mg)

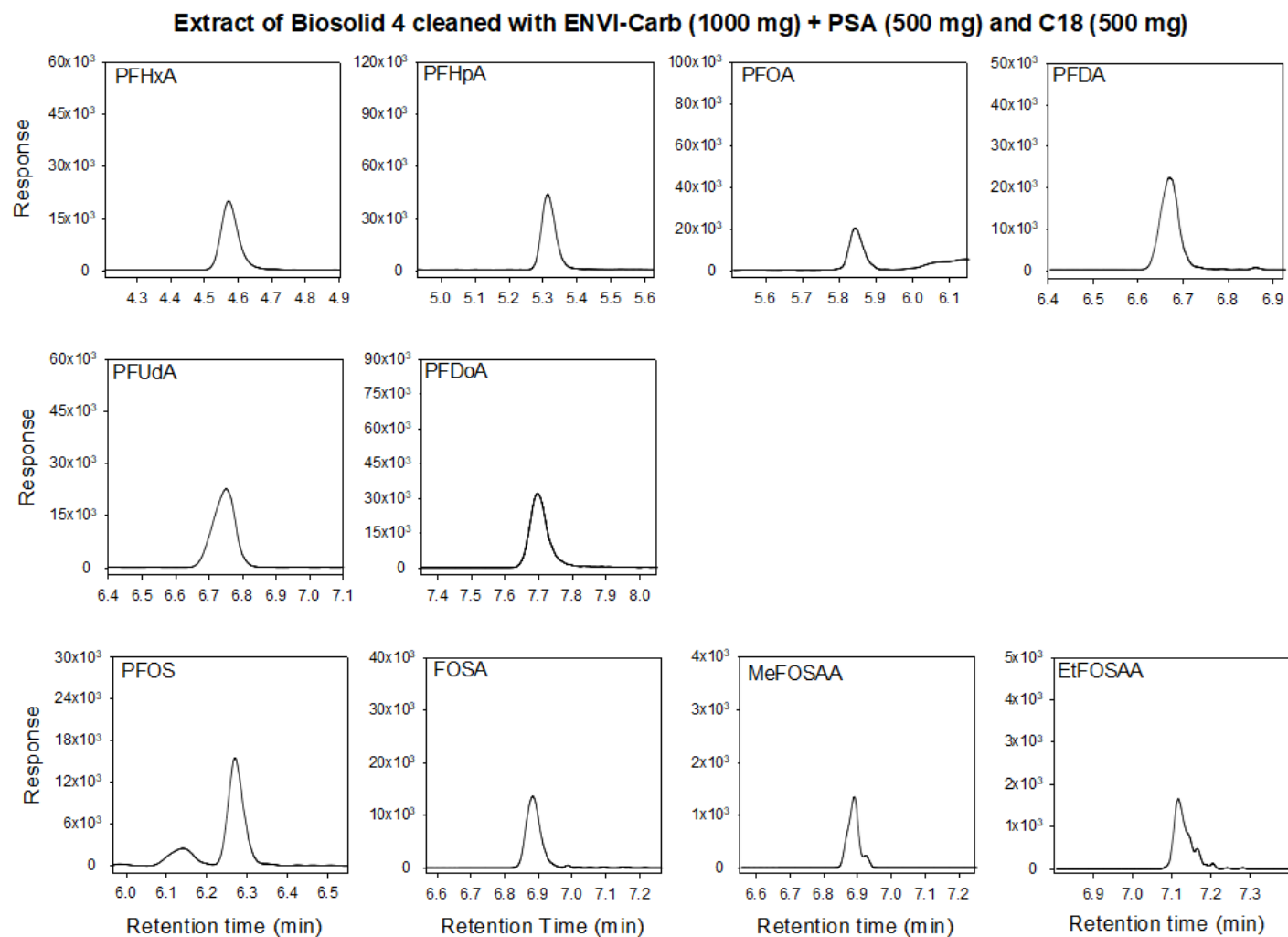


Figure S5-C. Chromatograms of all PFASs in the Biosolid 4 extract cleaned with ENVI-Carb (1000 mg), PSA (500 mg) and C18 (500 mg)

Extract of Biosolid 5 cleaned with ENVI-Carb (1000 mg) + PSA (500 mg) and C18 (500 mg)

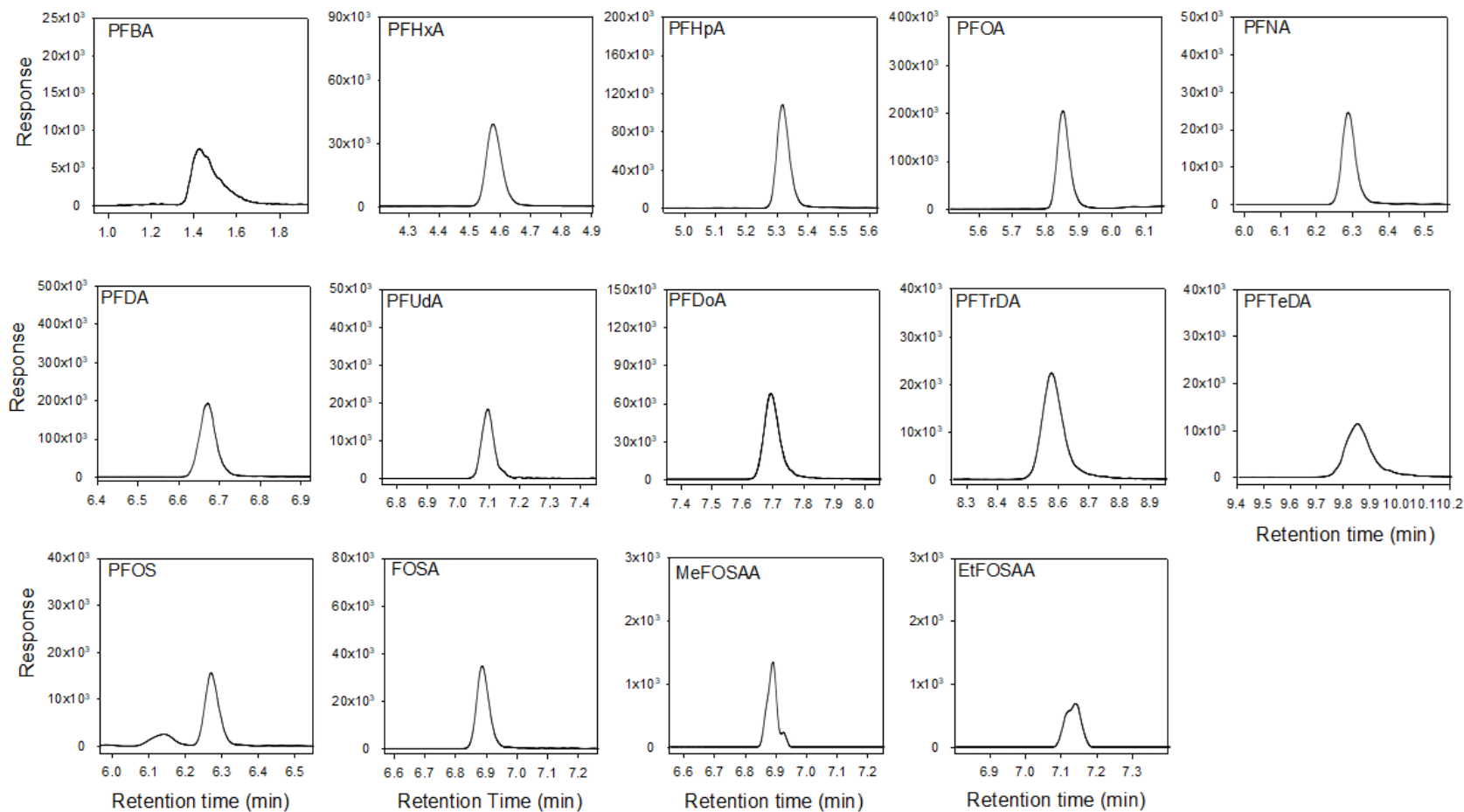


Figure S5-D. Chromatograms of all PFASs in the Biosolid 5 extract cleaned with ENVI-Carb (1000 mg), PSA (500 mg) and C18 (500 mg)

Extract of Biosolid 6 cleaned with ENVI-Carb (1000 mg) + PSA (500 mg) and C18 (500 mg)

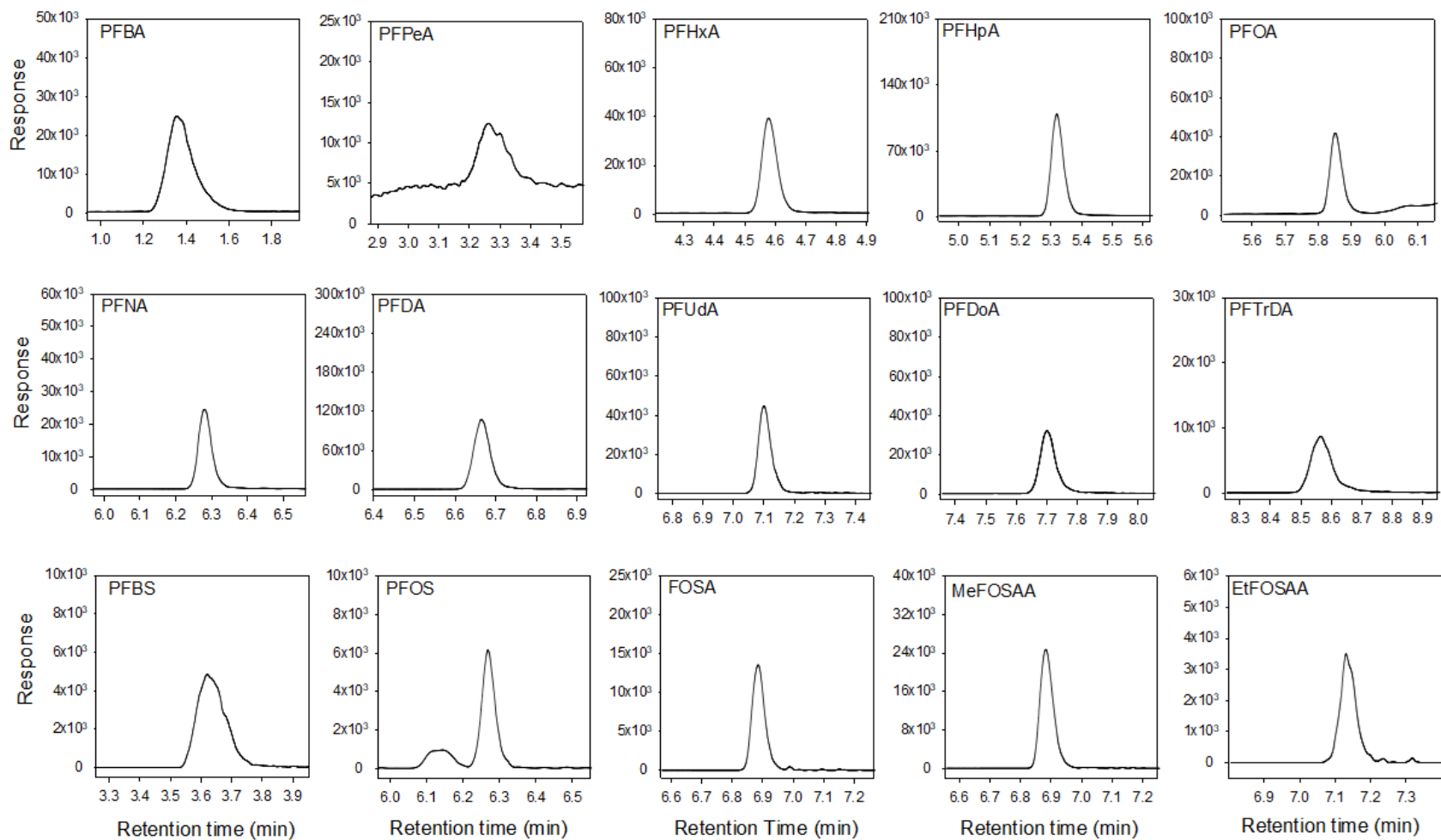


Figure S5-E. Chromatograms of all PFASs in the Biosolid 6 extract cleaned with ENVI-Carb (1000 mg), PSA (500 mg) and C18 (500 mg)

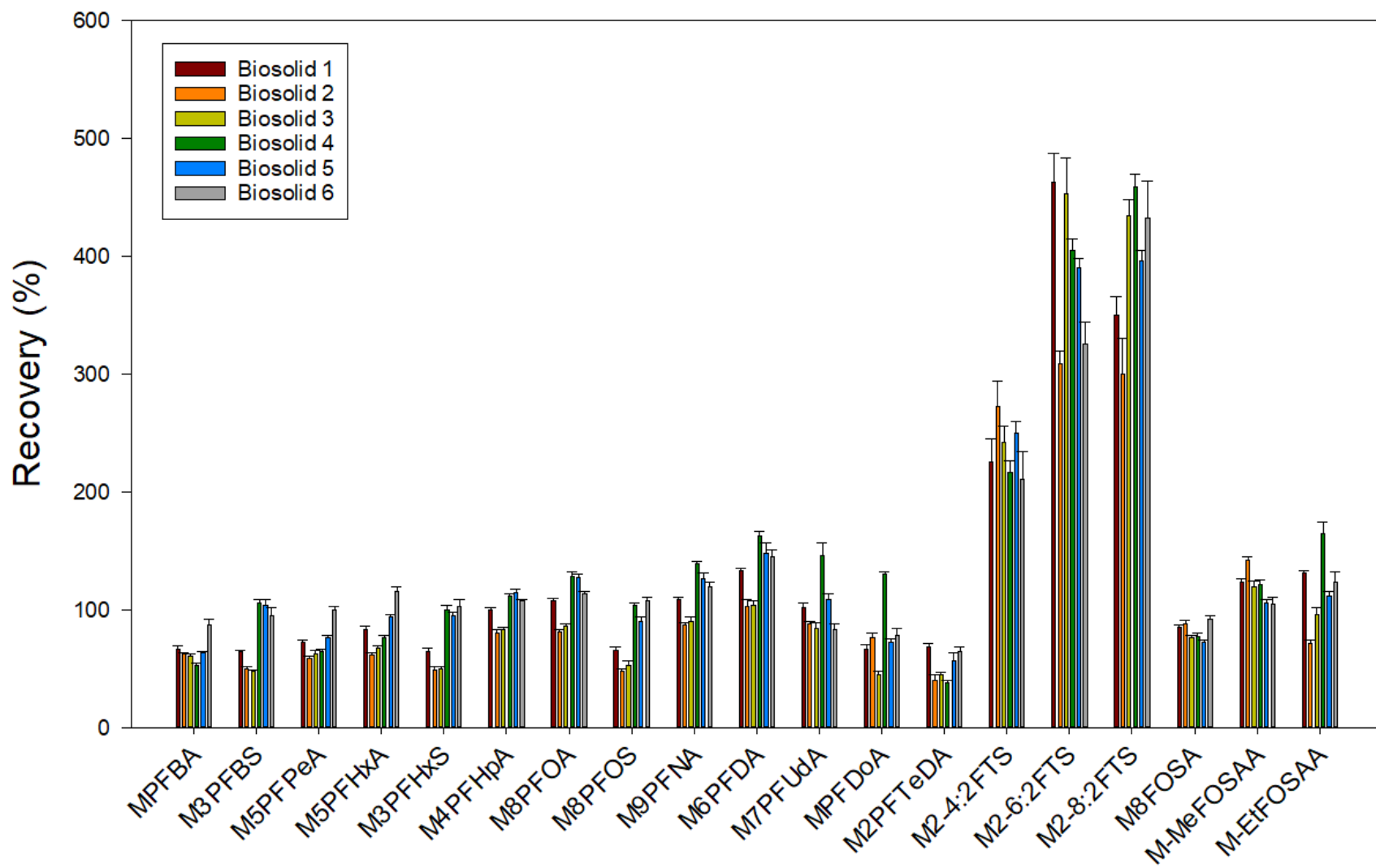


Figure S6. Mean Recovery Values (n=3) of mass-labelled PFAS of Biosolid 1, 2, 3, 4 and 5 cleaned with 1g ENVI-Carb + 0.5g PSA + 0.5g C18.