Extraction and Analytical Challenges for PFAS in Biosolids

Oliver Cawdell
Introduction

- PFAS sources in the environment.
- Why might PFAS be in biosolids, and why does it matter?
- Analytical challenges for biosolid and sludge matrices.
- Methods available for biosolids.
- Comparison of different extraction techniques.
- Summary of method performance
PFAS sources and pathways within the environment

Oliaei, F. et. al. (2012). PFOS and PFC releases and associated pollution from a PFC production plant in Minnesota (USA). Environmental science and pollution research international. 20.
- Biosolids are separated from wastewater during WWTP processing.
- Spreading of biosolids on farmland is common practice in North America.
- Land applied biosolids can cause PFAS to reenter the food chain creating a positive cycle.

Oliaei, F. et. al. (2012). PFOS and PFC releases and associated pollution from a PFC production plant in Minnesota (USA). Environmental science and pollution research international. 20.
Analytical challenges for biosolids

Currently no published EPA method for biosolids

Highly variable physical properties and chemistry between samples

Interferences Affecting Instrument Response:
High TOC, Lipids and Industrial contaminants

Analytes with Different Chemical Properties

Hydrophobic analytes at the interface of biphasal samples

Surface sorption, including glassware
Isotope Dilution: Crucial for difficult matrices

Results are automatically recovery-corrected for effects of the analytical process

Mitigates the effects of ion enhancement / suppression caused by interferences

Improved analyte identification when matrix affects retention times

Results are highly accurate and precise
Selecting a method for biosolid analysis

- No official solid matrix currently available.
  - 537.1 – method for potable waters only, limited to 18 analytes.
- Wet or dry solid processing
- Pre extractions to remove the solid component:
  - Methanol extraction. Simple extraction to aqueous phase.
  - Ion Pair. Matrix digestion before solvent extraction. (Zhang et al. 2018)
- Cleanup via SPE, GCB or Lipid cleanup column.

Method Comparison

Two different variables were tested in this study:

- Sample processing comparison: Air dried versus centrifuge and separate processing.

- Solid Matrix Pre-extraction comparison: Ion par extraction (Zhang et al. 2018) versus methanol solid/liquid extraction.

For consistency, these were kept constant:

- Internal standards were added before extraction (isotope dilution).
- 1g dry weight equivalent of each sample was extracted.
- All extracts went through SPE and GCB cleanup before analysis by UPLC-MS/MS.
Internal standard recovery from a lab sand matrix

- Methanol
- Ion Pair
Internal standard recovery from a biosolid matrix

- Methanol
- Ion Pair

Internal standard recovery (%)

- PFBA
- PFPeA
- PFBS
- HPO-DA
- 4:2 FTS
- PFHxA
- PFHpA
- PFHxS
- 6:2 FTS
- PFNA
- PFOS
- PFOA
- PFDA
- 8:2 FTS
- MeFOSAA
- EtFOSAA
- PFUdA
- PFDoA
- 10:2 FTS
- PFTeDA
- PFhDA
- MeFOSE
- EtFOSE
- MeFOSA
- EtFOSA
INTERNAL STANDARD RECOVERY (%)

Internal standard recovery in wet and dried biosolids

- Ion Pair Wet
- Ion Pair Dry

Chart showing the internal standard recovery for various compounds in wet and dried biosolids.
Summary

- Contaminated biosolids are a significant source of PFAS to the environment.

- Isotope Dilution must be used for confidence in the results for complex matrices such as biosolids.

- Wet sample extractions yield better recovery of PFAS.

- Aggressive digestion techniques improve long chain recovery.

- Clean up should be sample/site specific to remove known contaminants and interferences.