Quantitative LC-MS/MS Analysis for PFAS in Concrete Matrices

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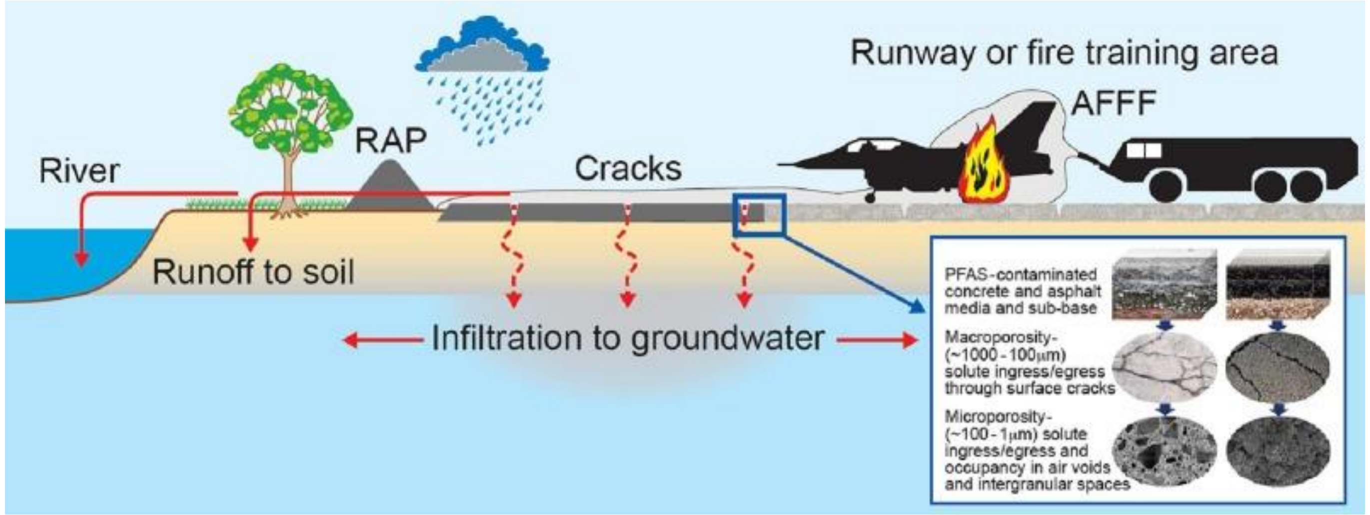
PFAS Introduction

- Per-and Polyfluorinated alkyl substances (PFAS) are a broad class of thousands of chemicals with various definitions that include carbon-fluorine bonds
- Concrete is widely used in construction, infrastructure, and industrial application that can serve as both a receptor and potential source of PFAS contamination
- Aqueous film-forming foam (AFFF) application to combat fires can impact concrete either through direct application or runoff
- Important to have analytical tool for characterization of concrete matrices to access degree of PFAS contamination



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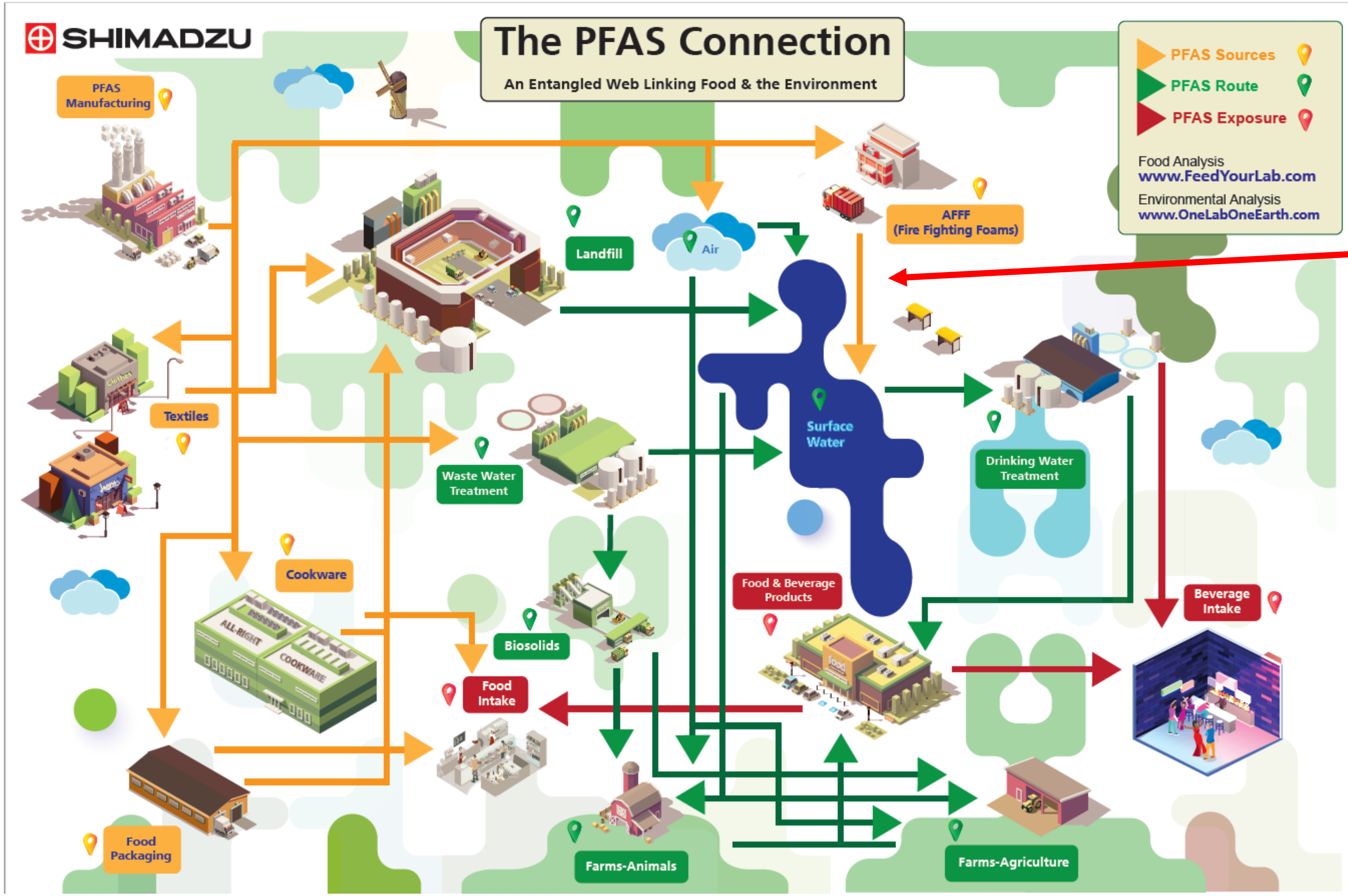
PFAS Connection from Source to Exposure



Building and infrastructure impacted from AFFF release

Collaboration Between RJ Lee Group and Shimadzu Scientific Instruments

- Collaboration was first initiated between the two companies to develop the first ASTM standard for the analysis of extractable PFAS in consumer products
    - ASTM F15.81; Consumer Products Subcommittee on PFAS
- Extension of this work was made to investigate PFAS in concrete matrices (for encapsulation and leaching projects)
- Purpose of work was to develop analytical method to assess PFAS in concrete matrices and for future work to investigate PFAS encapsulation within concrete
- Method currently has 45 target analytes and 25 surrogates with quantitation based on external standard calibration (internal standard quantification can be applied if necessary)

PFAS Target Analyte List

Analyte Name	Acronym	CAS Number
Perfluorotetradecanoic acid	PFTreA	376-06-7
Perfluorotridecanoic acid	PFTriA	72629-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorooctanesulfonamide	PFOSA	754-91-6
8:2 Fluorotelomer sulfonic acid	8:2 FTS	39108-34-4
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2
4:2 Fluorotelomer sulfonic acid	4:2 FTS	757124-72-4
N-Ethylperfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-Methylperfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorododecanesulfonic acid	PFDoS	79780-39-5
N-Methylperfluorooctanesulfonamide	NMeFOSA	31506-32-8
N-Ethylperfluorooctanesulfonamide	NEtFOSA	4151-50-2
N-Methylperfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7
N-Ethylperfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1

Analyte Name	Acronym	CAS Number
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
Pentafluorpropanoic acid	PFPrA	422-64-0
Perfluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Perfluoro(2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
2H,2H,3H,3H-Perfluorohexanoic Acid	3:3 FTCA	356-02-05
2H,2H,3H,3H-Perfluorooctanoic Acid	5:3 FTCA	914637-49-3
2H,2H,3H,3H-Perfluorodecanoic acid	7:3 FTCA	812-70-4
2H-perfluoro-2-octenoic acid	FHUEA	70887-88-6
2H-perfluoro-2-decenoic acid	FOUEA	70887-84-2
Lithium Bis(trifluoromethane)sulfonimide	HQ-115	90076-65-6
Bis[2-(perfluorohexyl)ethyl]phosphate	6:2-diPAP	57677-95-9

PFAS Surrogate List

Surrogates	Acronym	CAS Number
Perfluoro-n-[^{13}C4] butanoic acid	MPFBA	1017281-29-6
Perfluoro-n-[$^{13}C_5$] pentanoic acid	M5PFPeA	2283397-79-3
Perfluoro-n-[1,2,3,4,6-$^{13}C_5$] hexanoic acid	M5PFHxA	2328024-54-8
Perfluoro-n-[1,2,3,4-$^{13}C_4$] heptanoic acid	M4PFHpA	2328024-55-9
Perfluoro-n-[$^{13}C_8$] octanoic acid	M8PFOA	1350614-84-4
Perfluoro-n-[$^{13}C_9$] nonanoic acid	M9PFNA	2283397-80-6
Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$] decanoic acid	M6PFDA	2328024-56-0
Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$] undecanoic acid	M7PFUnA	N/A
Perfluoro-n-[1,2-$^{13}C_2$] dodecanoic acid	MPFDoA	960315-52-0
Perfluoro-n-[1,2-$^{13}C_2$] tetradecanoic acid	M2PFTreA	N/A
Perfluoro-1-[$^{13}C_8$] octanesulfonamide	M8FOSA	N/A
N-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	D3-N-MeFOSAA	N/A
N-ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid	D5-N-EtFOSAA	N/A
N-methyl-d_3-perfluoro-1-octanesulfanamide	D3-N-MeFOSA	N/A
N-ethyl-d_5-perfluoro-1-octanesulfanamide	D5-N-EtFOSA	1265205-97-7
2-(N-methyl-d_3-perfluoro-1-octanesulfonamido) ethan-d_4-ol	d7-N-MeFOSE	1265205-95-5
2-(N-ethyl-d_5-perfluoro-1-octanesulfonamido) ethan-d_4-ol	D9-N-EtFOSE	1265205-96-6
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy-$^{13}C_3$-propanoic acid	MHFPO-DA	N/A
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$] hexane sulfonate	M4:2FTS	2708218-88-4
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-octane sulfonate	M6:2FTS	2708218-89-5
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-decane sulfonate	M8:2FTS	2708218-90-8
Perfluoro-1-[$^{13}C_8$] octanesulfonate	M8PFOS	2522762-16-7
Perfluoro-1-[2,3,4-$^{13}C_3$] butanesulfonate	M3PFBS	2708218-84-0
Perfluoro-1-[1,2,3-$^{13}C_3$] hexanesulfonate	M3PFHxS	2708218-86-2
$(^{13}C_2)_2$ Bis[2-(perfluorohexyl)ethyl]phosphate	M4-6:2-diPAP	N/A

Materials and Methods: Calibration Curve

- Stocks were made from Accustandard and Wellington Laboratories purchased standards and were diluted using 95:5 (vol:vol) methanol:water into HDPE bottles and stored at 4^{o}C
- The stocks were used to prepare an 8- or 9-point calibration curve in 50:50 (vol:vol) methanol:water with 0.1% acetic acid at the concentrations listed in **Table 1**.

Table 1. *In-vial* Native and Surrogate Calibration Curve Concentrations (ng/L)

Analyte/Surrogate	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7	Cal 8	Cal 9
All Surrogates All Analytes Not Specified Below	5	10	20	40	60	80	100	150	200
3:3 FTCA, PFPeA	--	10	20	40	60	80	100	150	200
PFPrA, PFBA, 6:2-diPAP+Surr	--	50	100	200	300	400	500	750	1000

In-Vial to Product Range Concentration

- The curve is established at low ng/L concentrations in vial considering that the sample preparation procedure effectively dilutes the original concrete matrix by approximately 20 times
- Equation 1 shows in-vial (ng/L) to in concrete matrix (ng/kg) conversion

$$Cs\left(\frac{ng}{kg}\right) = \frac{\left[Ci\left(\frac{ng}{L}\right)\right] \times [Vs(L)]}{[Wd(kg)]}$$

where:

C_s = concentration of target analyte in sample,

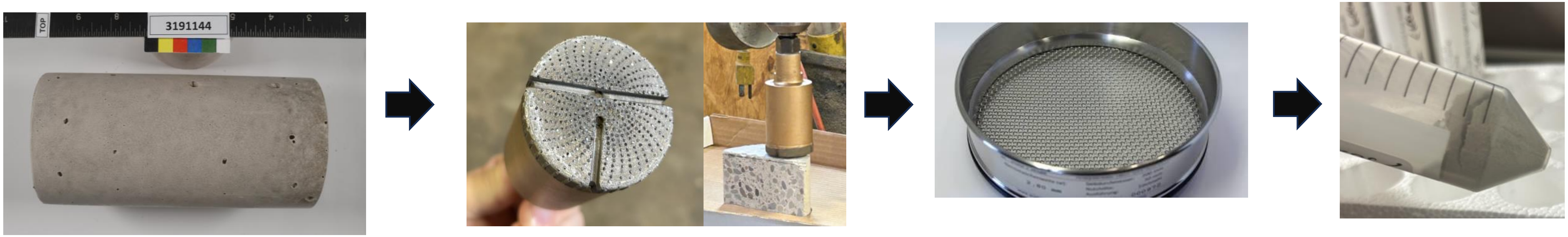
C_i = concentration of target analyte in sample from instrument

V_s = volume of sample

W_d = dry weight of sample

Materials and Methods: Sample Preparation

- Six concrete cylinders cast using 0.3% aqueous solution of AFFF gel to simulate PFAS-contaminated water (3 control samples were laboratory blank water)
- Three types of concrete were used: high strength, high early strength, and advanced pro-mix
- Cylinders were cast within ASTM C31 guidelines and cured for 30 days
- Samples were removed from the mold then cut into sub-samples with diamond-tipped saw then prepared for grinding
- Grinding was done with a diamond embedded brass bit and then passed through a series of stainless-steel sieves to achieve a final aggregate powder size between 38-600 µm



Materials and Methods: Sample Preparation

1. Weigh 0.5 g concrete into 50mL centrifuge tube

2. Add SSS, mix, equilibrate for 15 min
3. Add 10ml 50:50 MeOH:H_2O, vortex

4. Tumble for at least 1 hour

5. Centrifuge at 8ºC, 3000 rpm, 10 min

6. Filter through preconditioned 0.2µm PP syringe into 15mL centrifuge tube

7. Add acetic acid to pH 3-4, vortex

8. Centrifuge at 8ºC, 3000 rpm, 10 min

9. Aliquot to silanized glass vial with PE/silicone septa/cap

Materials and Methods: Analytical Method

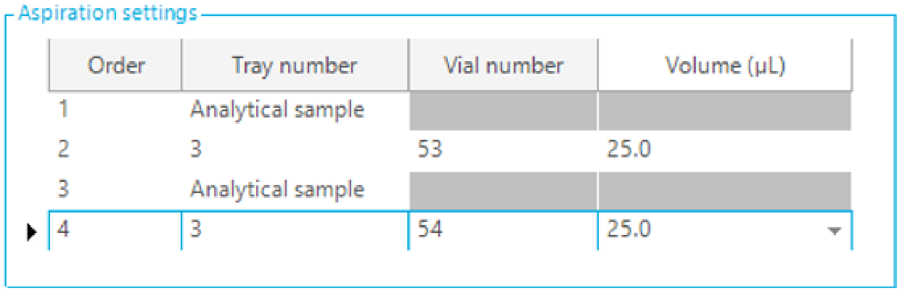
- Analysis was performed using a Shimadzu Nexera UHPLC consisting of 2 pumps (LC-40D X3, 130 MPa), autosampler (SIL-40C X3), system controller (SCL-40), and column oven (CTO-40C). The LC was coupled to a Shimadzu LCMS-8060NX with IonFocus ESI source.

[LC] Nexera	
Mobile Phase (LCMS Grades)	A: 2 mmol/L Ammonium Acetate in H_2O/ Acetonitrile = 95/5
	B: Acetonitrile
Delay Column	Shimadzu Nexcol PFAS Delay
	3.0 mm x 50 mm, 5 µm (P/N: 220-91394-09)
Analytical Column	Shim-pack Scepter C18-120
	2.1 mm x 100 mm, 3 µm (P/N: 227-31014-05)
Gradient (%B)	10% (0.5 min) ⇒22% (2.3-3.0 min) ⇒45% (6.0 min) ⇒ 75% (12.0 min) ⇒95% (12.1-14.0 min) ⇒10% (14.1-17.0 min)
Interface	IonFocus ESI (-)
Column Oven Temp.	45 ℃
Flow rate	0.45 mL/min
Injection volume	40 µL
Multiple draw injection program	Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O → Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O
Autosampler Rinsing	60/40 Acetonitrile/2-propanol, Before/After Aspiration 5 seconds

[MS] LCMS-8060NX	
Interface Temp.	170℃
Probe position	+3 mm
Nebulizer gas flow	3 L/min
Heating gas flow	15 L/min
Interface Voltage	-0.5 kV (same value for all compounds)
DL Temp.	200 ℃
Heatblock Temp.	300 ℃
Drying gas flow	8 L/min
Focus bias	-2 kV (same value for all compounds)
CID Cell Pressure	270 kPa; 350 kPa 6.6 - 7.6 min and 11.6 - 12.6 min

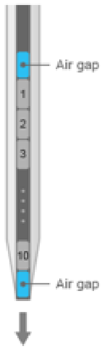
Materials and Methods: Autosampler Pretreatment

- Co-injection function provides the ability to inject samples in higher elution strength solvents than the initial mobile phase conditions.
- Injecting a weaker strength solvent, such as water, lowers the overall elution strength of the injection, improving early eluter peak shapes and the reliability of quantitative results

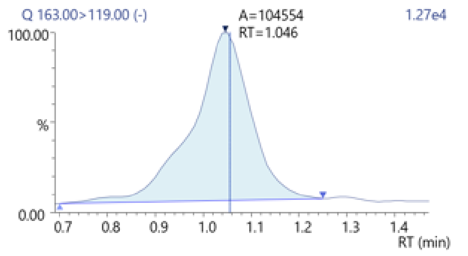
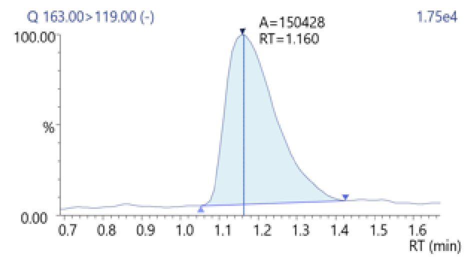
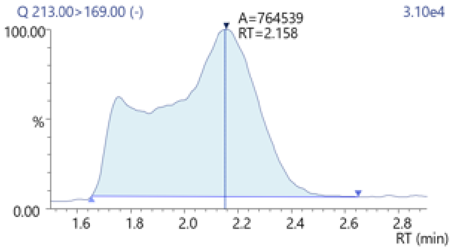
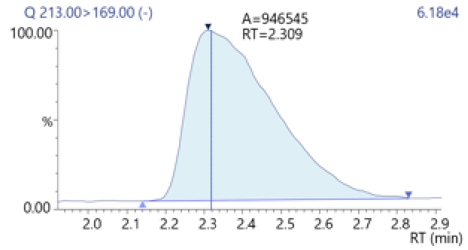
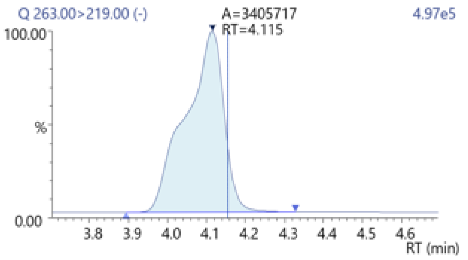
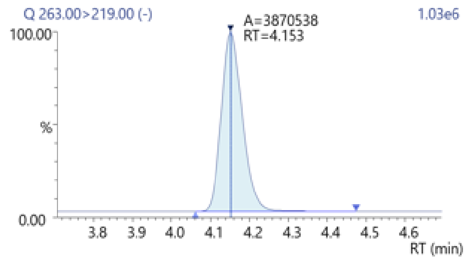


Aspiration settings

Order	Tray number	Vial number	Volume (µL)
1	Analytical sample		
2	3	53	25.0
3	Analytical sample		
4	3	54	25.0



- Final solvent composition for method is 50% methanol, starting mobile phase composition is 10%, impact of co-injection can be seen to right

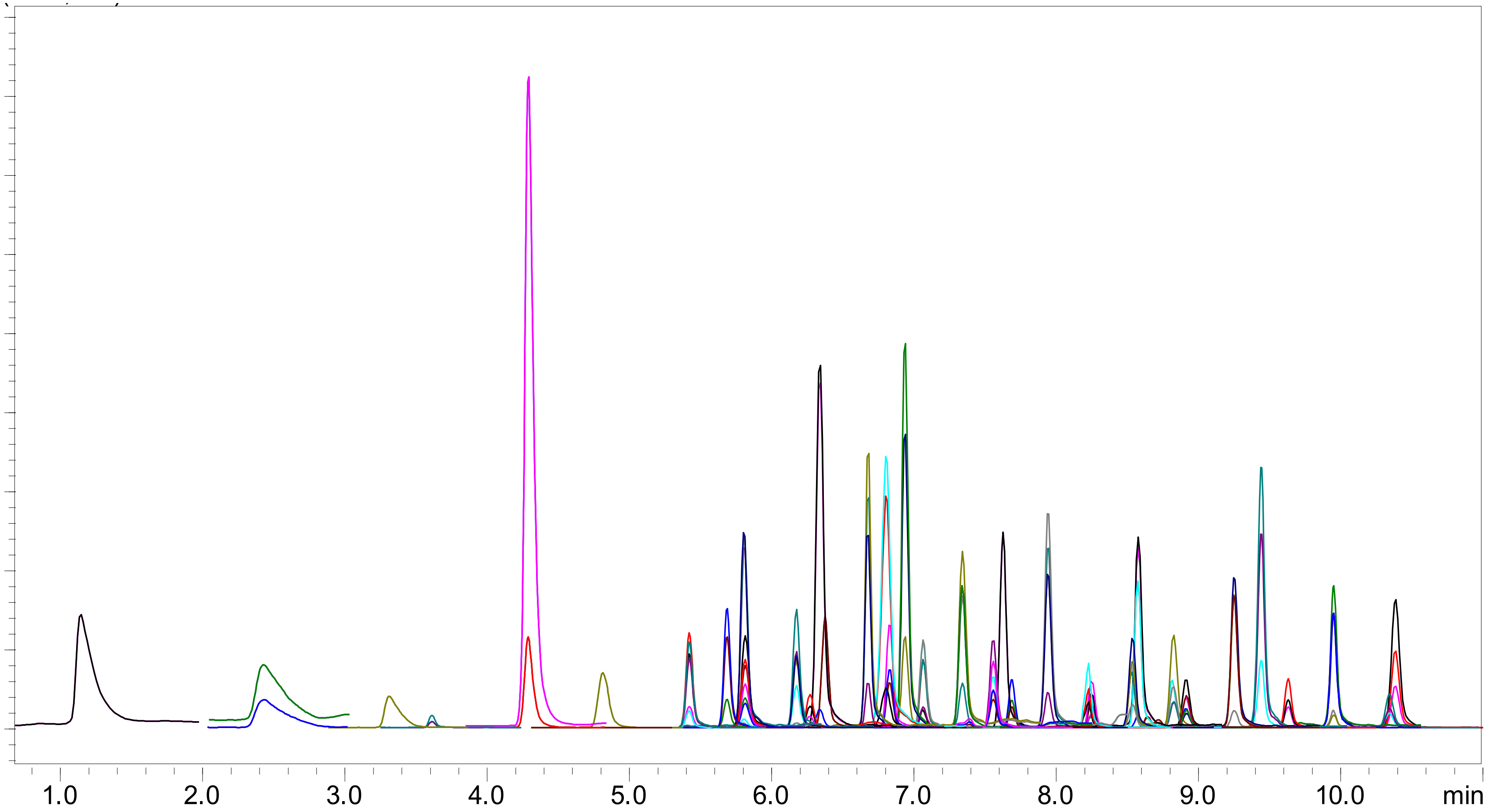
	40µL injection volume	**Co-injection w/ 50µL 0.1% AA in H$_2$0**
PFPrA		
PFBA		
PFPeA		

Results: Linearity Study

Compound	Calibration Range In-Vial (ng/L)	Calibration Curve Criteria	Reporting Range (ng/kg)
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFNA, PFOA, PFHpA, PFHxA, PFDS, PFNS, PFOS, PFHpS, PFHxS, PFPeS, PFBS, PFOSA, 8:2FTS, 6:2FTS, 4:2FTS, NEtFOSAA, NMeFOSAA, PFDoS, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, NFDHA, PFEESA, PFMPA, PFMBA, 5:3 FTCA, 7:3 FTCA, FHUEA, FOUEA, HQ-115, SURROGATES	5-200	$R^2 > 0.99$ RSE < 30% RF RSD < 30%	100-4000
PFBA, PFPrA, 6:2-diPAP	50-1000		1000-20000
PFPeA	25-1000		500-20000
3:3 FTCA	10-200		200-4000

Results: Example Chromatogram

- Mid-point calibrator of targets and surrogates



Results: Surrogate Recovery (n=3)

Lower long chain recovery as matrix complexity increases (carbon fiber content?)

Surrogate	Spike Conc. ng/kg	High Strength %Recovery	High Strength %RSD	High Early Strength %Recovery	High Early Strength %RSD	Adv. Pro Mix %Recovery	Adv. Pro Mix %RSD
13C4-PFBA	1600	90.1	2.6	93.0	3.7	95.1	0.9
13C5-PFPeA	1600	92.5	2.9	93.7	3.8	96.3	0.9
13C5-PFHxA	1600	90.7	4.2	96.4	3.9	97.2	2.3
13C4-PFHpA	1600	94.1	5.8	95.8	4.2	96.8	2.7
13C8-PFOA	1600	93.1	1.8	96.8	4.4	97.6	2.0
13C9-PFNA	1600	94.1	4.6	91.1	4.8	92.4	1.2
13C6-PFDA	1600	94.5	3.1	91.4	5.3	89.6	2.1
13C7-PFUnA	1600	92.2	3.6	91.2	3.1	85.8	1.3
13C2-PFDoA	1600	87.8	2.9	85.9	3.7	72.6	0.9
13C2-PFTeDA	1600	53.8	9.4	52.5	3.1	36.1	4.7
13C8-PFOSA	1600	91.9	3.5	94.0	4.8	91.5	0.7
D3-NMeFOSAA	1600	84.8	4.4	82.2	1.4	77.9	3.1
D5-NEtFOSAA	1600	84.3	3.5	85.4	4.2	76.7	2.0
D3-NMeFOSA	1600	92.8	5.6	92.4	4.2	94.3	4.2
D5-NEtFOSA	1600	94.1	6.8	93.3	2.7	91.0	8.2
D7-NMeFOSE	1600	92.6	0.5	89.9	1.0	88.7	3.5
D9-NEtFOSE	1600	91.8	1.7	89.1	3.2	86.8	5.5
13C3-HFPO-DA	1600	91.3	3.3	92.3	3.8	94.6	6.4
13C2-4:2FTS	1600	70.7	1.3	70.9	4.9	70.2	10.0
13C2-6:2FTS	1600	90.3	2.0	91.2	1.1	105.7	2.6
13C2-8:2FTS	1600	93.2	6.9	82.0	12.2	80.4	6.6
13C8-PFOS	1600	94.5	2.7	91.5	2.1	93.7	3.1
13C3-PFBS	1600	91.7	2.3	94.8	5.5	96.0	3.7
13C3-PFHxS	1600	95.2	5.2	97.6	8.2	99.8	0.7
M4-6:2 diPAP	1600	73.2	2.8	83.7	3.2	57.9	9.4

Comparison of AFFF Neat to AFFF/High Strength Pre-cast

- Diluted neat AFFF and diluted AFFF with concrete mix was prepared with method to compare PFAS target results prior to casting the cores
  - Results showed very consistent target recoveries (AFFF sample only has subset of targets within the method)

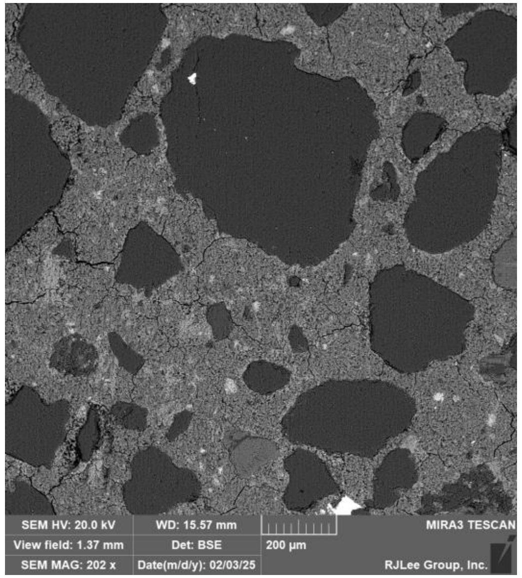
	Diluted AFFF Only	**High Strength spiked with Diluted AFFF**		**Casted High Strength**	**Casted High Early Strength**	**Casted AdvProMix**
	Concentrations in ng/kg, (n=3)					
PFDoA	176	126		202	232	176
PFDA	338	346		526	536	580
PFNA	---	--		158	166	288
PFOA	1130	1212		1224	1404	1544
PFHpA	202	236		322	334	368
PFHxA	2766	2606		2116	2332	2378
PFPeA	234	230		282	290	508
8:2 FTS	22762	22418		15214	15774	14358
6:2 FTS	62786	65888		33974	33350	32132

%RSD of triplicates less then 11%

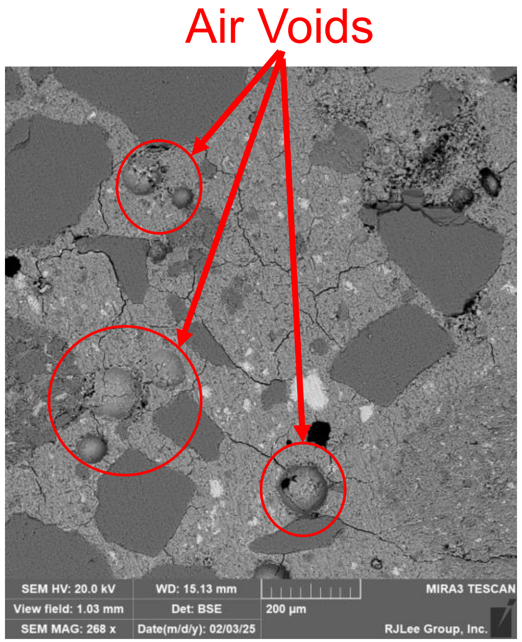
Conclusion and Future Directions

- Extraction procedure, chromatography, and mass spectrometry conditions were optimized to ensure optimal sensitivity for co-solvation sample preparation procedure
- Developed method eliminates need for solid phase extraction to simplify extraction process
- Target analytes/surrogates are quantitated using external standard method resulting in a reporting range for majority of analytes from 100-4,000 ng/kg (can use internal standard quantification if desired)

- Investigation of concrete encapsulation with native mixes and with doping the concrete with additives and exposing the cores to environmental chambers to determine degree of leaching (remediation tool to take foam fractured leachate and solidify into concrete blocks for landfills)
- Blank concrete exposure studies to determine PFAS impact and infiltration into various types of concrete and impact on their petrography (also cross section mass spec imaging to investigate distribution patterns)



PFAS Free Water



AFFF Contaminated Water