Poly- and Perfluoroalkyl Substances (PFAS) in Soil/Sediment and Tissue Samples by Liquid Chromatography/Tandem Mass Spectrometry

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ISO 17025 Accredited Method

Introduction

Poly- and perfluoroalkyl substances, also known as PFAS compounds, are found in numerous components, most notably in non-stick and waterproof items that are used in everyday life, including Teflon. Even items like the inside of microwave popcorn bags, fast food wrappers, and aqueous fire-fighting foams (AFFF) contain PFAS compounds.

While these compounds are not acutely toxic, PFAS are known to be bioaccumulative, i.e. they collect in organ tissue over time and are potentially carcinogenic and contribute to other health issues. Because of the pervasiveness and stability of PFAS, these compounds are being detected in many areas of the environment, including water, sediment/soil, and in the tissues and organs of marine and terrestrial wildlife.

To test for the ubiquity of PFAS compounds in the environment, soil and vacuum dust samples were collected from various parts of the Bryan/College Station area. Additionally, four samples of canned seafood were purchased and were analyzed by liquid chromatography/tandem mass spectrometry.

The PFAS Challenge

PFAS' prevalence and stable nature are the very reasons these compounds are challenging for environmental analytical chemists in all areas, from extraction to detection.

The most common way to detect PFAS is by liquid chromatography/triple quadrupole mass spectrometry (LC/MS/MS). In nearly all instances, LC solvent delivery systems are made of Teflon components due to its inert nature, leading to elevated levels of background PFAS. This concern is addressed by installing a smaller LC column between the pump and the LC autosampler, delaying the elution of interfering compounds.

Chemically, PFAS contain a strong carbon-fluorine chain. They also maintain charged functional groups in the form of sulfonates, carboxylic acids, telomer sulfonates, and sulfonamides, with ever-growing variations to add to the PFAS family. Because of the strong nature of the carbon-fluorine bond, these compounds are nearly impossible to fragment using LC/MS/MS, a soft ionization technique. Furthermore, the inability of these compounds to break down has contributed to their pervasiveness in the environment and status as carcinogens and contaminants of concern.

The unique nature of PFAS makes them difficult to extract from complex matrices such as soil and tissue. In some cases, because of their charged functional group, an ion-pairing agent is used to form an uncharged compound that will partition into an organic phase.

The individuals performing the tasks of sampling and analysis must understand that these compounds can be found throughout laboratory implements, such as aluminum foil, traditional homogenizers and blenders, and solvent bottles. For best results, a method that intentionally uses polypropylene implements that have not been washed with detergent should be developed.

Materials and Extraction

Sample Preparation

- Soil/Sediment: 1g Dry Weight
- Tissue: 1g Wet homogenized Weight
  - Add: Buffers, pH ~10

Organic Solvents

- Soil/Sediment: Add organic solvent
- Tissue: Add organic solvent

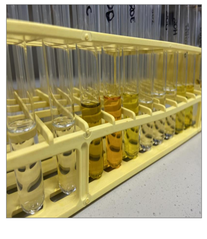
Extraction

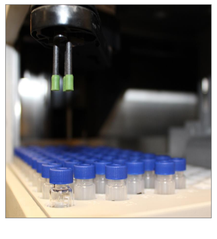
- Soil/Sediment: Sonicate for ~10 minutes (1X solvent extraction)
- Tissue: Sonicate for ~10 minutes (2X solvent extraction)

After each sonication, the samples were centrifuged to pellet the solid material and the organic solvents removed and dried to a residue using nitrogen and a heated water bath (N-Evap). Each sample was re-suspended in a specific blend of water and methanol, and external standard (M9PFNA). Each sample was transferred to a polypropylene vial for analysis.

Analysis by LC/MS/MS

LC	MS/MS
Mobile Phases: ~5 mM Ammonium Acetate in water (A) and methanol (B)	Ionization Mode: HESI-
Flow Rate: 0.7-1.0 mL/min	CE: compound-specific
Injection volume: 10-20 µL	Segmented SRM
Gradient Start: 85%A/15%B	Peak Resolution: 0.7 FWHM





Target Analytes

- There are 28 PFAS compounds, 14 isotopically-labeled internal standards, and 1 external standard included in this analysis.

Quantitative Analysis

- Analytes were quantitated using analyte/internal standard peak area ratios to correct for extraction deficiencies and matrix interferences.

Qualitative Analysis

- Analytes are identified based on their retention time and transition ions, where applicable (some do not fragment).

Results

The results from this study are summarized in Figures 1 and 2 for soils/sediments/house dust and canned seafood, respectively.

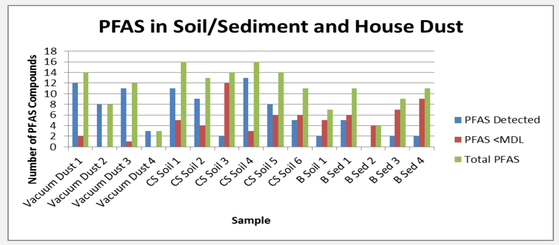


Figure 1. Total PFAS detected in soil/sediment and vacuum dust samples.

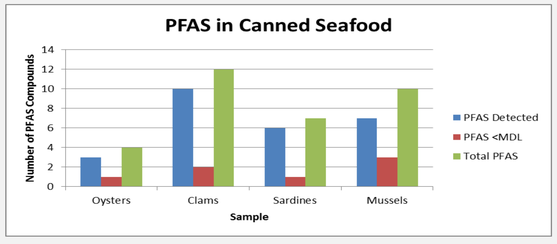
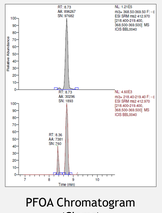
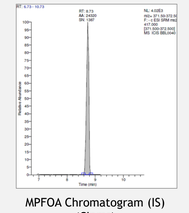


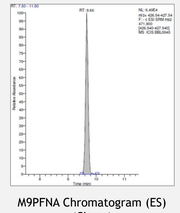
Figure 2. Total PFAS detected in canned seafood samples.



PFOA Chromatogram (Clams)



MPFOA Chromatogram (IS) (Clams)



M9PFNA Chromatogram (ES) (Clams)

Conclusion

PFAS were detected in all samples analyzed, showing the pervasiveness of these chemicals in our environment and in the food and drink we consume every day. Additionally, the vacuum dust samples were of special interest due to the various PFAS chemicals that are known to be used in carpet manufacture, for example, Scotch Guard.

References

White, N., et al. Elevated levels of perfluoroalkyl substances in estuarine sediments of Charleston, SC. Science of the Total Environment. 2015.

Martin, J., et al. Bioconcentration and Tissue Distribution of Perfluorinated Acids in Rainbow Trout (*Onchohynchus mykiss*). Environmental Toxicology and Chemistry. 2003.

Acknowledgements

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