A DIRECT INJECT APPROACH FOR ANALYSIS OF LEGACY AND EMERGING PERFLUOROALKYL SUBSTANCES (PFAS) IN ENVIRONMENTAL WATER AND SOIL SAMPLES

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INTRODUCTION

Perfluoroalkyl substances (PFAS) are common, man-made, persistent environmental contaminants that are used in the production of many consumer products as non-stick coatings, surfactants, and for stain and water resistance coatings. PFAS are also a major component of fire fighting foams used for suppression of fuel fires. Global widespread use of these compounds over many decades has led to their release into the environment. Their chemical properties make them bioaccumulative and they are found in all types of environmental samples, including water and soil. Current advisory guidelines around the globe require parts per trillion (ppt) detection of PFAS in various types of environmental samples.

An approach based upon direct injection of a large sample volume was developed for the determination of a wide range of legacy and emerging (e.g. ADONA, F53-B) PFAS compounds in environmental water and soils. This approach utilizes little sample preparation and requires a highly sensitive mass spectrometer for detection. Environmental water samples assessed using this method including surface, ground, and waste water. Sand, silt, and clay were evaluated as the soil samples. By simplifying the sample preparation step, sample throughput can be drastically increased as well as reducing chances for sample contamination from inherent PFAS in typical laboratory supplies. The performance and scope of the method makes it a suitable approach for the testing of water and soil samples for a wide range of PFAS, legacy and emerging, at relevant concentrations.
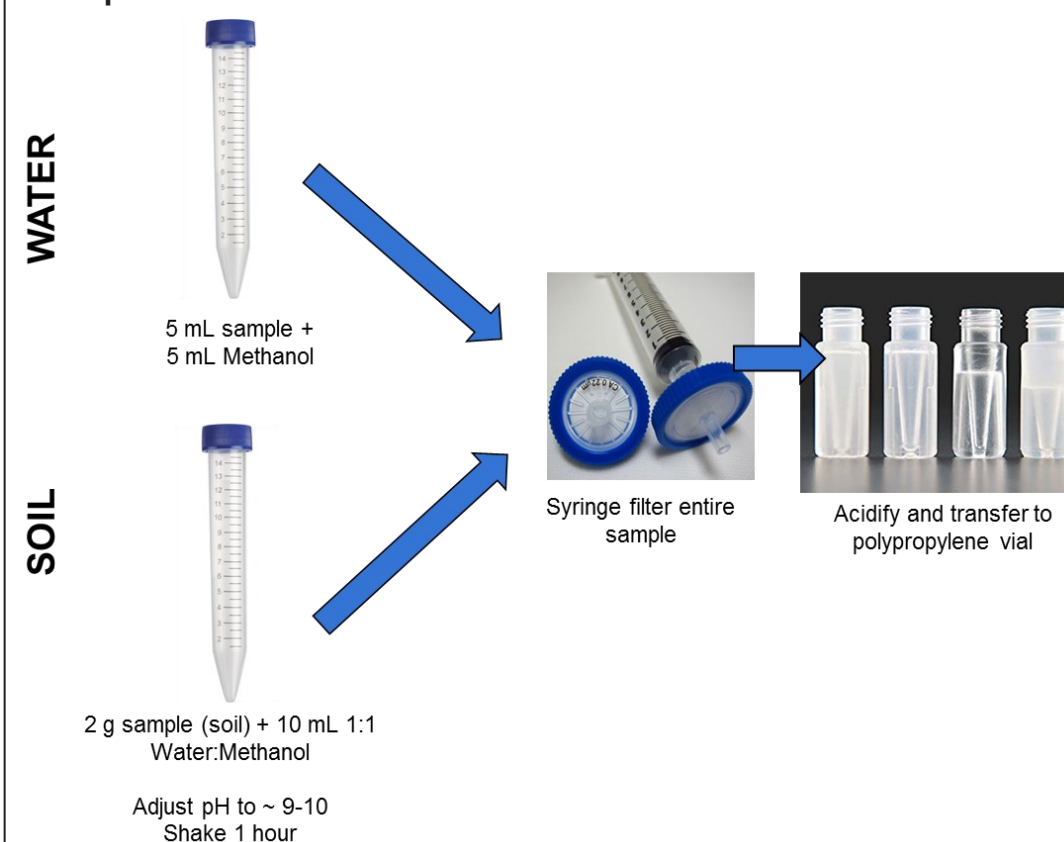
METHODS

Water Samples
- Water samples were provided by the United States Environmental Protection Agency (USEPA). Samples included reagent, surface, ground, influent, and effluent water blindly spiked with low and high concentrations of PFAS compounds.
- 5 mL of sample was provided in a 15 mL Eppendorf tube.

Soil Samples
- Soil samples were provided by the United States Environmental Protection Agency (USEPA). Samples included sand, silt, fat clay, and lean clay blindly spiked with unknown concentrations of PFAS compounds.
- 2 g of sample was provided in a 15 mL Eppendorf tube.

Sample Pretreatment

WATER

5 mL sample +
5 mL Methanol

Syringe filter entire sample

Acidify and transfer to polypropylene vial

SOIL

2 g sample (soil) + 10 mL 1:1 Water:Methanol

Adjust pH to ~ 9-10
Shake 1 hour

Figure 1. Overview of the sample pre-treatment method used for all water and soil samples.

LC-MS/MS Conditions
LC System: ACQUITY™ UPLC™ I-Class Plus fitted with PFC kit

Column: CSH Phenyl Hexyl 2.1 x 100 mm, 1.7 µm

Column Temp: 35°C

Sample Temp: 10°C

Injection Volume: 30 µl

Mobile Phase A: 95:5 Water:Methanol + 2 mM ammonium acetate

Mobile Phase B: Methanol + 2 mM ammonium acetate

Gradient:

Time (min)	Flow Rate (mL/min)	% A	% B
0	0.3	100	0
1	0.3	80	20
6	0.3	55	45
13	0.3	20	80
14	0.4	5	95
17	0.4	5	95
18	0.3	100	0
22	0.3	100	0

MS System: Xevo™ TQ-XS

Ionization Mode: ESI-

Capillary Voltage: 1.0 kV

Desolvation Temp: 500°C

Desolvation Gas Flow: 1100 L/hr

Cone Gas Flow: 150 L/hr

Source Temperature: 100°C

MRM parameters for each compound were optimized using the QuanOptimize tool in MassLynx™.

RESULTS AND DISCUSSION

Water Samples
Samples provided were spiked with only the PFAS currently written into the ASTM 7979 method prior to receiving them. All PFAS were detected in both low and high concentration spikes. Figure 2 shows an example of all the PFAS detected in the low concentration level spike of a surface (river) water sample.
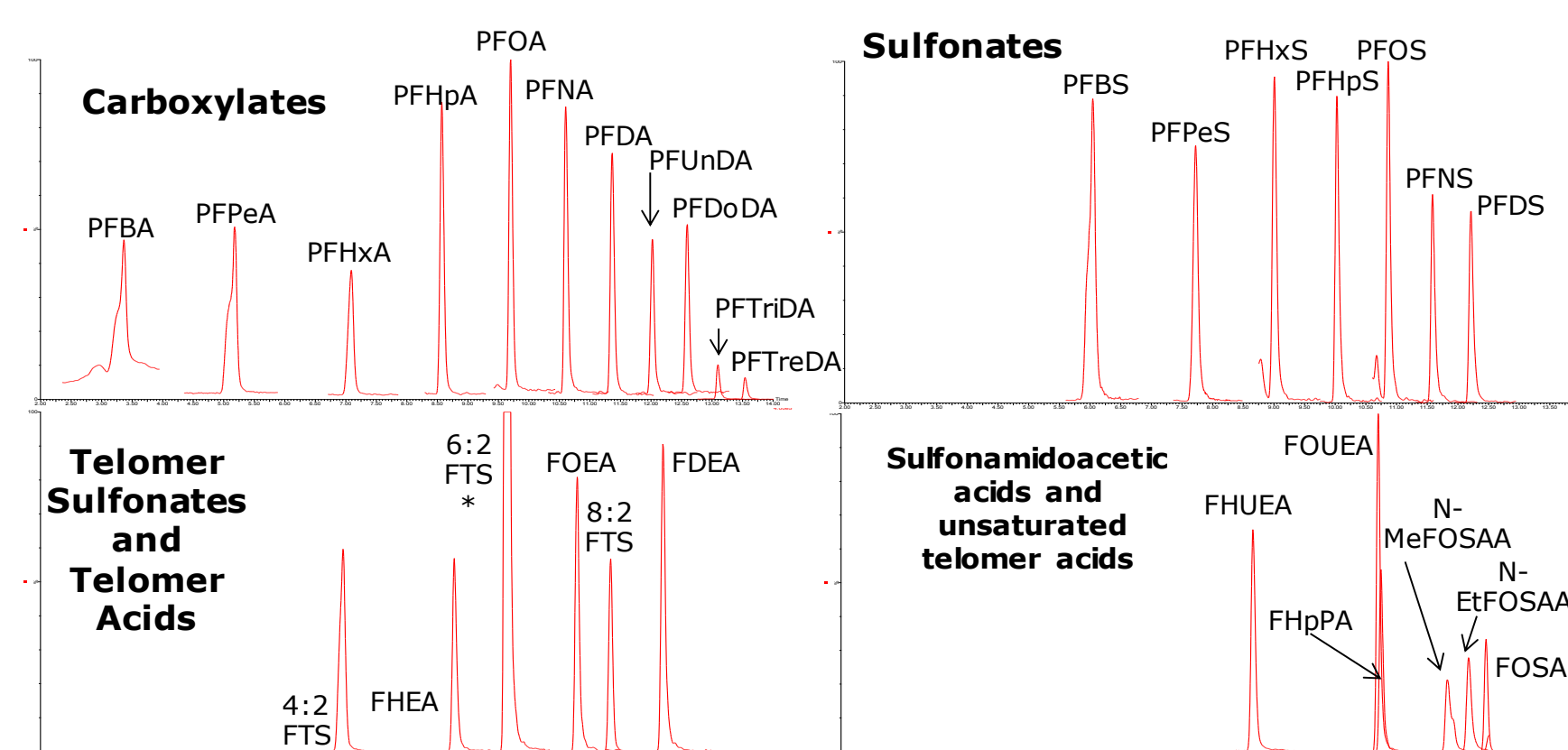

Figure 2. All PFAS compounds detected in low concentration spiked surface water sample. PFBA and PFPeA at 300 ng/L; 4:2, 6:2, and 8:2 FTS at 1200 ng/L; all other compounds at 60 ng/L. (*) this compound shown off scale.

Recovery was determined using isotope labelled surrogate standards that were spiked into the samples prior to sample pre-treatment and analysis. Table 1 shows recovery results for an example of PFOS in all sample types. Overall recoveries were in the range of 80-125%, with a few outliers due to matrix effects. Those effects could be mitigated by using matrix matched calibrations or by using isotope labelled standards as a correction factor during calculation of concentration.

Robustness was assessed by performing 20 replicate injections of a surface water extract. An example of peak area for PFOS over these 20 injections is shown in Figure 3. Percent RSD of peak area for all PFAS over these 20 injections was < 10% demonstrating the method is robust.

Matrix	% Recovery PFOS
Reagent Water	92.8
Ground Water	90.6
Surface Water	94.6
Influent Water	94.1
Effluent Water	93.5

Overall Recoveries: 80 – 125%

*PFTreDA, PFTriDA ~ 200% - matrix effects

Table 1. Percent recovery in all water sample types for example of PFOS.

n = 20 injections

RSD: 5.5625
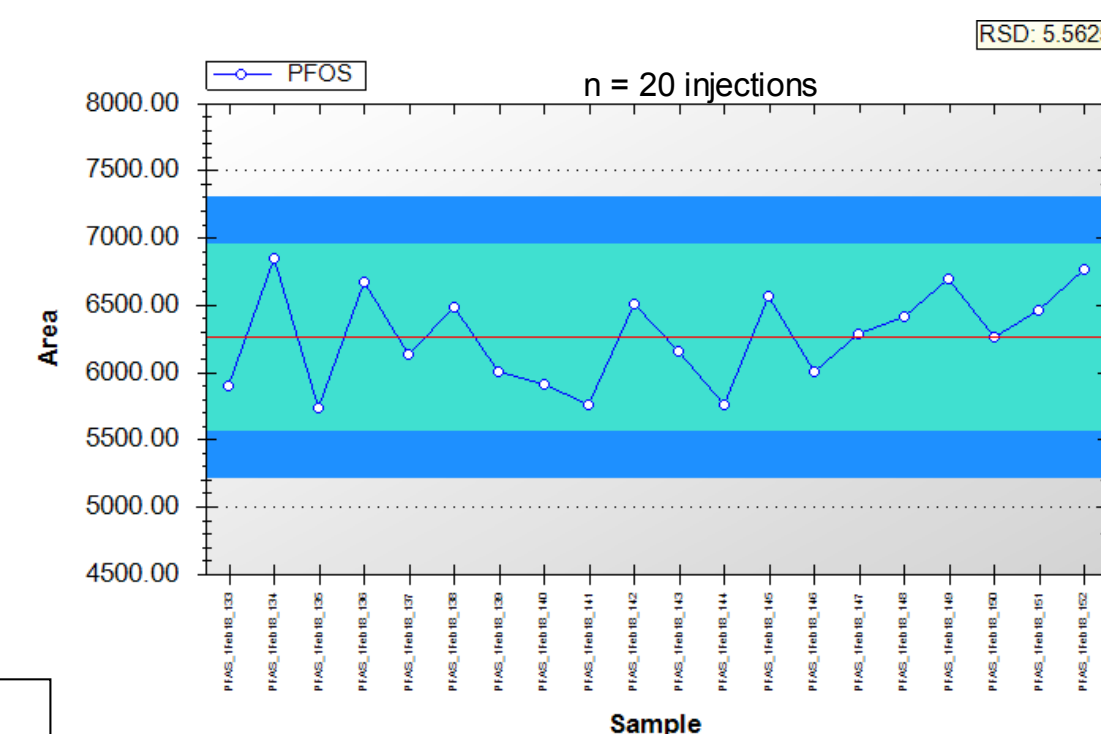
Overall RSD: < 10 %

Figure 3. Robustness of peak areas over 20 injection of surface water sample for example of PFOS.

For full details on this method, please see Waters Application Note 720006329EN

Soil Samples
Samples provided were spiked with an unknown concentration of PFAS prior to receiving them. All PFAS were detected in both low and high concentration spikes. Figure 4 shows an example of all the PFAS detected in the low concentration level spike of a lean clay sample.
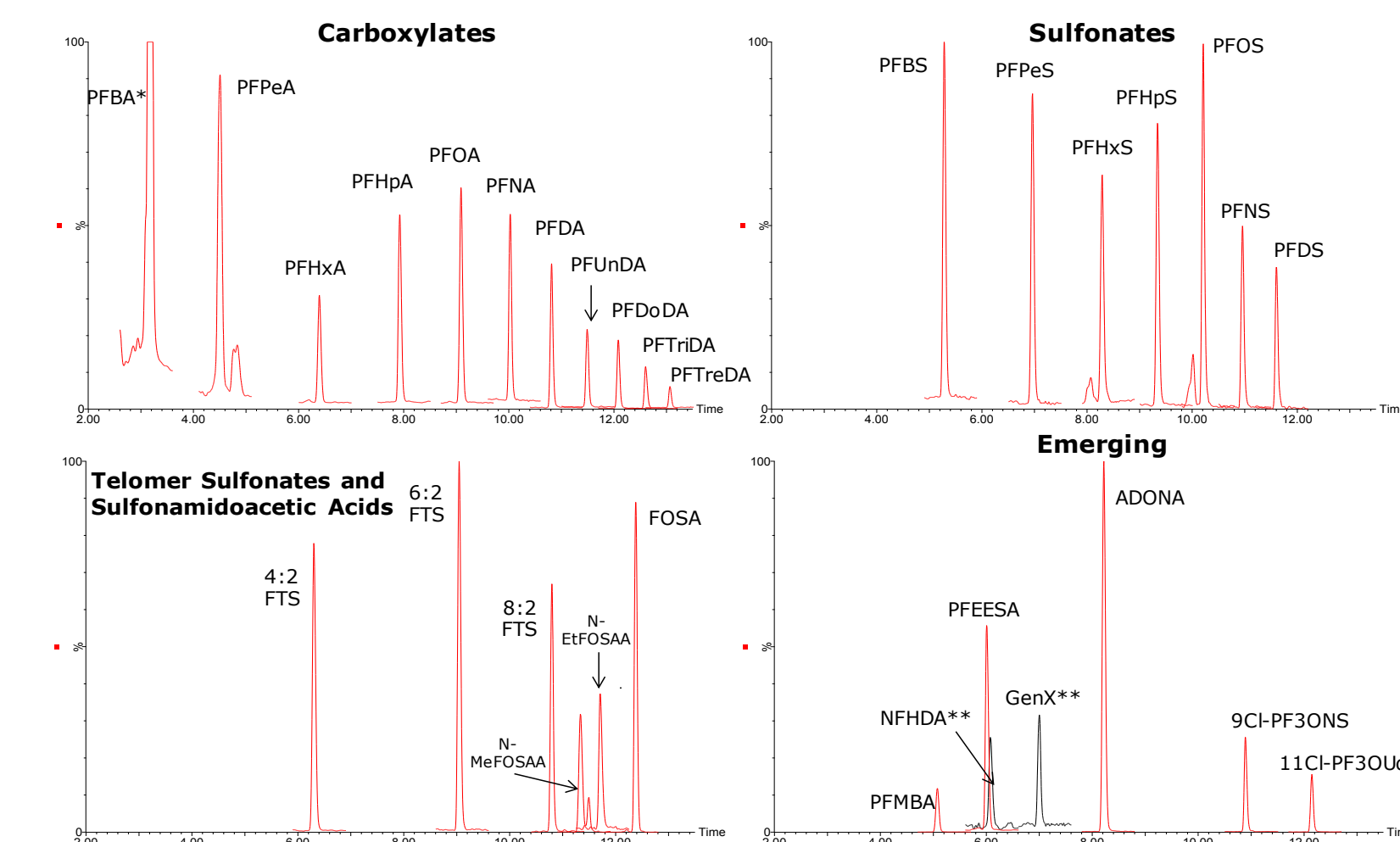

Figure 4. All PFAS compounds detected in low concentration spiked surface water sample. (*) this compound shown off scale. (**) compounds shown zoomed.

Similar to the water sample, recovery for soils was assessed using isotope labelled surrogate standards spiked into the samples prior to sample pre-treatment. Overall recoveries were all within the range of 70-130%. An example of the % recovery results for PFOA are shown in Table 2.

Some emerging PFAS of interest were also spiked into the samples to assess these new compounds of interest. All emerging compounds behaved similar to the legacy compounds in terms of recovery and robustness. Figure 5 below shows GenX detected at 10 ng/L (in vial) or 40 ng/kg (in sample).

Matrix	% Recovery PFOA
Silt	96.3
Sand	93.8
Lean Clay	95.0
Fat Clay	95.8

Table 2. Percent recovery in all soil sample types for example of PFOA.

6.95;602
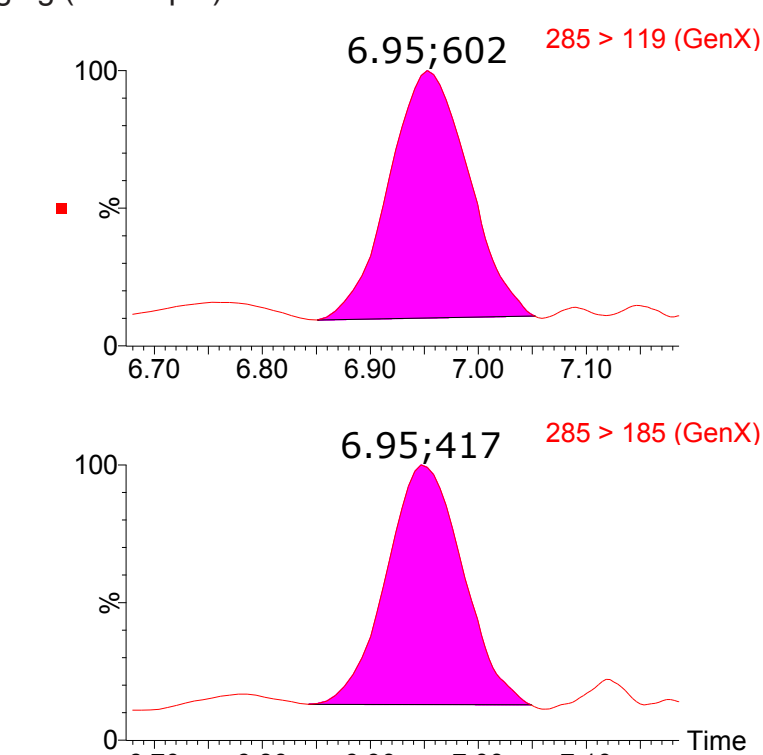285 > 119 (GenX)

6.95;417
285 > 185 (GenX)

Figure 5. GenX detected at 10 ng/L in vial or 40 ng/kg in sample. (top) MRM transition 285>119 (bottom) MRM transition 285>185

CONCLUSIONS

- Direct injection methods such as ASTM 7979 allow for quick sample turnaround time due to minimal sample preparation.

- The direct injection approach works well for both water and soil matrices.

- Results meet and exceed the ASTM method requirements.

- Results meet and exceed the EPA health advisory acute levels of 70 ng/L PFOS in water.

- The large volume direct injection method used on the Xevo TQ-XS was extremely sensitive with method detection limits for most compounds in the low ng/L range in water and ng/kg range for soils.

- All targeted PFAS compounds were detected in the water and soil samples analyzed at both low and high concentrations with excellent recovery and reproducibility.

- The direct injection approach is suitable for legacy and emerging PFAS.

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