

Cleanup of Per- and Polyfluoroalkyl Substances in Soil Extracts Using EPA Method 1633 with Automated Solid Phase Extraction - Turbo Trace PFC

Per- and polyfluoroalkyl substances (PFAS) constitute a group of compounds characterized by perfluorinated or polyfluorinated carbon chain moieties, typically denoted by structures such as $F(CF_2)_n$ or $F(CF_2)_n-(C_2H_4)_n$. Due to their unique properties, these substances have found extensive application in various industrial and consumer products.

Recent developments in the United States have led to the introduction of EPA method 1633, which addresses the need for robust methodologies to monitor and analyze PFAS. This method, unveiled in early 2024, enables comprehensive analysis across various matrices, including wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. EPA Method 1633 represents a significant advancement in the analytical toolkit for assessing PFAS contamination and understanding their distribution and behavior in diverse environmental compartments.

Method 1633 has provided a framework for analysis of solid materials for PFAS. Extraction of these compounds from solids can be carried out either automatically or manually. The subsequent cleanup step is described here using a fully automated Solid Phase Extraction system. Laboratories can greatly increase their sample throughput with automated cleanup even when using a manual extraction technique for solid materials.

Instrumentation

- FMS Turbo Trace PFC™ System The system is modular in nature and can be extended to a total of 4 modules for a total of 8 samples processed in parallel.
- Vacuum pump
- Agilent 6475 TripleQuad LC/MS

Consumables

- FMS Inc. PFAS Carbon/WAX SPE Cartridge, 50/200 mg
- Ultrapure DI water
- Methanol pesticide grade
- Ammonium hydroxide
- Formic acid
- Relevant PFAS spiking standards

Method

- Five gram dry weight soil samples were spiked with relevant PFAS standards and extracted manually with 30 mL 0.3 % ammonia in methanol.
- Extracts were then concentrated in an automated evaporator (FMS SuperVap®) and diluted with 50 mL water.
- Up to 8 extracts (50 mL) in sample bottles can be loaded onto system and cartridges installed.
- Rinse bottles are automatically filled during procedure
- Use positive pressure (nitrogen) for pumping solvents and mixes through the system and use vacuum to load the samples
- Condition cartridges with 15 mL 1% methanolic ammonium hydroxide followed by 5 mL of 0.3M formic acid.
- Load samples across the cartridges at 5-10 mL/min (vacuum ~ 8-inch Hg)
- Sample bottles rinsed with 5 mL reagent water (twice) followed by 5 mL of 1:1 0.1M formic acid/methanol and load rinses across the cartridges
- Dry 2 min
- Rinse sample bottles with 5 mL 1% methanolic ammonium hydroxide
- Load rinses across cartridges and collect in polypropylene tubes
- As per the method no further concentration is carried out.
- Further relevant standards were added prior to LC/MS analysis.



Analysis

- Take aliquot from final 5 mL extract (Method 1633 does not require volume reduction of final extract)
- Agilent 1290 Infinity II LC System
- Agilent 6475 Triple quad LC/MS
- Agilent Zorbax Eclipse Plus C18 column 2.1 x 50 mm, 1.8 μ m
- Column temperature 40 °C
- Injection 5.0 μ L
- Mobile phase 5 mM ammonium acetate in 95% water, 5% acetonitrile (A) and methanol (B)
- Gradient
 - 0 min 98% A 2% B
 - 0.2 min 98% A 2% B
 - 10 min 5% a 95% B
- Stop time 12.2 min
- Dynamic MRM negative electrospray
- T (gas) = 230 °C
- T (sheath) = 355 °C



TurboTrace PFC
System



	Soil-1	Soil-2	Soil-3	Soil-4		
Name	Final Conc.	Final Conc.	Final Conc.	Final Conc.	Average	RSDs (%)
11Cl-PF3OUdS	0.000	0.000	0.000	0.000	0.000	0.0
3-3 FTCA	0.000	0.000	0.000	0.000	0.000	0.0
4-2 FTS	0.000	0.000	0.000	0.000	0.000	0.0
5-3 FTCA	0.000	0.000	0.000	0.000	0.000	0.0
6-2 FTS	0.043	0.039	0.051	0.040	0.044	12.6
7-3 FTCA	0.000	0.000	0.000	0.000	0.000	0.0
8-2 FTS	0.105	0.122	0.137	0.108	0.118	12.3
9Cl-PF3ONS	0.000	0.000	0.000	0.000	0.000	0.0
ADONA	0.000	0.000	0.000	0.000	0.000	0.0
EtFOSE	0.000	0.000	0.000	0.000	0.000	0.0
HFPO-DA	0.000	0.000	0.000	0.000	0.000	0.0
MeFOSE	0.000	0.000	0.000	0.000	0.000	0.0
N-EtFOSA	0.000	0.000	0.000	0.000	0.000	0.0
N-EtFOSAA	0.000	0.000	0.000	0.000	0.000	0.0
NFDHA	0.000	0.000	0.000	0.000	0.000	0.0
N-MeFOSA	0.000	0.000	0.000	0.000	0.000	0.0
N-MeFOSAA	0.000	0.000	0.000	0.000	0.000	0.0
PFBA	0.679	0.506	0.516	0.462	0.541	17.6
PFBS	0.420	0.400	0.446	0.575	0.460	17.0
PFDA	1.078	1.185	0.990	1.020	1.068	8.0
PFDoA	0.569	0.585	0.527	0.586	0.567	4.9
PFDoS	0.000	0.000	0.000	0.000	0.000	0.0
PFDS	0.000	0.000	0.000	0.000	0.000	0.0
PFEESA	0.000	0.000	0.000	0.000	0.000	0.0
PFHpA	0.327	0.334	0.450	0.474	0.396	19.4
PFHpS	0.000	0.000	0.000	0.000	0.000	0.0
PFHxA	0.697	1.012	1.078	1.026	0.953	18.2
PFHxS	0.000	0.000	0.000	0.000	0.000	0.0
PFMBA	0.000	0.000	0.000	0.000	0.000	0.0
PFMPA	0.000	0.000	0.000	0.000	0.000	0.0
PFNA	0.433	0.426	0.498	0.421	0.444	8.1
PFNS	0.075	0.053	0.051	0.072	0.063	20.0
PFOA	0.946	1.283	1.031	1.250	1.127	14.6
PFOS	4.328	3.431	3.823	3.507	3.772	10.8
PFOSA	0.000	0.000	0.000	0.000	0.000	0.0
PFPeA	0.523	0.625	0.618	0.589	0.589	7.9
PFPeS	0.000	0.000	0.000	0.000	0.000	0.0
PFTDA	0.256	0.212	0.223	0.162	0.213	18.2
PFTTrDA	0.200	0.212	0.190	0.152	0.188	13.8
PFUnA	0.492	0.451	0.648	0.524	0.529	16.1

Table 1. Average native PFAS (ng/g) in 5 g soil and RSDs (%) for 40 PFAS (1633) using manual extraction and Turbo Trace PFC cleanup (n=4).



	SOIL-01	SOIL-02	SOIL-03	SOIL-04			EPA
Name	% Recoveries	% Recoveries	% Recoveries	% Recoveries	Average	RSD (%)	Window
13C2-4-2 FTSA	73	86	82	83	81	6.9	40-200
13C2-6-2 FTS	72	78	68	87	76	10.8	40-200
13C2-8-2 FTSA	88	91	81	79	85	6.7	40-300
13C2-PFDoDA	98	86	77	87	87	9.9	10-130
13C2-PFTDA	94	86	82	85	87	5.9	10-130
13C3-HFPO-DA	69	89	103	112	93	20.1	40-130
13C3-PFBS	92	84	97	81	89	8.3	40-135
13C3-PFHxS	84	120	91	96	98	16.0	40-130
13C4-PFBA	99	110	101	91	100	7.8	5-130
13C4-PFHpA	103	101	95	99	100	3.4	40-130
13C5-PFHxA	98	99	98	101	99	1.4	40-130
13C5-PFPeA	93	97	100	103	98	4.3	40-130
13C6-PFDA	85	79	84	74	81	6.3	40-130
13C7-PFUnA	97	80	74	89	85	11.9	30-130
13C8-PFOA	89	83	86	81	85	4.1	50-200
13C8-PFOS	97	112	111	93	103	9.4	50-200
13C8-PFOSA	83	108	96	93	95	10.8	40-130
13C9-PFNA	86	95	99	105	96	8.3	40-130
2H3-N-MeFOSA	89	118	81	85	93	18.0	10-130
2H3-N-MeFOSAA	98	117	104	85	101	13.2	40-170
2H5-N-EtFOSA	87	94	86	107	94	10.4	10-130
2H5-N-EtFOSAA	83	107	110	93	98	12.8	25-135
2H7-MeFOSE	97	105	88	95	96	7.3	10-130
2H9-EtFOSE	88	102	84	98	93	9.0	10-130

Table 2. Recoveries (%), RSDs (%) and acceptance windows (%) for 24 surrogate PFAS in manual soil extraction and Turbo Trace PFC cleanup (n=4).

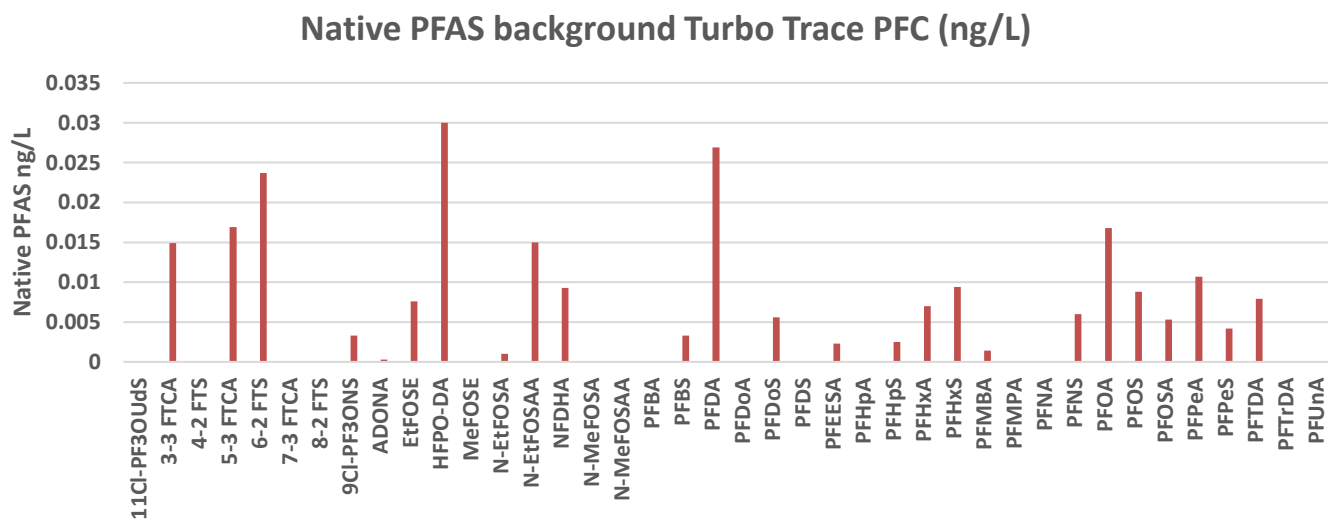


Figure 1. Native PFAS background with Turbo Trace PFC for method 1633 (in ng/L).



Discussion and Conclusions

40 native PFAS compounds were analyzed using EPA method 1633 (Table 1) in 5 g soil samples with manual extraction and cleanup across the fully automated Turbo Trace PFC SPE system. Native concentrations were low at 0-6 ng/g. Table 2 shows the recoveries in percent of the 24 surrogates with all results between 75-120 % with low RSDs (%). The data shows excellent recoveries and in Figure 1 very low native PFAS background contribution from the system (in ng/L).

The Turbo Trace PFC system produces data that is as good as other more expensive fully automated SPE systems. The system is easy to operate and has fewer valves reducing chance of breakdown and contamination. Cleaning the system between runs is quick and easy.

The automated cleanup step in the sample processing is fast with total run time ~ 30-45 min. Compared to drinking water and wastewater samples that typically have 500 mL volumes for 1633 the 50 mL volumes of the soil cleanup have fast loading times.

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