Northeast Residuals & Biosolids Conference

The Extraction and Analysis of PFAS in Biosolids: Method Performance, Matrix Effects, and Optimization Strategies

November 18th, 2025

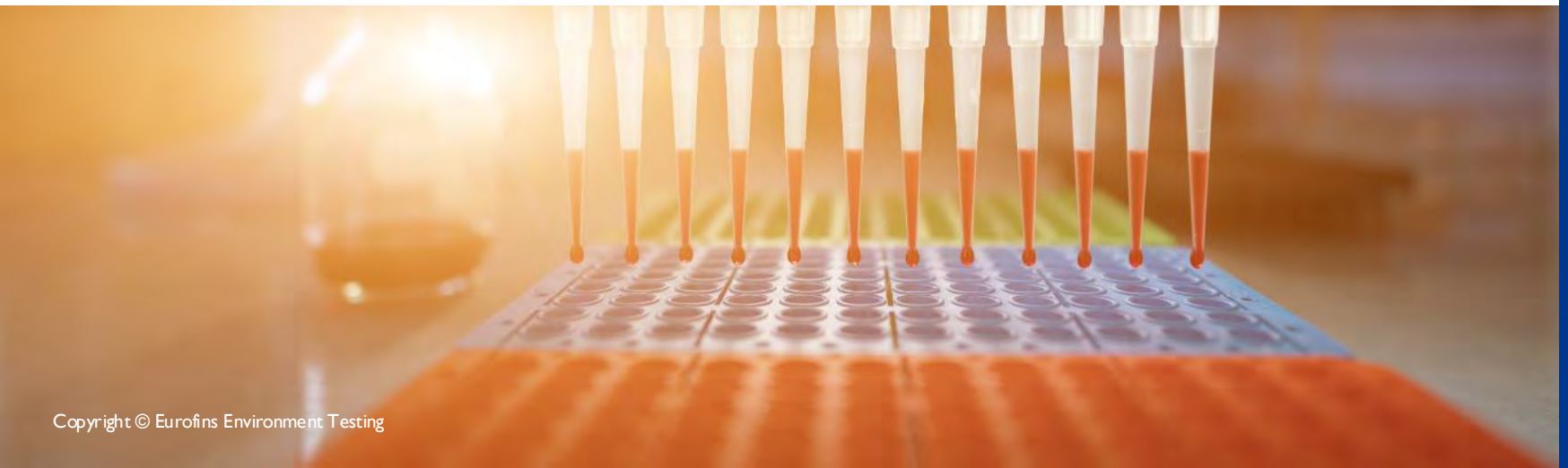
Jonathan Thorn

Technical Director & PFAS Practice Leader

eurofins | Environment Testing

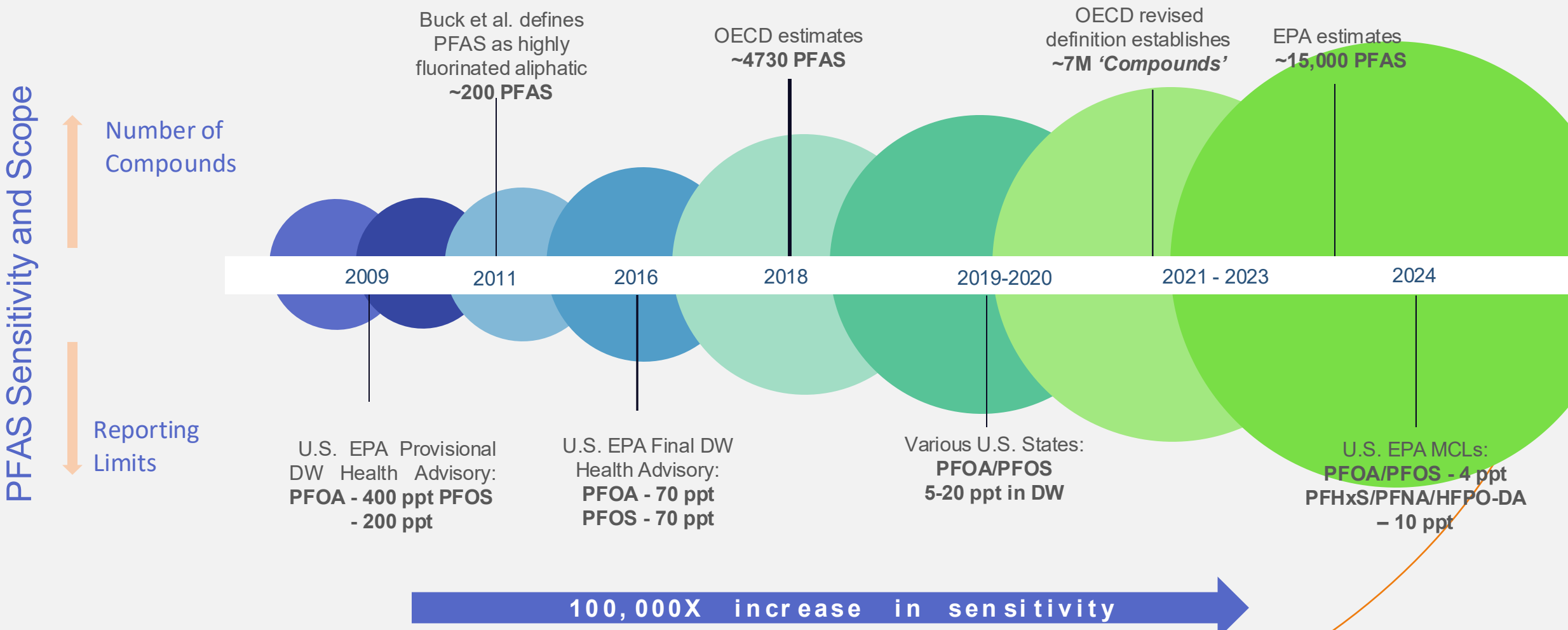
Presentation Topics

- Available methods for biosolids
- Considerations for real world samples
- Biosolid data

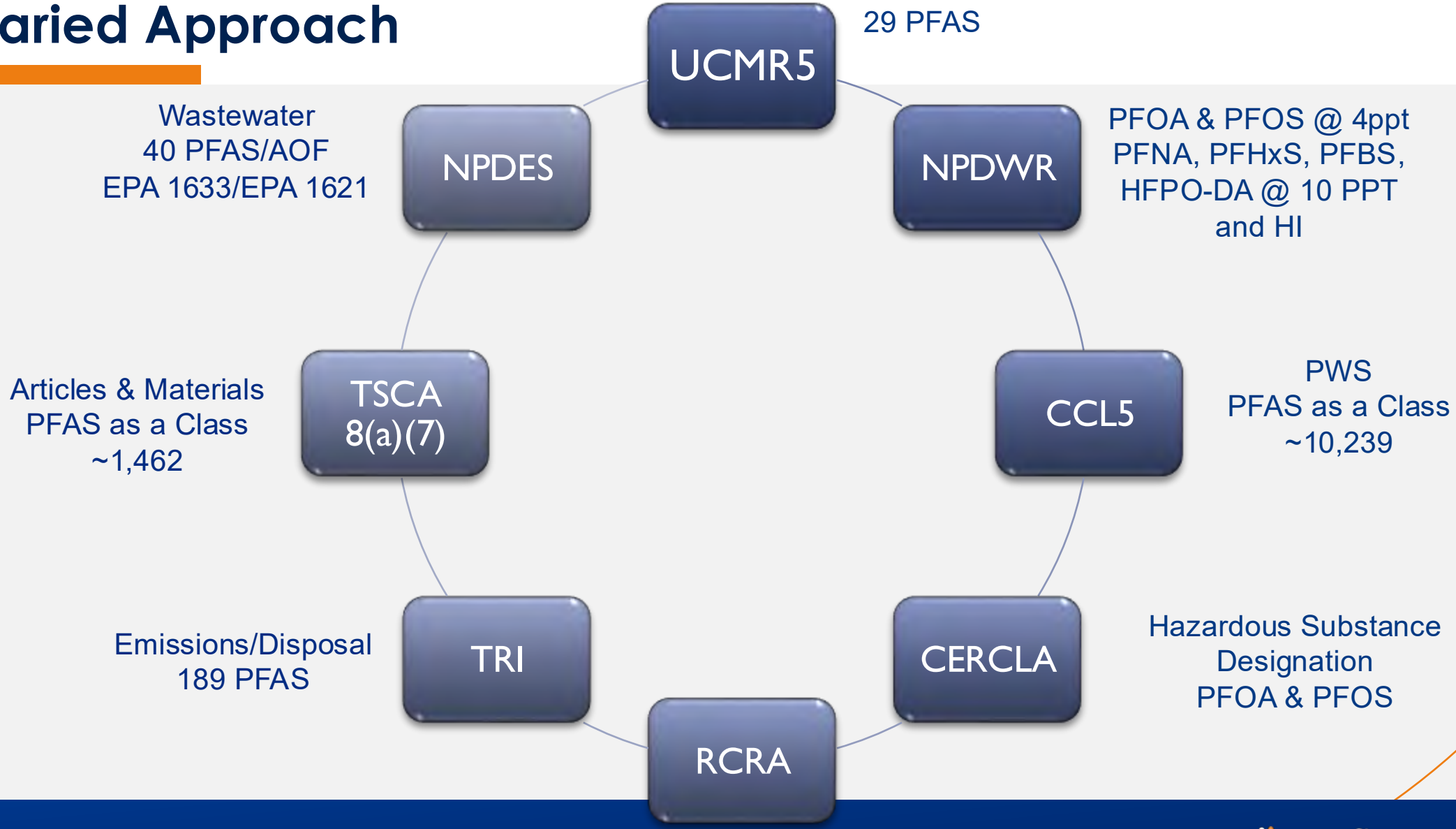


eurofins | Environment Testing

Evolving Definition of "PFAS

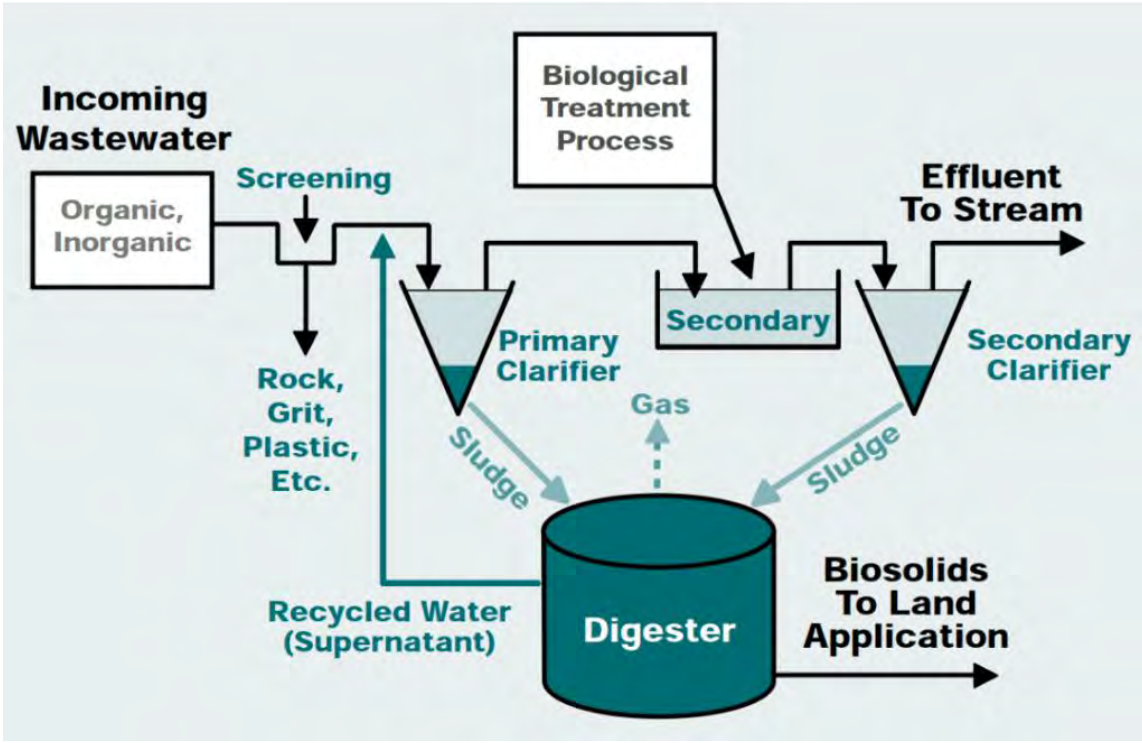


Varied Approach



What are Biosolids?

Biosolids are sewage sludge that has been treated to meet EPA regulatory standards under 40 C.F.R. Part 503 and is intended for beneficial land application as a soil conditioner or fertilizer. While the terms "biosolids" and "sewage sludge" are often used interchangeably by the public, biosolids specifically refers to the treated, nutrient-rich product that results when domestic sewage undergoes processing at wastewater treatment plants to separate liquids from solids, followed by additional treatment to meet federal safety and quality requirements for land use.



Understanding Biosolid Management in Modern Agriculture | Shapiro

eurofins | Environment Testing

PFAS Methods for Biosolids

eurofins | Environment Testing

eurofins | Environment Testing

EPA 1633A

- Multi-lab validated for surface water, groundwater, wastewater, landfill leachate, soil, sediment, biosolids, fish, and shellfish tissue
- 0.5-gram dry weight basis for extraction
- Serial extraction with basic solvent
- Weak Anion Exchange SPE
- Carbon cleanup
- LC/MS/MS
- Isotope dilution quantification
- 40 target analytes

Multi-lab Validation Study

- 8 commercial labs / 1 state lab
- 3 biosolid samples
  - Southern CA WWTP – Wet Cake
  - Mid-Atlantic WWTP – Biosolids#1 East
  - Pacific NW WWTP – WWTP Biosolid
- Samples homogenized prior to sub-sampling
- Good statistical data across the labs
  - Lower recoveries for PFDoS

Links to MLV Study Reports:

- Wastewater, Surface Water, and Groundwater
- Soild and Sediment
- Biosolids and Landfill Leachate
- Tissue

eurofins | Environment Testing

EPA 1633A – Target Analytes

PFCA

- PFBA
- PFPeA
- PFHxA
- PFHpA
- PFOA
- PFNA
- PFDA
- PFUnA
- PFDoA
- PFTrDA
- PFTeDA

PFSA

- PFBS
- PFPeS
- PFHxS
- PFHpS
- PFOS
- PFNS
- PFDS
- PFDoS

FTS

- 4:2 FTS
- 6:2 FTS
- 8:2 FTS

FTCA

- 3:3 FTCA
- 5:3 FTCA
- 7:3 FTCA

PFOSA

- PFOSA
- NMeFOSA
- NEtFOSA

FOSAA

- NMeFOSAA
- NEtFOSAA

FOSE

- NMeFOSE
- NEtFOSE

PFECA

- HFPO-DA
- ADONA
- PFMPA
- PFMBA
- NFDHA

PFESA

- 9Cl-PF3ONS
- 11Cl-PF3OUdS
- PFEESA

EPA 1633A – Section 9.1.2

In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements.

These options include alternative extraction, concentration, and cleanup procedures, and changes in sample volumes, columns, and detectors.

Alternative determinative techniques and changes that degrade method performance are not allowed without prior review and approval (see 40 CFR 136.4 and 136.5).

Types of Quantification

- External Standard
  - Only uses native analytes
  - Prone to matrix effects
  - EPA 8327 and ASTM D8421
- Internal Standard
  - Uses labeled internal standard
  - Compensates for variation in sample preparation and instrument performance
  - EPA 537.1
- Isotope Dilution
  - Labeled extracted and internal standards
  - Compensates for matrix effects, extraction efficiency, and instrument variation
  - EPA 533, EPA 1633, option for ASTM D8421

How does isotope dilution work?

Fortify

- Add known amount of IDA

Equilibration

- Critical step to ensure IDA behaves the same as the native in the sample!

Sample Preparation

- IDA and native will behave the same (losses, enhancements)

Analysis

- Loss or enhancement of native is corrected by the IDA undergoing same loss or enhancement!

eurofins | Environment Testing

The Power of Isotope Dilution - Wastewater

		External Standard		Internal Standard		Isotope Dilution			
		MS	MSD	MS	MSD	MS	MSD		
Analyte	CAS No.	% Rec	% Rec	% Rec	% Rec	% Rec	% Rec	Lower	Upper
PFBA	375-22-4	0	0	0	0	61	84	40	150
PFHxA	307-24-4	63	85	64	79	90	122	40	150
PFOA	335-67-1	135	131	119	106	118	111	40	150
PFNA	375-95-1	135	134	98	96	107	109	40	150
PFDA	335-76-2	106	110	76	77	92	98	40	150
PFBS	375-73-5	87	104	62	72	70	92	40	150
PFHxS	355-46-4	97	105	74	79	96	80	40	150
PFOS	1763-23-1	110	104	80	75	98	88	40	150
4:2FTS	757124-72-4	136	140	104	110	96	99	40	150
6:2FTS	27619-97-2	290	288	200	203	94	102	40	150
8:2FTS	39108-34-4	277	241	210	186	99	84	40	150
HFPO-DA	13252-13-6	48	49	70	66	97	98	40	150

1633A Expanded...

eurofins | Environment Testing

1633A EXP… What is that??

- Section 1.6: In addition, under the allowance for flexibility and method modifications described at 40 CFR 136.6, laboratories may include additional PFAS compounds as target analytes and/or alternative labeled PFAS compounds as authentic standards become commercially available without the need for the EPA review and approval, provided that they complete the requirements in Section 9 for those new analytes.
- 1633A EXP – 59 additional analytes, 15 new EIS

1633A EXP - Analytes

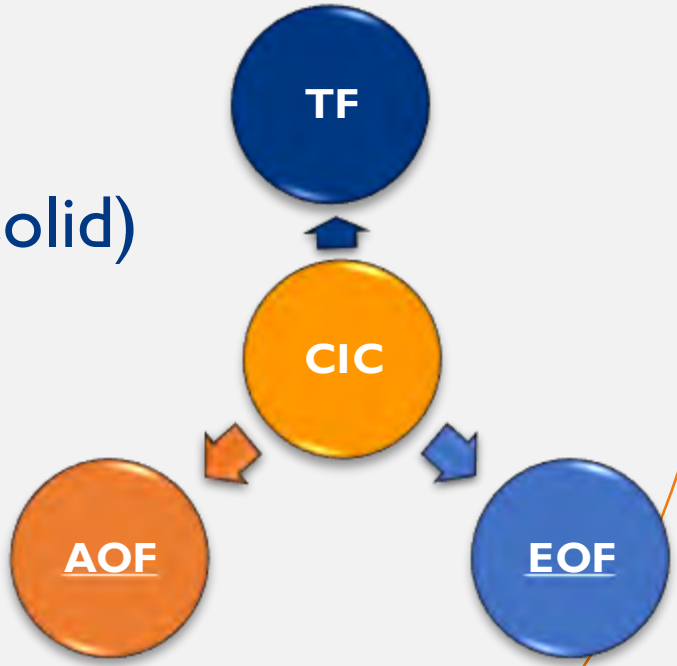
	EPA 1633	1633 EXP	Combined
Perfluoroalkyl carboxylic acids (PFCA)	11	3	14
Perfluoroalkyl sulfonic acids (PFSA)	8	4	12
Fluorotelomer sulfonic acids (FTSA)	3	1	4
Perfluorooctane sulfonamides (PFOSA)	3	6	9
Perfluorooctane sulfonamidoacetic acids (FOSAA)	2	0	2
Perfluorooctane sulfonamide ethanols (FOSE)	2	0	2
Per- and Polyfluoroether carboxylic acids (PFECA)	5	15	20
Perfluoroalkyl ether sulfonic acids (PFESA)	3	6	9
Fluorotelomer carboxylic acids (FTCA)	3	3	6
Perfluoroalkyl Phosphinates (PFPIA)	0	4	4
Polyfluoroalkyl Phosphate di-esters (diPAP)	0	4	4
Fluorotelomer unsaturated carboxylic acids (FTUCA)	0	3	3
Diprotic	0	3	3
perfluorinated sulfonylimides (PFSI)	0	2	2

Total PFAS and Proxy Methods

eurofins | Environment Testing

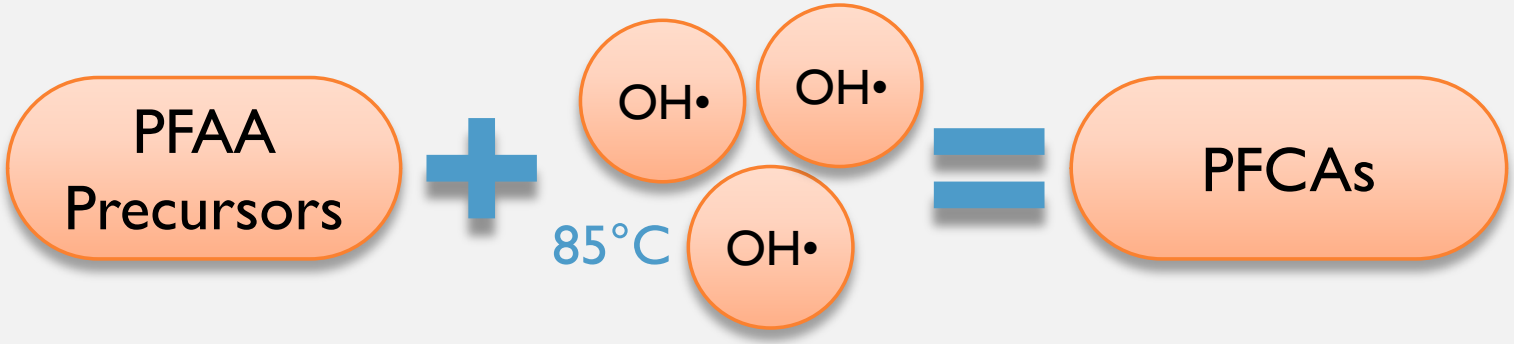
Total Fluorine, Organic Fluorine, and Inorganic Fluorine

- Combustion Ion Chromatography
- Total Fluorine (TF)
  - Reporting Limits ~ 200 ppb (aqueous) / 200 ppb (solid)
- Adsorbable Organic Fluorine (AOF)
  - Reporting Limits ~ 2 ppb (aqueous)
- Extractable Organic Fluorine (EOF)
  - Reporting limits ~ 300 ppb (solids)



Total Oxidizable Precursor (TOP) Assay

- Cons
  - Matrix interference
  - Forms non-measurable transformation products
  - Not robust
  - Over & Under oxidation
- Pros
  - Quantify precursor PFAS with Chain length



6:2 FTS PFHxA

Under-oxidation = 6:2 FTS untransformed
Over-oxidation = PFHxA, PFPeA, PFBA, PFPrA, PFEtA, TFA

eurofins | Environment Testing

Real World Samples

eurofins | Environment Testing

Are all Biosolids the Same?

- Varied moisture
  - Liquid biosolids 95-99%
  - Dewatered biosolids 70-85%
  - Dried biosolids 10-50%
  - Heat-dried biosolids 5-10%
- Enriched organic matter
  - Varies from 40-70% of the dry weight
- Heterogeneous

Are all Biosolids the Same?

Are all Biosolids the Same?

Real World Samples… What Could Happen?

- High moisture biosolids
  - Require large mass to reach 0.5g dry weight basis
  - Increased RL
  - Too much matrix
- High organic matter
  - Matrix effects (suppression and/or enhancement)
- Non-homogeneous samples
  - Poor reproducibility

What About Drying?

- Oven drying
  - Reduce moisture
  - Increase homogeneity of sample
- Decrease in total concentration at higher temperatures
- Studies at 30 C and 105 C

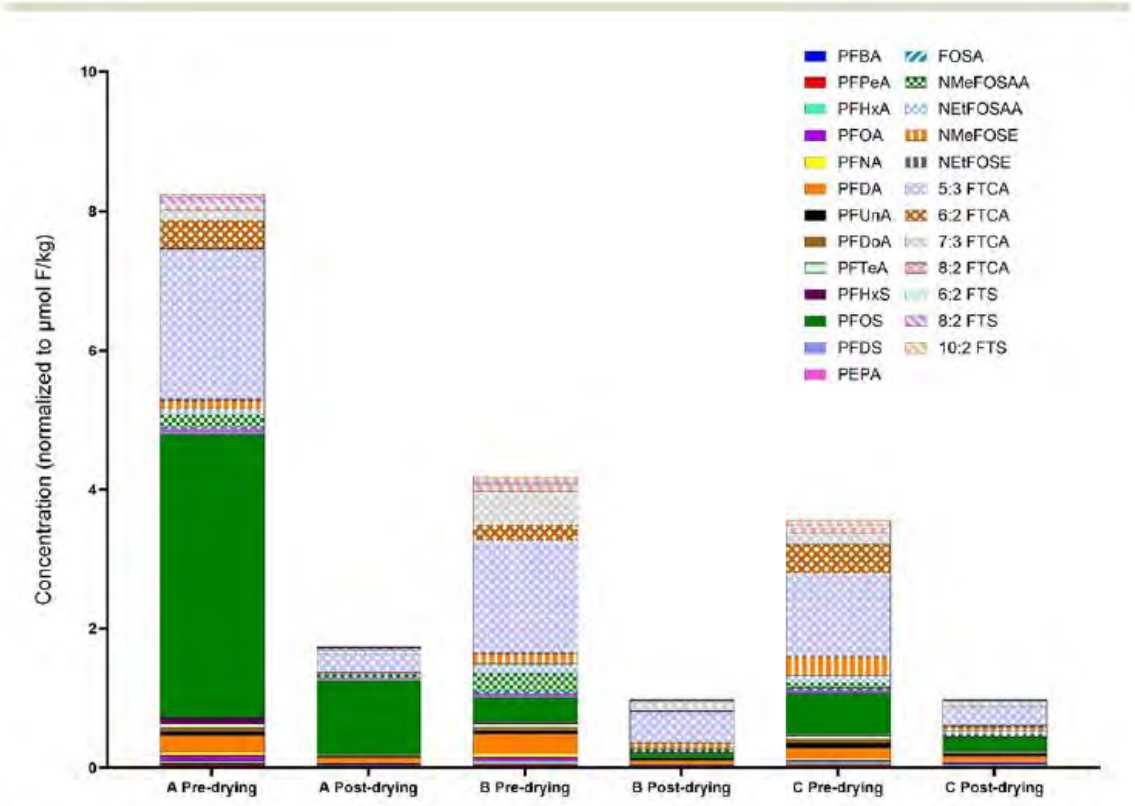


Fig. 4 Lab-scale oven drying reduced measurable PFAS in samples from three different WRRFs. Reprinted with permission. © The Water Research Foundation.[39]

Drying reduces the total PFAS concentration in biosolids and alters the PFAS profile - Environmental Science: Water Research & Technology (RSC Publishing)

eurofins | Environment Testing

All is not lost!

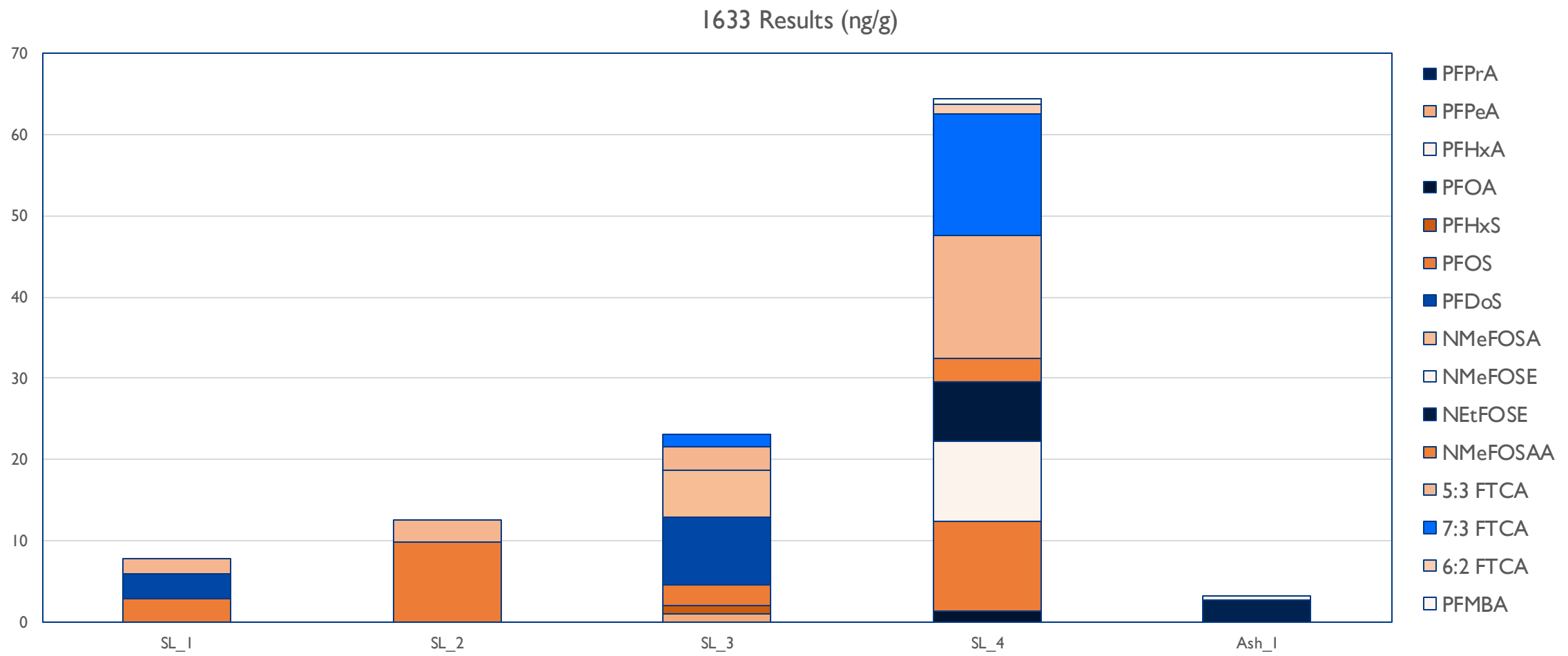
- Higher moisture / organic matter may lead to higher MDL and RL values
- Isotope dilution corrects for matrix enhancement / suppression!

Native	% Recovery	EIS	% Recovery
PFBA	111%	13C4-PFBA	25%
6:2 FTS	85%	13C2-6:2 FTS	162%
8:2 FTS	109%	13C2-8:2 FTS	245%

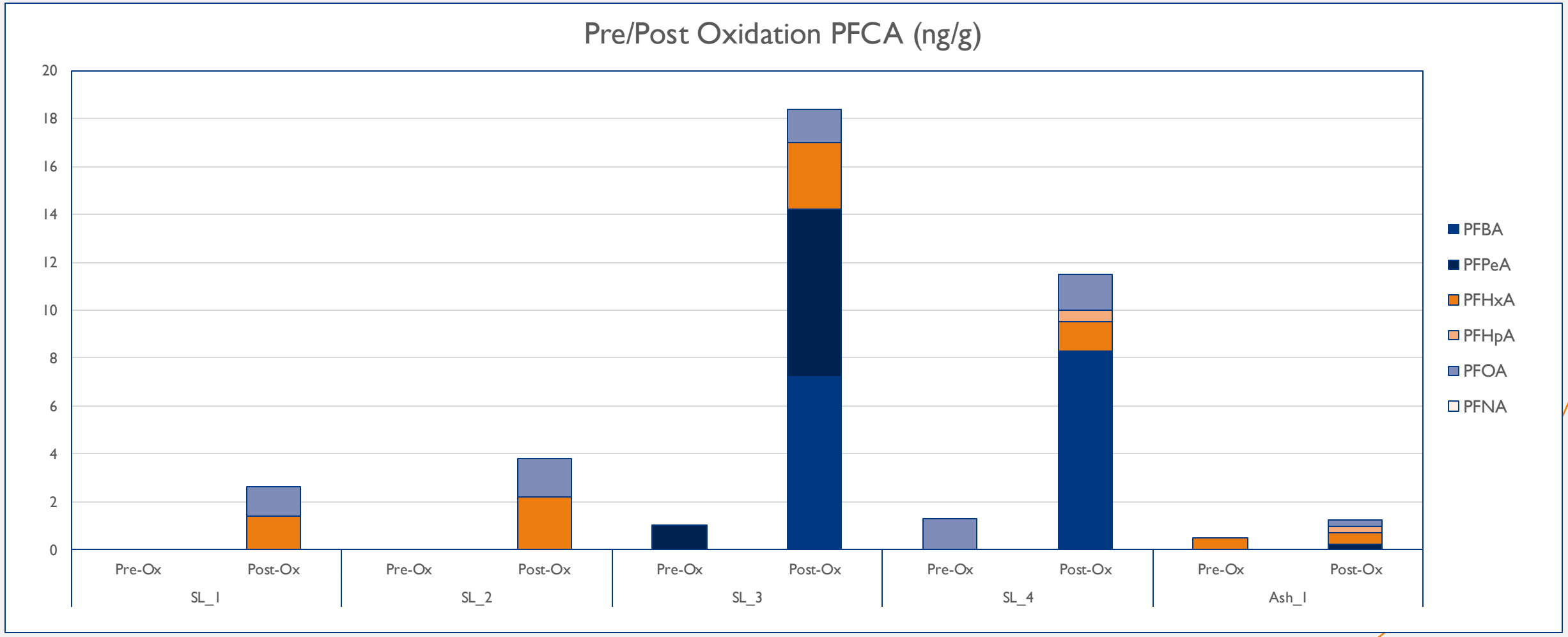
Analytical Results

eurofins | Environment Testing

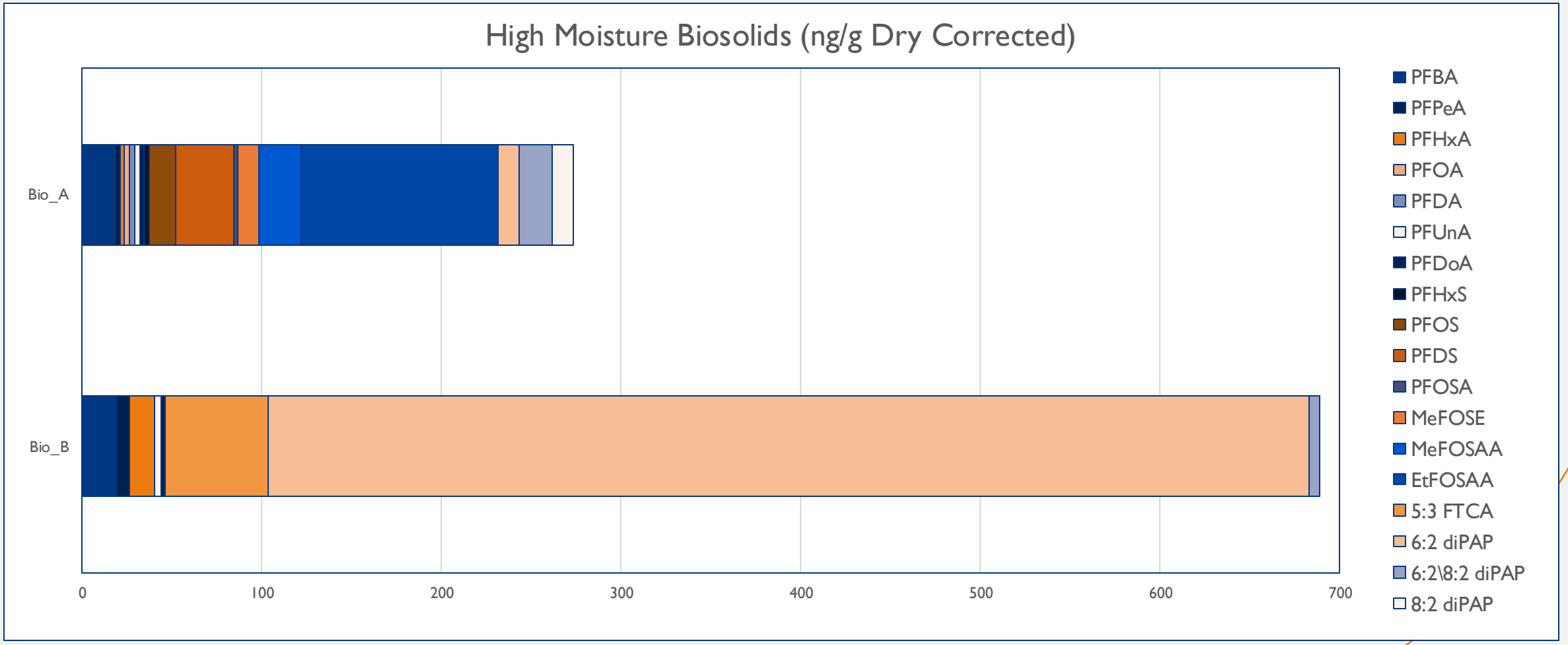
EPA 1633



Pre/Post Oxidation – C4 to C9 PFCA

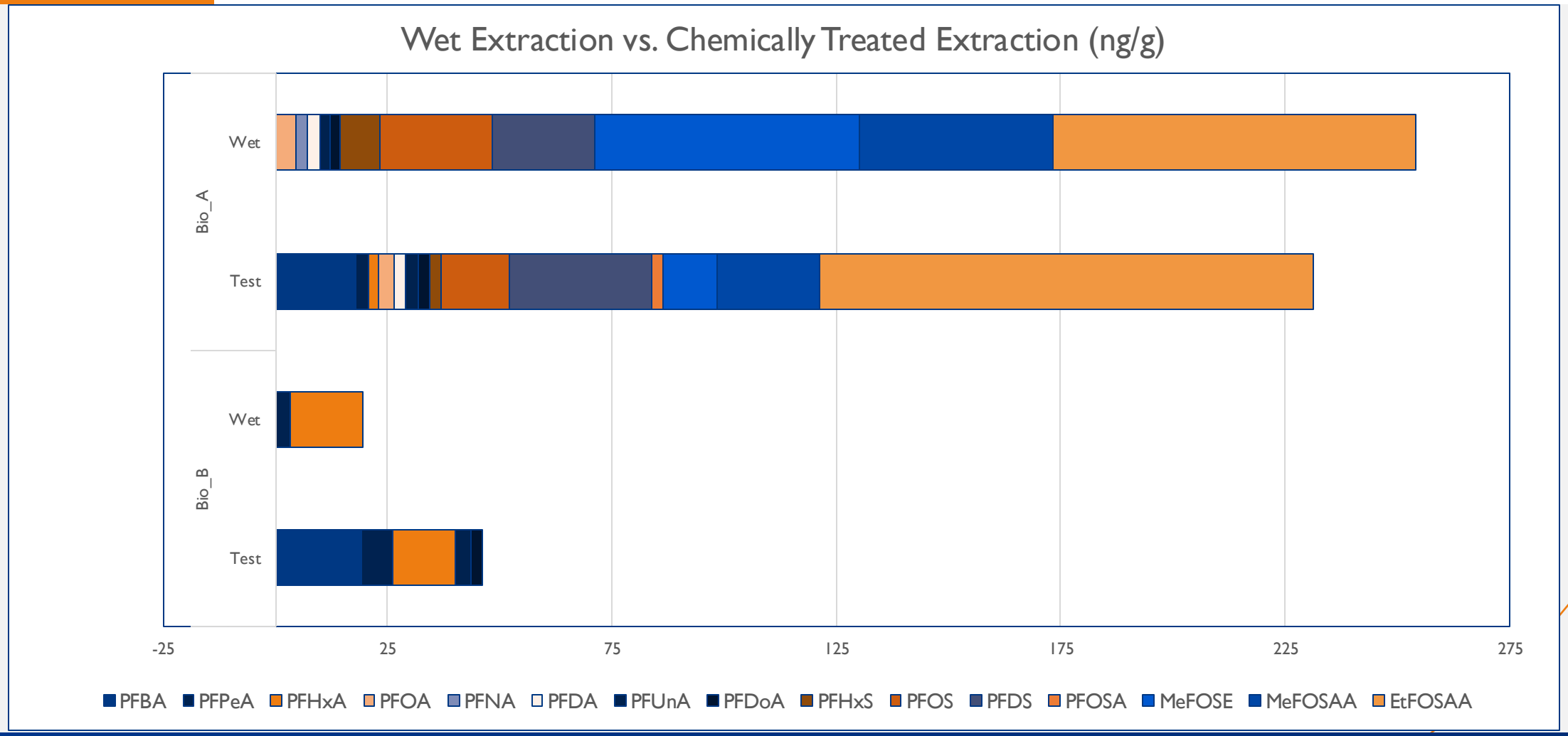


EPA 1633A - Expanded



eurofins | Environment Testing

High Moisture Biosolids



High Moisture Biosolids: EIS Recoveries

	Biosolid_B			
	Test	Wet	Lower	Upper
13C3-PFPrA	50.1		20	150
13C4-PFBA	57.6	84.4	8	130
13C5-PFPeA	56.1	93.8	35	130
13C5-PFHxA	58.5	82.2	40	130
13C4-PFHpA	56	71	40	130
13C8-PFOA	62.4	78.9	40	130
13C9-PFNA	58.8	53.1	40	130
13C6-PFDA	59	27.9	40	130
13C7-PFUdA	55.6	9.86	40	130
13C2-PFDoA	52.7	7.55	40	130
13C2-PFTrDA	55.7		20	150
13C2-PFTeDA	55.2	5.51	20	130
13C2-PFHxDA	52.8		20	150
13C3-PFPrS	73.4		20	150
13C3-PFBS	70.8	90.8	40	135
13C3-PFHxS	62.9	76.8	40	130
13C8-PFOS	59.7	34.5	40	130
13C3-PFDS	53		20	150
13C3-PFUdS	57		20	150
13C8-PFOSA	52.1	26.5	40	130

	Biosolid_B			
	Test	Wet	Lower	Upper
d3-MeFOSA	49.7	11.5	10	130
d5-EtFOSA	51.9	8.46	10	130
d7-MeFOSE	51.4	8.96	20	130
d9-EtFOSE	47.1	6.19	15	130
13C3-MeFOSAA	54.6	13.2	20	150
13C4-EtFOSAA	82.2	11.2	20	150
13C2-4:2FTS	93.2	207	40	165
13C2-6:2FTS	84	180	40	215
13C2-8:2FTS	102	95.1	40	275
13C2-10:2FTS	93.1		20	150
13C2-6:2FTCA	53.5		20	150
13C2-8:2FTCA	51.2		20	150
13C2-10:2FTCA	107		20	150
13C2-6:2FTUCA	63		20	150
13C2-8:2FTUCA	56.4		20	150
13C2-10:2FTUCA	116		20	150
13C4-6:2 diPAP	88.8		20	150
13C4-8:2 diPAP	83		20	150
13C3-HFPO-DA	56	61.9	40	130