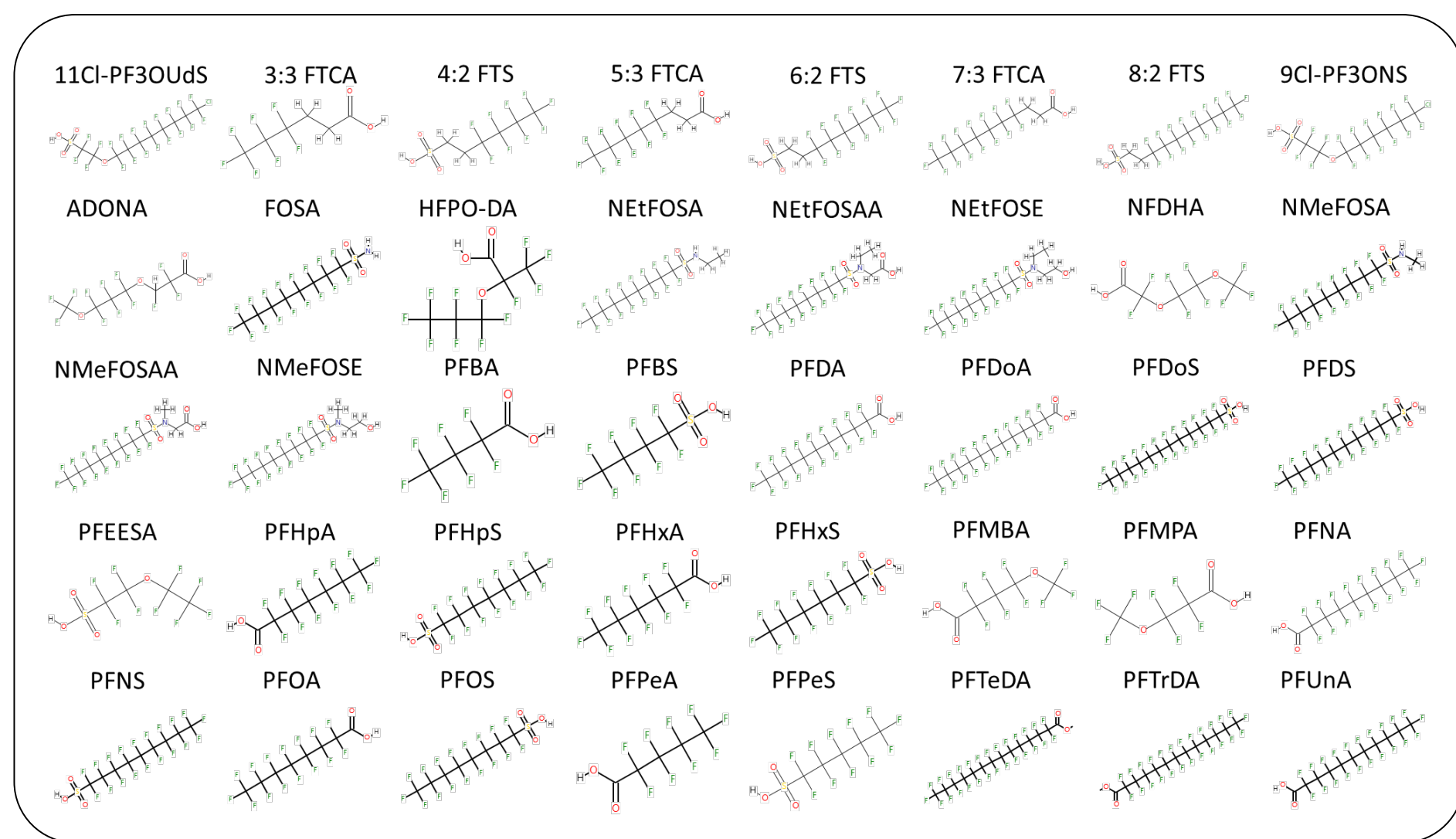


Untargeted PFAS identification and targeted PFAS library screening workflows for groundwater analysis using a QTOF mass spectrometer

Ethan Hain, Om Shrestha, Kathleen Luo, Christopher Gilles, Evelyn Wang, Xiaomeng Xia, Robert English, Tiffany Liden
Shimadzu Scientific Instruments, 7102 Riverwood Dr., Columbia, MD 21046 U.S.A.

Introduction

Per- and poly-fluoroalkylated substances (PFAS) have garnered increasing regulatory and public health interest as a result of the widespread occurrence and validated toxicity of these emerging contaminants. Although there are several specific PFAS that are currently being regulated on a federal and state level, there are potentially thousands of different PFAS that may exist in the environment. The toxicity associated with each of these individual PFAS will drive regulations; therefore, the identification of novel PFAS is a critical primary step in documenting the need for individual PFAS regulations. Once novel PFAS are characterized, these analytes of interest can be quickly identified in environmental matrices (e.g., groundwater) through targeted screening for easier monitoring.



Structures of PFAS studied.

Methods

A neat standard and spiked groundwater sample containing the 40 PFAS from Environmental Protection Agency (EPA) Method 1633 were chromatographically separated using a Shim-pack Scepter C18-120 column (2.1 × 100 mm; 3 μm) with a Shim-pack Scepter C18-120 delay column (2.1 × 50 mm; 3 μm) and mobile phases of 5 mM ammonium acetate in water and methanol (no additives) at a flow rate of 0.25 mL/min. Data were acquired on a Shimadzu LCMS-9030 quadrupole time-of-flight mass spectrometer using a negative mode MS scan ranging from 40-950 *m/z*, targeted MS/MS scans based off of target analyte *m/z*, and data-independent acquisition (DIA) MS/MS scans of a variable precursor isolation width and collision energy spread of 5-55 V. LabSolutions and LabSolutions Insight Explore software were used to obtain the data and perform data analyses.

Table of LC and LCMS parameters

Nexera LC		LCMS-9030	
Flow Rate:	0.25 mL/min	Nebulizing Gas:	3 L/min
Oven Temp.:	45 °C	Drying Gas:	5 L/min
Injection Vol.:	1 μL	Heating Gas:	15 L/min
Mobile Phase:	A: 5 mM Ammonium acetate in water B: Methanol	Desolvation Temp.:	160 °C
Delay Column:	Shim-pack Scepter C18-120 (2.1 × 50 mm; 3 μm)	DL Temp.:	150 °C
Analytical Column:	Shim-pack Scepter C18-120 (2.1 × 100 mm; 3 μm)	Heat Block Temp.:	250 °C
Time Course:	0 min %B = 5; 1 min %B = 40; 8 min %B = 95; 8.1 min %B = 100; 13 min %B = 100; 13.1 min %B = 5; 18 min %B = 5	Interface Temp:	100 °C
		Probe Position:	+1 mm
		Interface:	ESI

EPAM1633PFAS Library

EPAM1633 PFAS spiked into groundwater (15.625-390 ppb) and identified by DIA.

Name	Formula	Theoretical <i>m/z</i>	Acquired <i>m/z</i>	Mass Error (ppm)	Found RT	RT Diff.	Lib. SI
11CI-PF3OUdS	C ₁₀ HClF ₂₀ O ₄ S	630.8892	630.8876	-2.504	8.726	0.04	100
3:3 FTCA	C ₆ H ₅ F ₇ O ₂	241.0105	241.0095	-4.025	5.143	0.02	94
4:2 FTS	C ₆ H ₅ F ₉ O ₃ S	326.9743	326.9732	-3.272	5.909	0.03	94
5:3 FTCA	C ₈ H ₅ F ₁₁ O ₂	341.0041	341.0034	-2.023	6.847	0.03	97
6:2 FTS	C ₈ H ₅ F ₁₃ O ₃ S	426.9679	426.9670	-2.084	7.288	0.05	100
7:3 FTCA	C ₁₀ H ₅ F ₁₅ O ₂	440.9977	440.9967	-2.449	7.966	0.04	98
8:2 FTS	C ₁₀ H ₅ F ₁₇ O ₃ S	526.9615	526.9604	-2.220	8.235	0.03	99
9CI-PF3ONS	C ₈ HClF ₁₆ O ₄ S	530.8956	530.8945	-1.997	8.011	0.04	94
ADONA	C ₇ H ₂ F ₁₂ O ₄	376.9689	376.9680	-2.334	6.779	0.03	100
FOSA	C ₈ H ₂ F ₁₇ NO ₂ S	497.9462	497.9450	-2.510	8.638	0.02	100
HFPO-DA	C ₆ HF ₁₁ O ₃	284.9779	284.9772	-2.421	6.221	0.04	97
NEtFOSA	C ₁₀ H ₆ F ₁₇ NO ₂ S	525.9775	525.9761	-2.662	9.564	0.01	100
NEtFOSAA	C ₁₂ H ₆ F ₁₇ NO ₄ S	583.9830	583.9816	-2.363	8.600	0.03	93
NEtFOSE	C ₁₂ H ₁₀ F ₁₇ NO ₃ S	630.0249	630.0233	-2.492	9.533	0.01	100
NFDHA	C ₅ HF ₉ O ₄	294.9658	294.9646	-4.272	5.852	0.03	97
NMeFOSA	C ₉ H ₄ F ₁₇ NO ₂ S	511.9619	511.9608	-2.070	9.358	0.01	100
NMeFOSAA	C ₁₁ H ₆ F ₁₇ NO ₄ S	569.9673	569.9660	-2.281	8.426	0.04	95
NMeFOSE	C ₁₁ H ₈ F ₁₇ NO ₃ S	616.0092	616.0079	-2.143	9.332	0.01	100
PFBA	C ₄ HF ₇ O ₂	212.9792	212.9785	-3.146	4.038	0.02	93
PFBS	C ₄ HF ₉ O ₃ S	298.9430	298.9424	-2.107	5.236	0.02	100
PFDA	C ₁₀ HF ₁₉ O ₂	512.9600	512.9585	-3.100	8.220	0.04	89
PFDa	C ₁₂ HF ₂₃ O ₂	612.9537	612.9520	-2.773	8.909	0.05	90
PFDs	C ₁₂ HF ₂₅ O ₃ S	698.9174	698.9158	-2.332	9.149	0.05	100
PFES	C ₁₀ HF ₂₁ O ₃ S	598.9238	598.9225	-2.204	8.558	0.04	100
PFESAA	C ₄ HF ₉ O ₄ S	314.9379	314.9372	-2.350	5.602	0.03	99
PFHpA	C ₇ HF ₁₅ O ₂	362.9696	362.9688	-2.369	6.704	0.04	92
PFHpS	C ₇ HF ₁₅ O ₃ S	448.9334	448.9325	-2.027	7.289	0.03	100
PFHxA	C ₆ HF ₁₁ O ₂	312.9728	312.9720	-2.460	5.993	0.04	93
PFHxS	C ₆ HF ₁₃ O ₃ S	398.9366	398.9360	-1.404	6.707	0.03	100
PFMBA	C ₅ HF ₉ O ₃	278.9709	278.9701	-2.904	5.400	0.03	94
PFMPA	C ₄ HF ₇ O ₃	228.9741	228.9735	-2.489	4.456	0.02	100
PFNA	C ₉ HF ₁₇ O ₂	462.9632	462.9620	-2.592	7.798	0.04	88
PFNS	C ₉ HF ₁₉ O ₂ S	548.9270	548.9256	-2.587	8.200	0.04	100
PFOA	C ₈ HF ₁₅ O ₂	412.9664	412.9657	-1.768	7.291	0.04	97
PFOS	C ₈ HF ₁₇ O ₃ S	498.9302	498.9290	-2.465	7.779	0.04	100
PFPeA	C ₅ HF ₉ O ₂	262.9760	262.9751	-3.422	5.112	0.03	92
PFPeS	C ₅ HF ₁₁ O ₃ S	348.9398	348.9388	-2.780	6.045	0.03	100
PFTeDA	C ₁₄ HF ₂₇ O ₂	712.9473	712.9452	-2.875	9.433	0.06	98
PFTrDA	C ₁₃ HF ₂₅ O ₂	662.9505	662.9491	-2.006	9.188	0.05	97
PFUnA	C ₁₁ HF ₂₁ O ₂	562.9568	562.9553	-2.665	8.593	0.04	98

EPAM1633 PFAS were identified by targeted library screening and untargeted analysis.

The Assign function can be used to search ChemSpider or PubChem based off the acquired mass or a formula.

The compound table shows the name, formula, theoretical and acquired precursor *m/z*, mass error, many more compound specific parameters.

Acquired MS/MS spectra are compared and fragments are assigned with relevant structures and formula.

Conclusions

The 40 PFAS from EPAM1633 were used to generate a library from a single mixture, and then were confirmed to function for targeted library screening and untargeted identification in groundwater using the Insight Explore Assign function.