



Vista
Analytical Laboratory

Extraction and Analytical Challenges for PFAS in Biosolids

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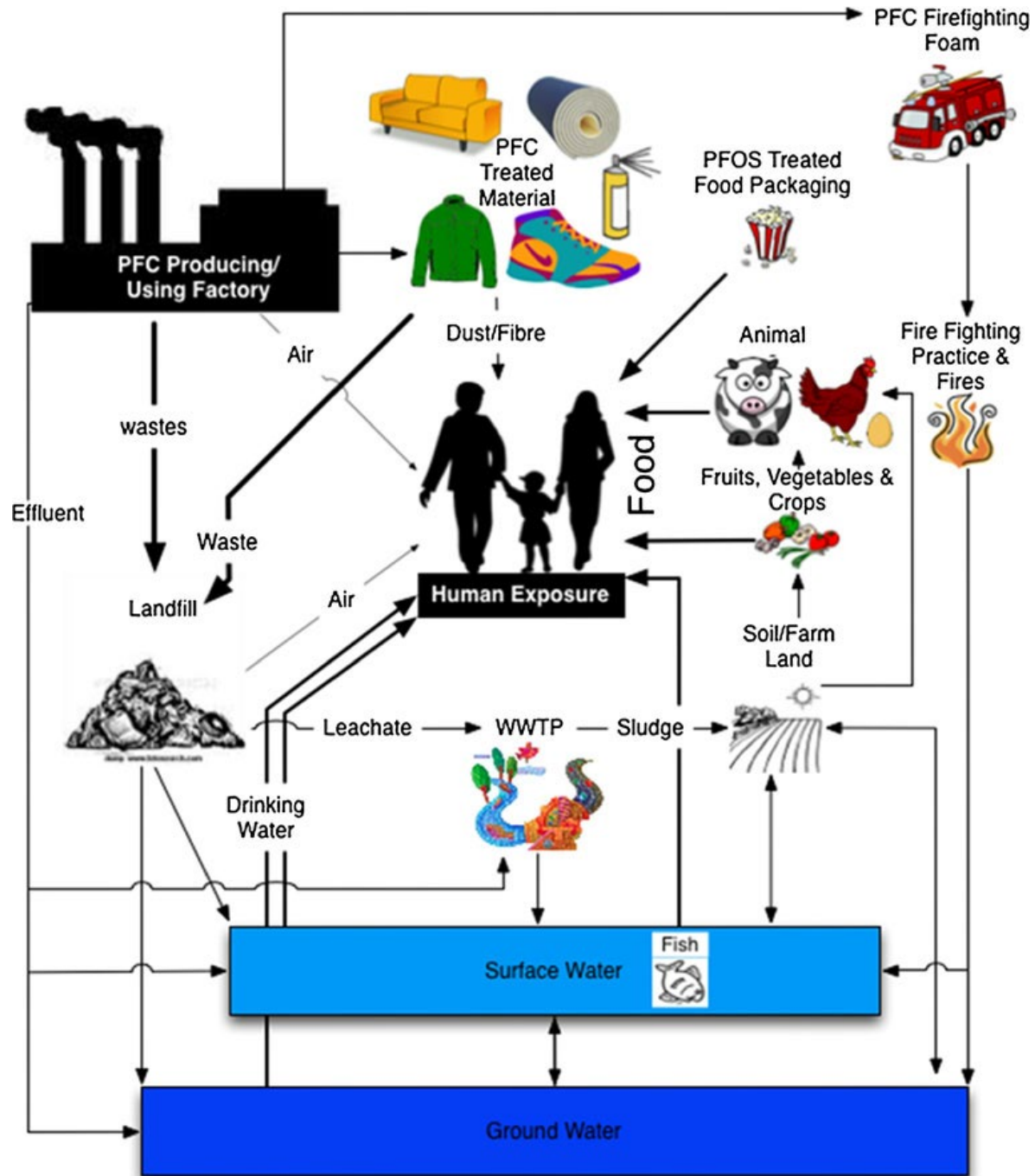


Introduction

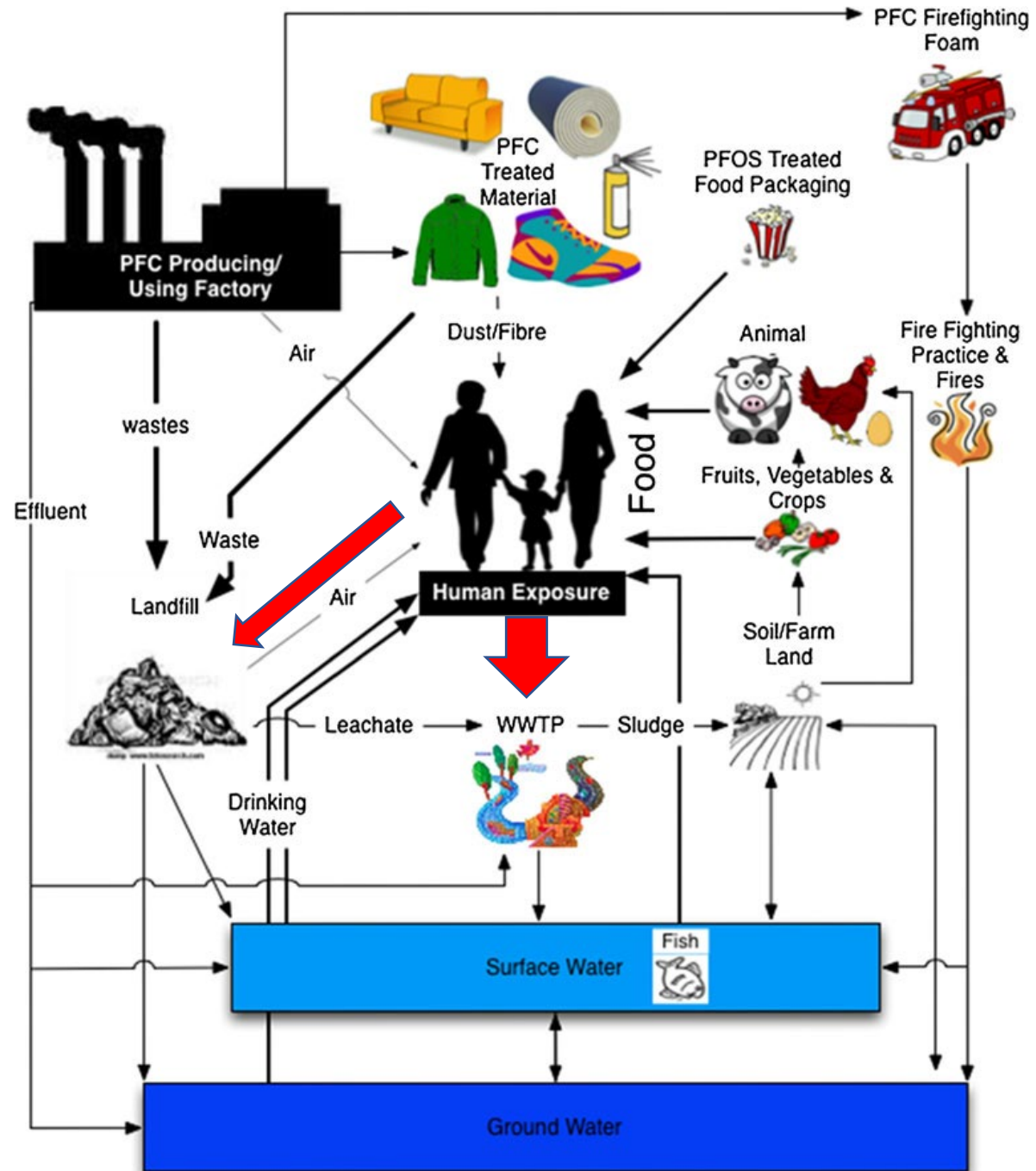
- ▶ Why might PFAS be in biosolids, and why does it matter?
- ▶ Analytical challenges for biosolid and sludge matrices.
- ▶ Methods available for biosolids.
- ▶ Comparison of different extraction techniques.
- ▶ Summary of method performance



PFAS sources and pathways within the environment



- ▶ 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.





News reporting and public interest in PFAS is growing

‘I don’t know how we’ll survive’: the farmers facing ruin in Maine’s ‘forever chemicals’ crisis

Maine faces a crisis from PFAS-contaminated produce, which is causing farms to close and farmers to face the loss of their livelihoods

Lethal ‘forever chemicals’ taint our food, water and even blood.

There is no longer any population or place on earth untouched by PFAS contamination.

Michigan beef found to contain dangerous levels of ‘forever chemicals’

Contamination at a small farm discovered after sewage sludge was tested for PFAS, but officials downplayed incident as ‘isolated’

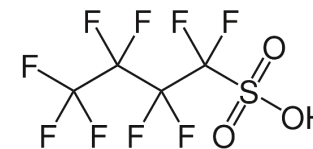
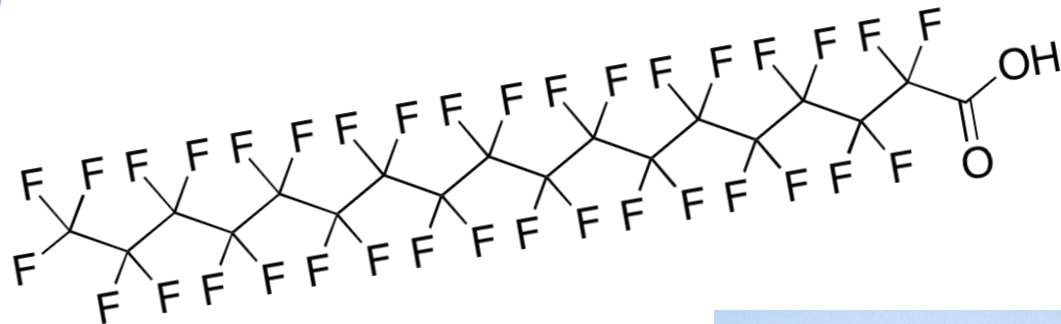
‘Forever chemicals’ found in home fertilizer made from sewage sludge

Alarming toxic PFAS levels revealed in new report raise concerns that the chemicals are contaminating vegetables

Toxic ‘forever chemicals’ have made their way from sewage to fertilizer to American beef

Analytical challenges for biosolids

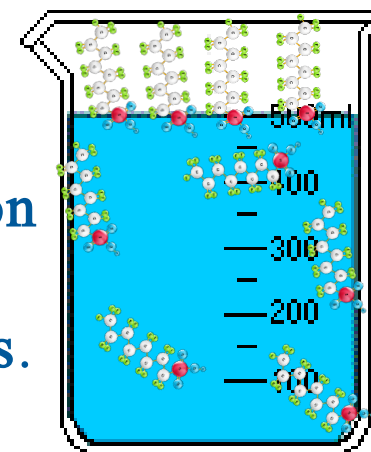
Complex Matrix



Contaminants from waste water sources such as metals, hydrocarbons and personal care products



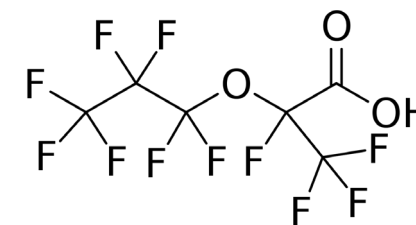
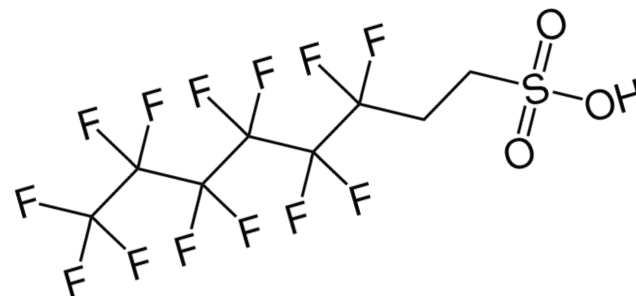
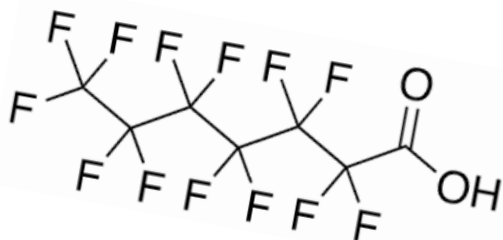
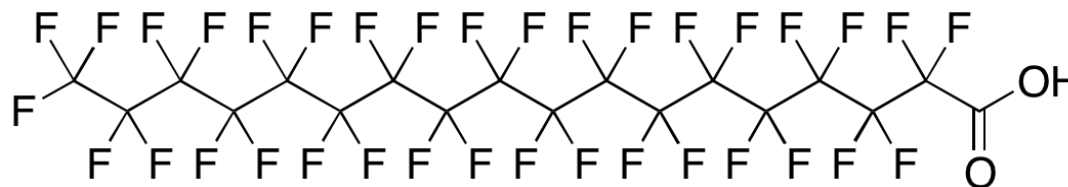
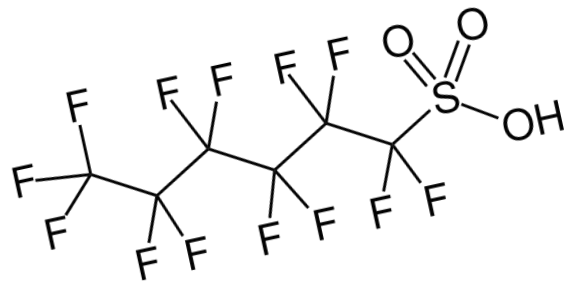
Hydrophobic analytes at the interface of biphasic samples



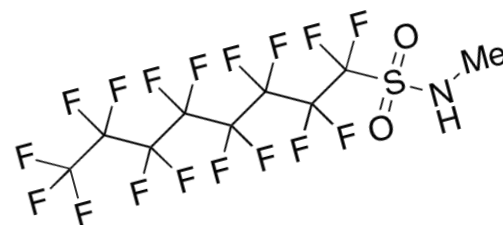
Interferences affecting instrument response: High total organic matter, lipids

Surface sorption on to particles and container surfaces.

Per- and Poly-Fluoroalkyl Substances

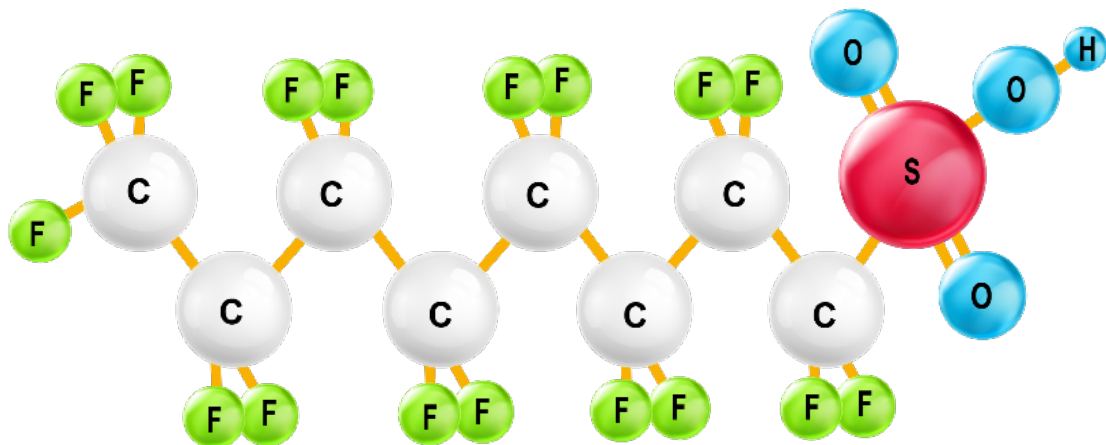


Highly variable physical properties such as particle size and percent moisture.

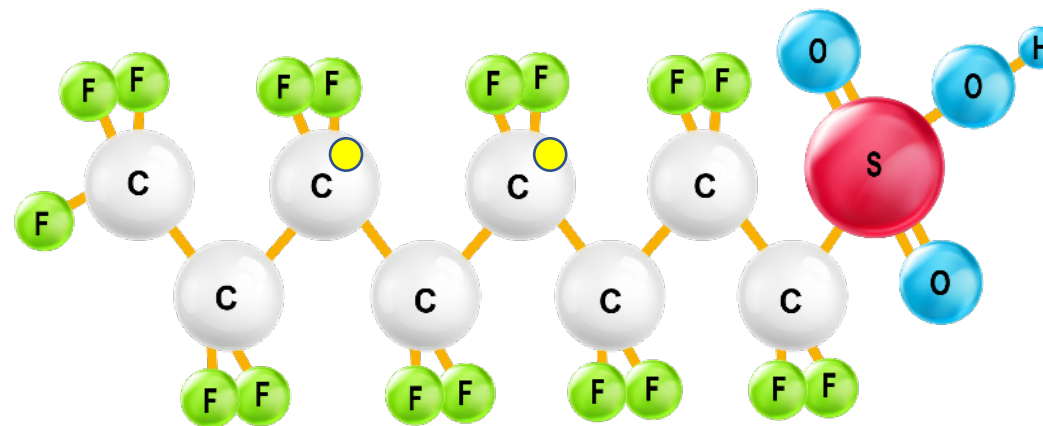


Analytes with Different Chemical Properties

Quantitation Technique: Isotopically-Labeled Standards



PFOS



$^{13}\text{C}_2$ -PFOS

Atoms with the same number of protons,
but different neutrons; e.g., Carbon-12, Carbon-13



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 To Maximize Internal Standard Recovery



- ▶ Isotope dilution methods:
 - ▶ Proprietary isotope dilution methods optimized for solids.
 - ▶ Draft Method 1633

- ▶ Wet or dry solid processing
- ▶ Pre-extraction procedures
- ▶ Cleanup via SPE and/or ENVI-Carbï

Zhang et al. (2018) Determination of perfluoroalkyl acid isomers in biosolids, biosolids-amended soils and plants using ultra-high performance liquid chromatography tandem mass spectrometry. *Journal of Chromatography B*, 1072



Method Comparison

Two different variables were tested in this study:

- ▶ Sample processing before extraction:
 - ▶ Air drying a 5% biosolid sludge for solid only extraction.
 - ▶ Centrifuging and splitting the total biosolid into solids and aqueous components. The solid component was extracted and the aqueous fraction added in before SPE.
- ▶ Solid Matrix Pre-extraction comparison:
 - ▶ Basic Methanol solid/liquid extraction
 - ▶ Ion pair extraction (Zhang et al. 2018)



Method Comparison

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 the same SPE and cleanup.
 - ▶ Weak Anion Exchange SPE
 - ▶ ENVI-Carbï
 - ▶ Analysis by LC-MS/MS





Basic Methanol extraction

- ▶ Digestion in basic solution for solid matrix
- ▶ SPE followed by ENVI-Carb® cleanup
- ▶ Can be expensive and time consuming
- ▶ Best results for the short-chain aqueous-amenable PFAS. Internal standard recoveries for the long chains can be low.





Basic Methanol extraction

Similarities to Draft EPA Method 1633:

Same cleanup steps, although sorbent size was different.

(1633 SPE 15mg, 10mg of dispersive ENVI-Carbⁱ).

Methanolic ammonium hydroxide pre extraction

Differences:

1g d.w. vs 0.5g (1633)

Extract was not concentrated before SPE

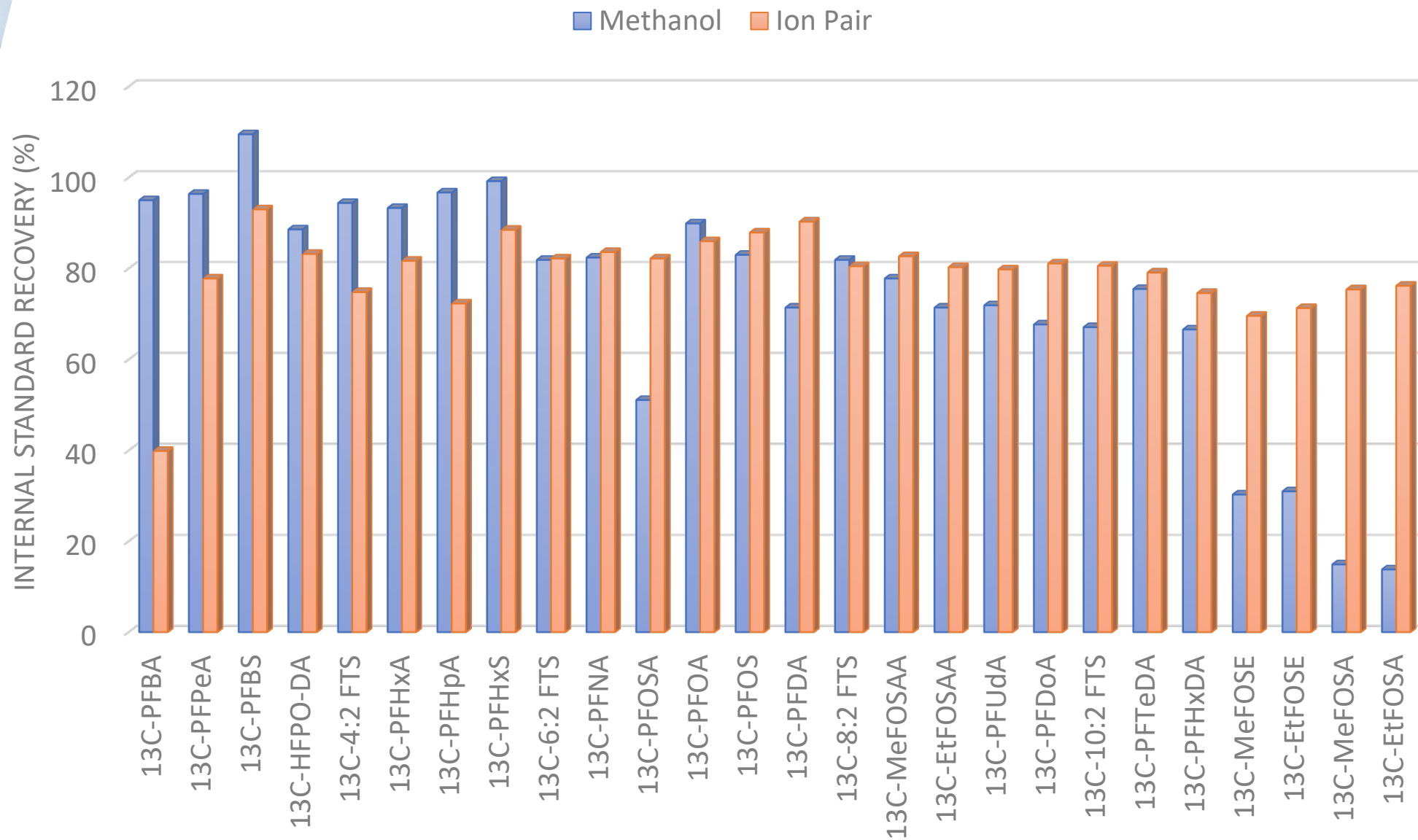
Mobile phase

Recoveries quantified by response area, not against a separate standard

Ion Pair extraction

- ▶ Tetrabutylammonium hydrogen sulfate (TBAHS), sodium carbonate (Na_2CO_3) are added to the samples, as the ion pair reagents.
- ▶ Aids the extraction of ionized analytes into organic phases by adding an oppositely charged ion to the extract.
- ▶ Uses an alternate extraction solvent, MTBE.
- ▶ Requires only basic laboratory equipment and skills.
- ▶ Can still be used with traditional cleanup techniques.
- ▶ Lesser used extraction technique that would require more research to full optimize for all PFAS chemistries and matrices.

Internal standard recovery in lab sand

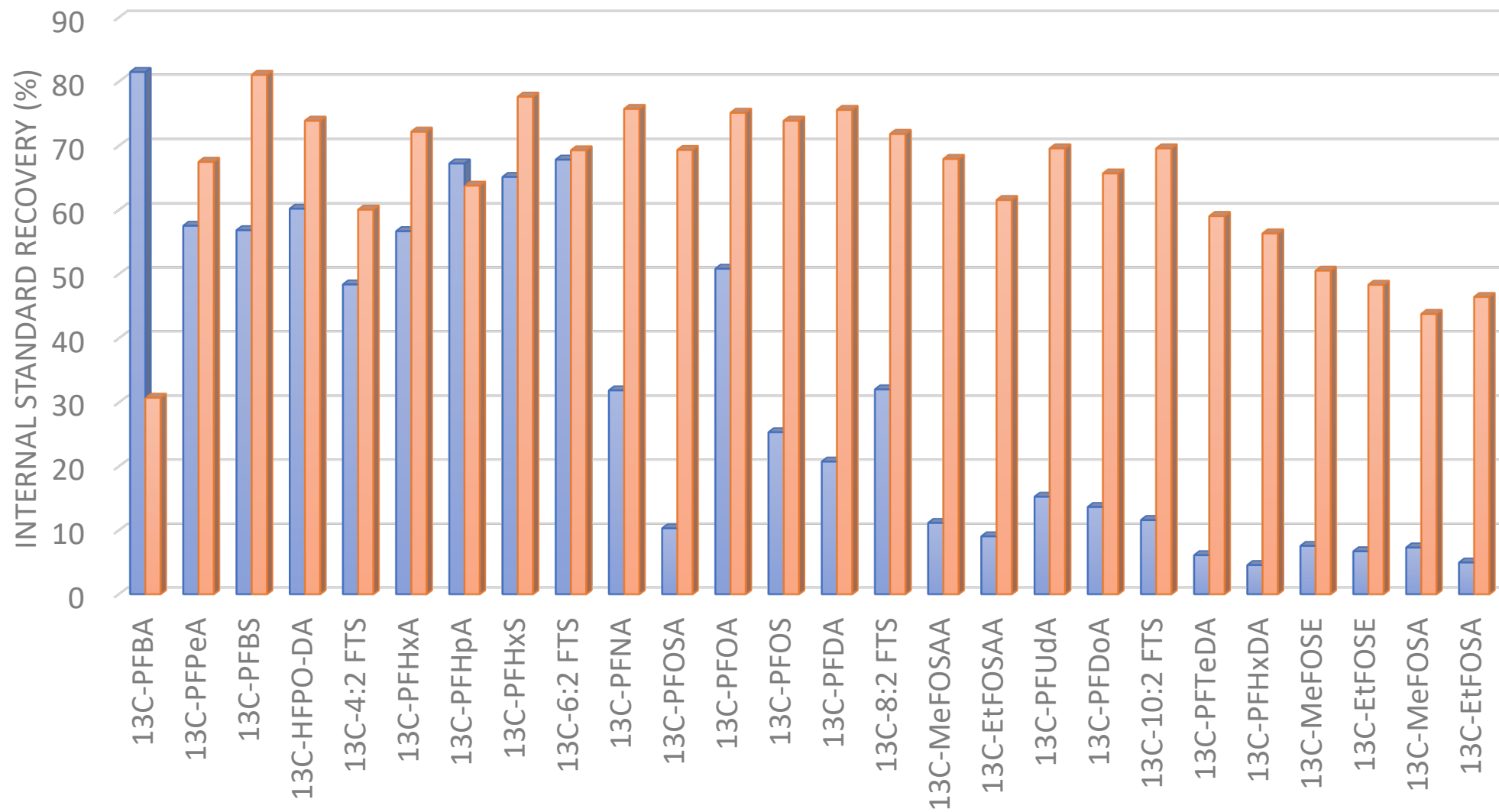




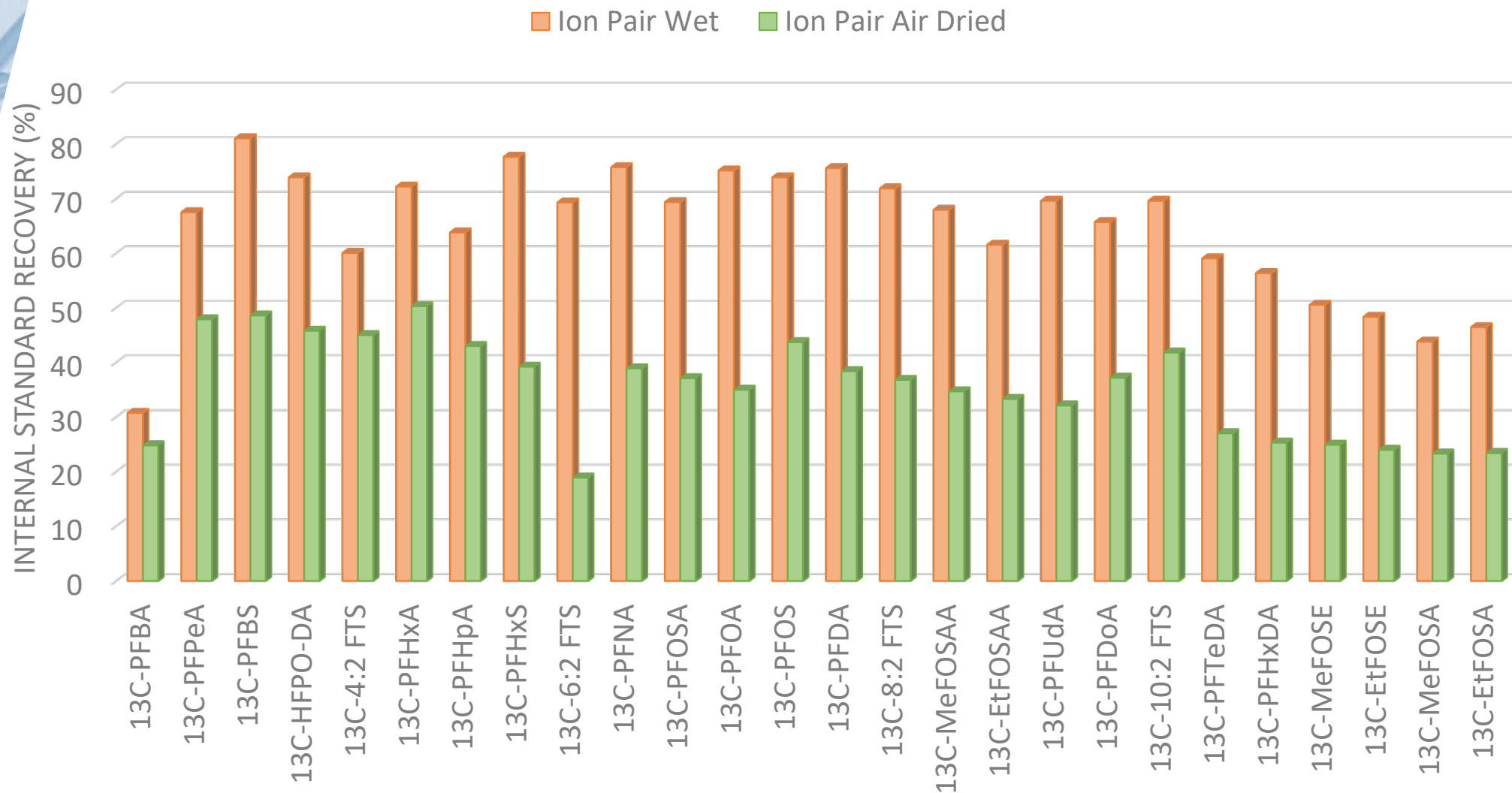
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Internal standard recovery in a 5% biosolid matrix

■ Methanol ■ Ion Pair



Internal standard recovery for Ion Pair in wet and air dried biosolids





Summary

- ▶ Contaminated biosolids can be 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 yielded higher recoveries of PFAS.
- ▶ Ion Pair extraction techniques improved recoveries of the long chain and neutral PFAS tested.



thank you

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