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Excellence in Science

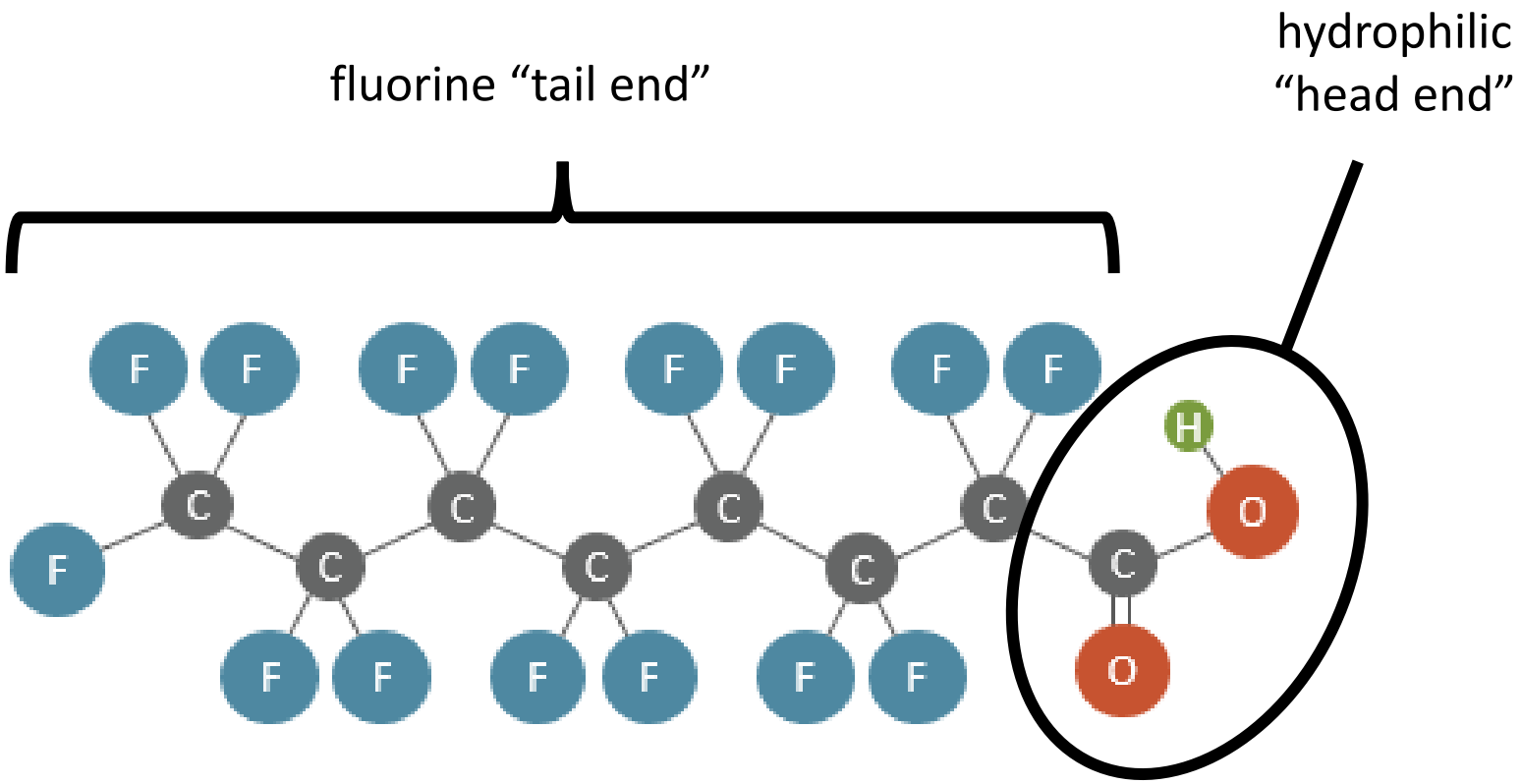
Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Leachate by EPA Method 1633A Using LC-MS/MS

August 4, 2025

Tiffany Liden, PhD

PFAS & Leachate

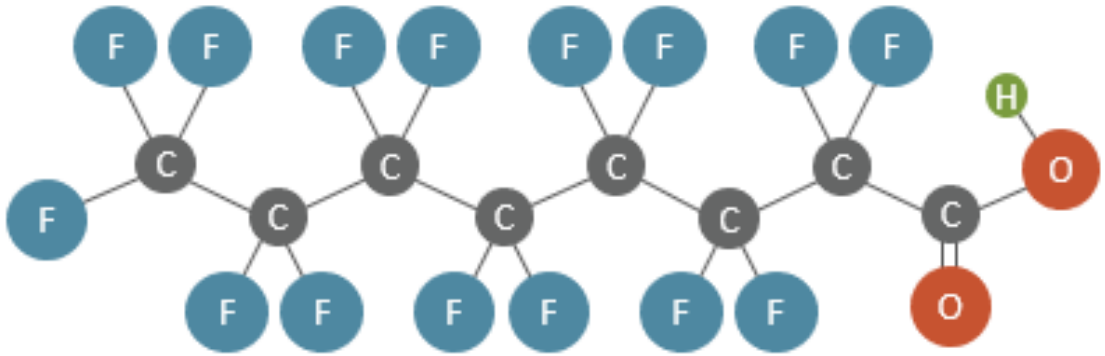
Per- and Polyfluoroalkyl Substances (PFAS)



PFAS & Leachate

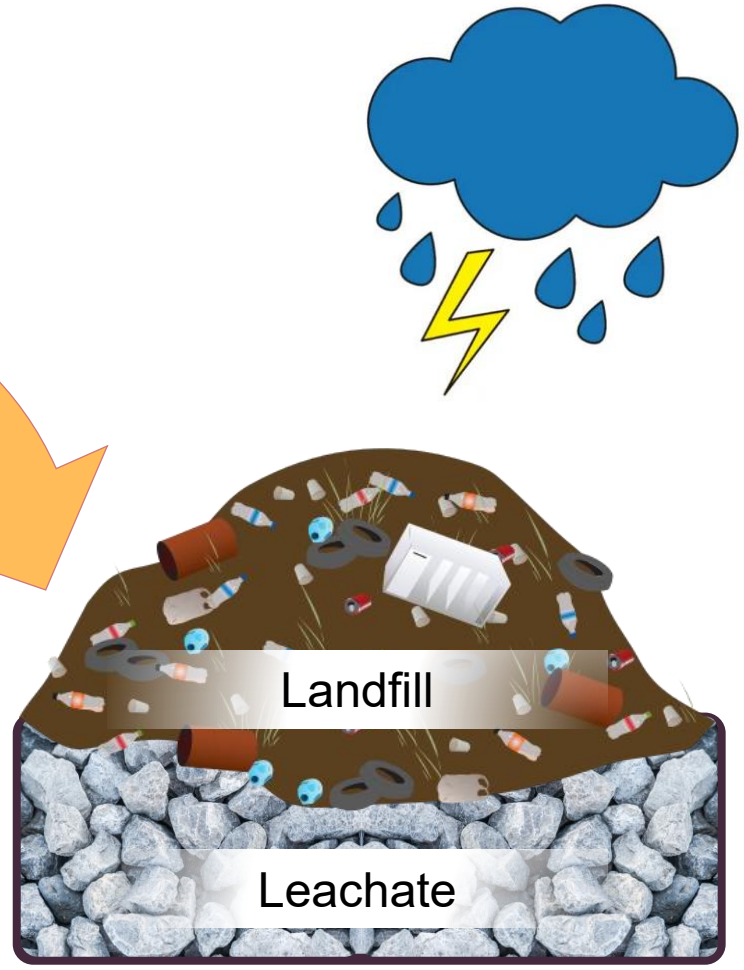
Per- and Polyfluoroalkyl Substances (PFAS)
<u>are used to make household products</u>.

PWC Fayetteville's Home Town Utility, https://www.faypwc.com/pfas-facts/



PFAS & Leachate

Per- and Polyfluoroalkyl Substances (PFAS) are used to make household products that <u>are discarded</u>.

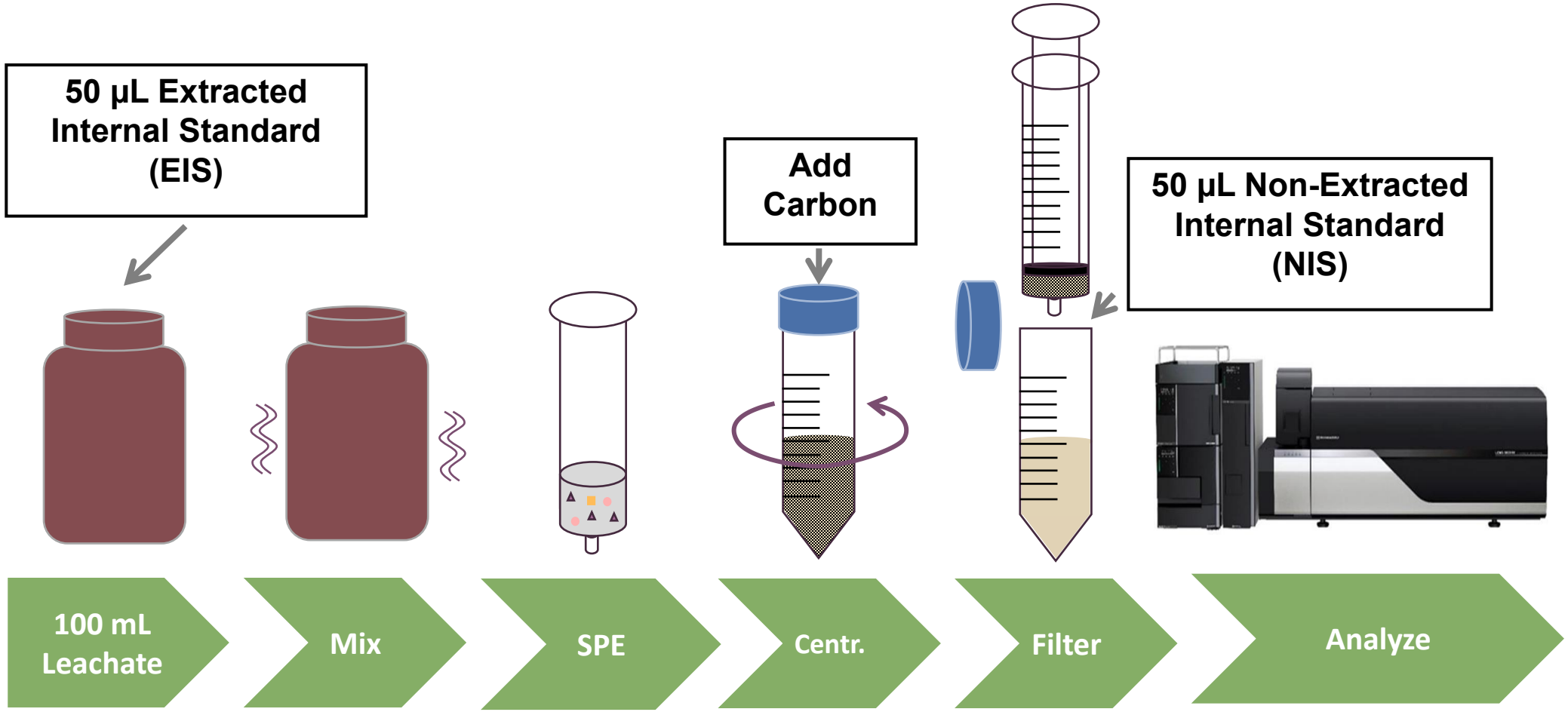


PWC Fayetteville's Home Town Utility, https://www.faypwc.com/pfas-facts/

Leachate Source

- **Pooled Sample**
- **From the central-southern U.S.**

EPA 1633A Sample Prep



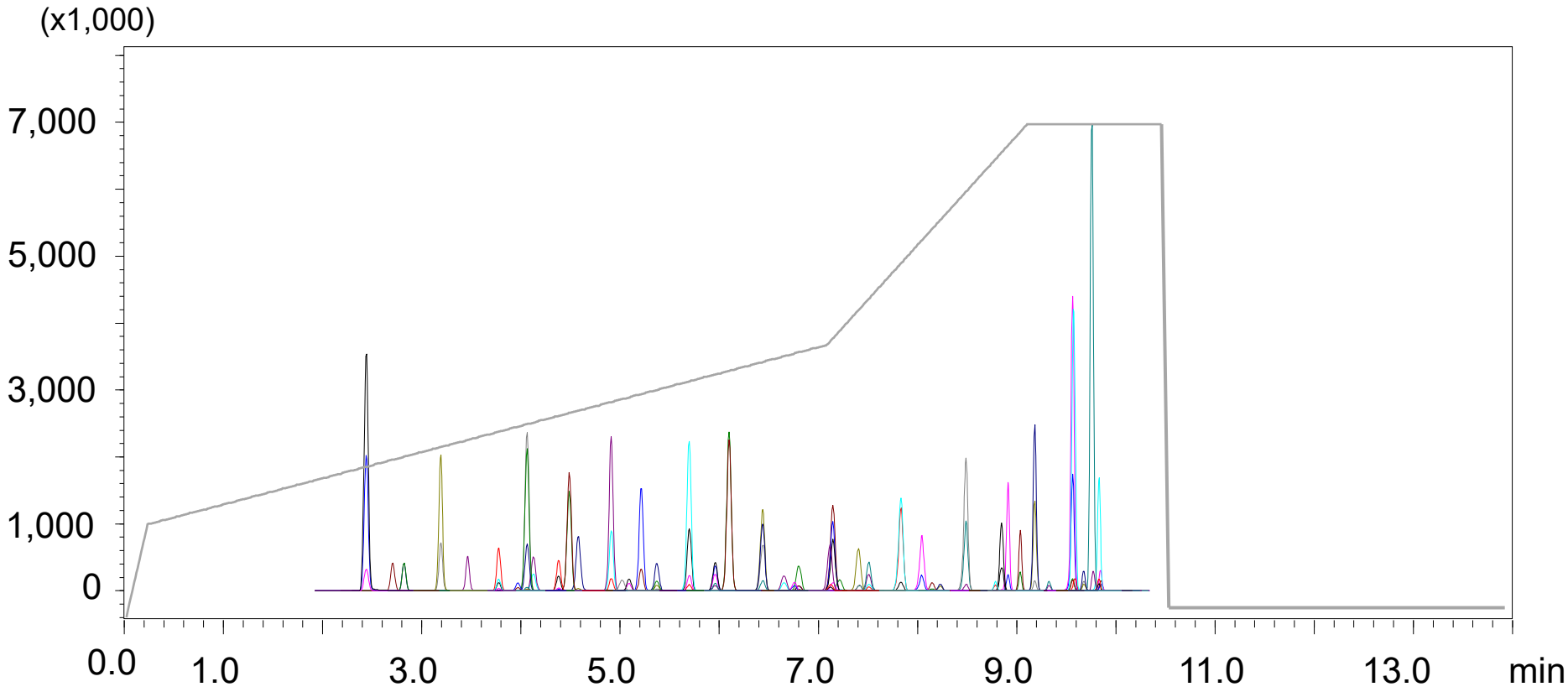
Instrument Parameters

LCMS-8060	Parameters	LC	Parameters
Nebulizing gas	3.0 L/min	**Delay Column**	Nexcol PFAS Delay Column (50 x 3.0mm, 5 µm)
Heating gas	15.0 L/min	**Analytical Column**	Shim-pack Scepter C18-120 Column (50 × 2.1 mm, 3 µm)
Drying gas	5.0 L/min	**Flow rate**	0.4 mL/min
Interface Temperature	250 ° C	**Mobile phase A**	2mM Ammonium Acetate in Water
DL Temperature	200° C	**Mobile phase B**	Acetonitrile
Heat Block Temperature	300° C	**Column oven temperature**	40 ° C
Diluent	Methanol with 4% water, 1% ammonium hydroxide and 0.625% acetic acid		

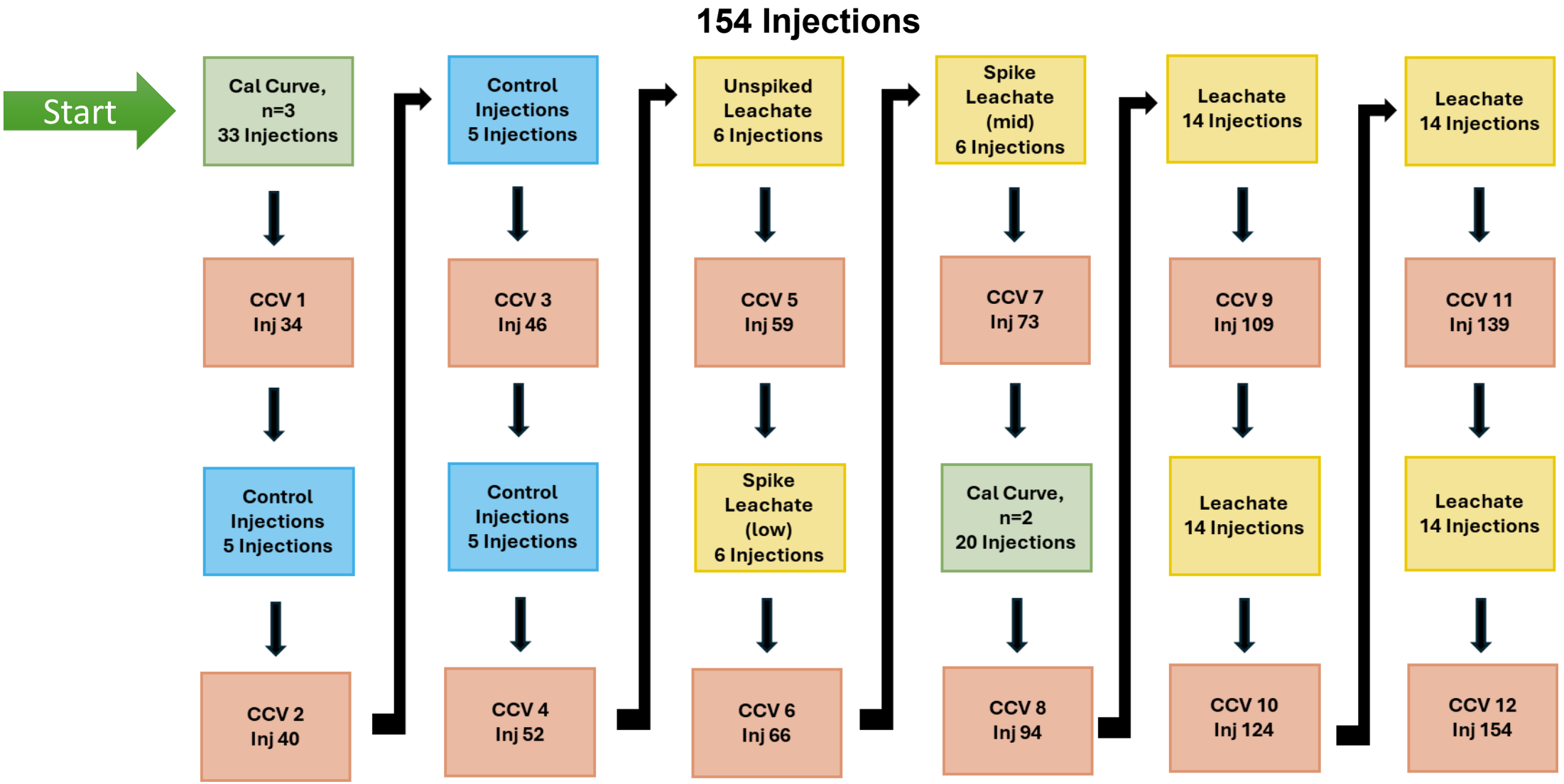
Gradient

LC Gradient	
Time (min)	%B
0	2
0.20	20
7.00	55
9.00	98
10.00	98
10.01	2
14.00	Stop

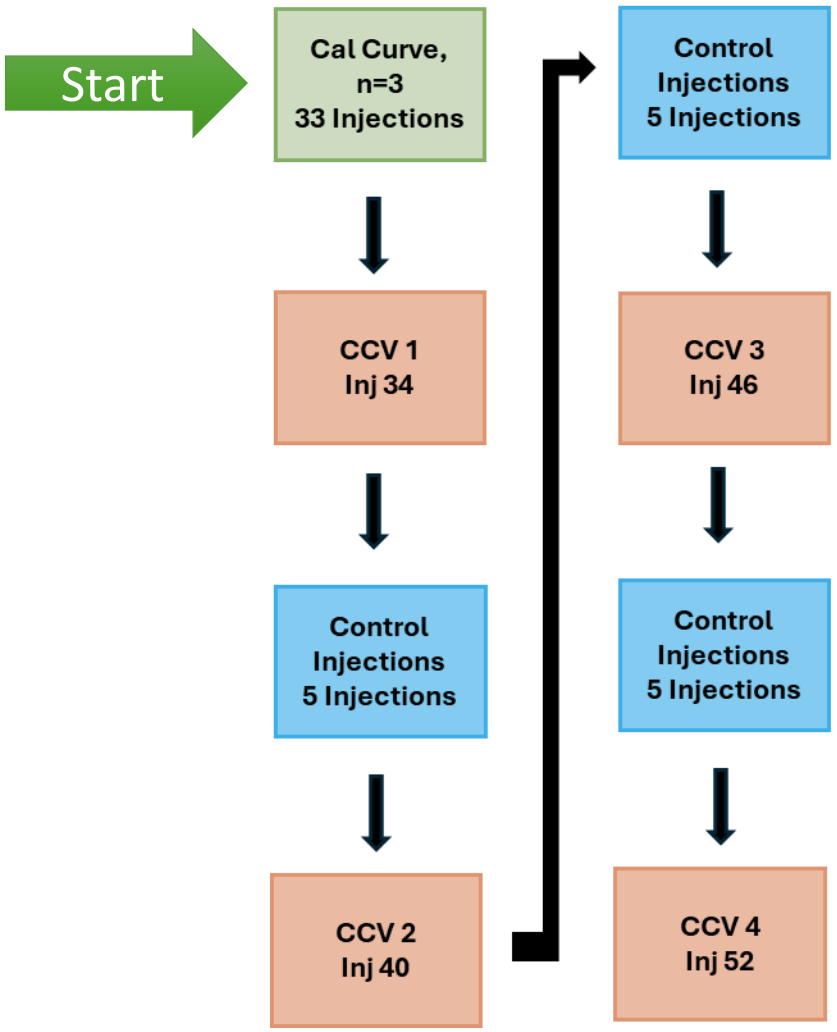
PFAS- EPA 1633A



Injection Sequence



Injection Sequence



Calibration Curve

- Based on EPA 1633A ranges
- Repeated 3X included blanks

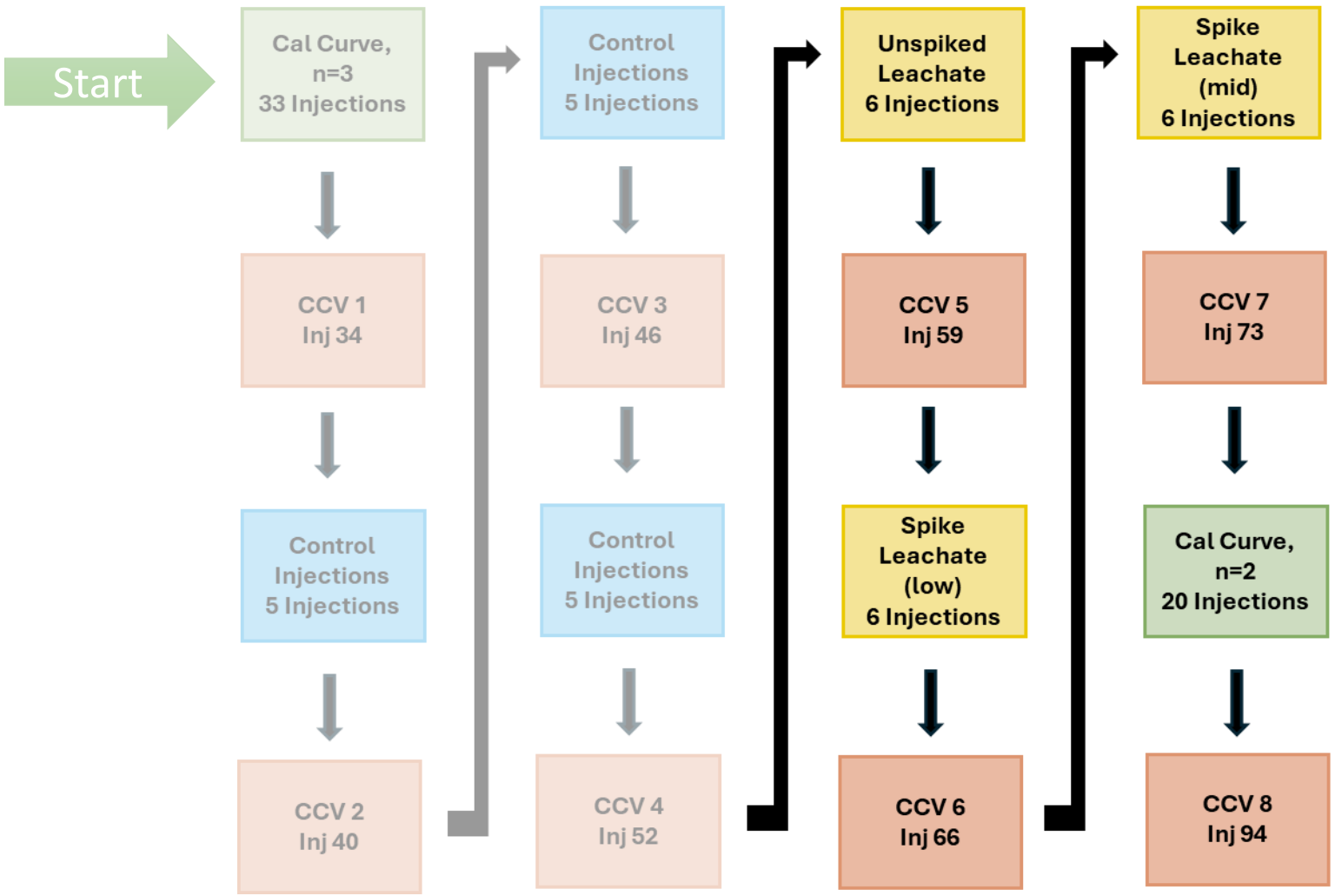
Continuous Calibration Verification (CCV)

- Equivalent to Cal 4

Extracted Lab Controls

- Repeated 3x
- Consisted of
  - Method Blank
  - 2 LLC (Spiked 2x Cal 1)
  - 2 MLC (Spiked Cal 4)

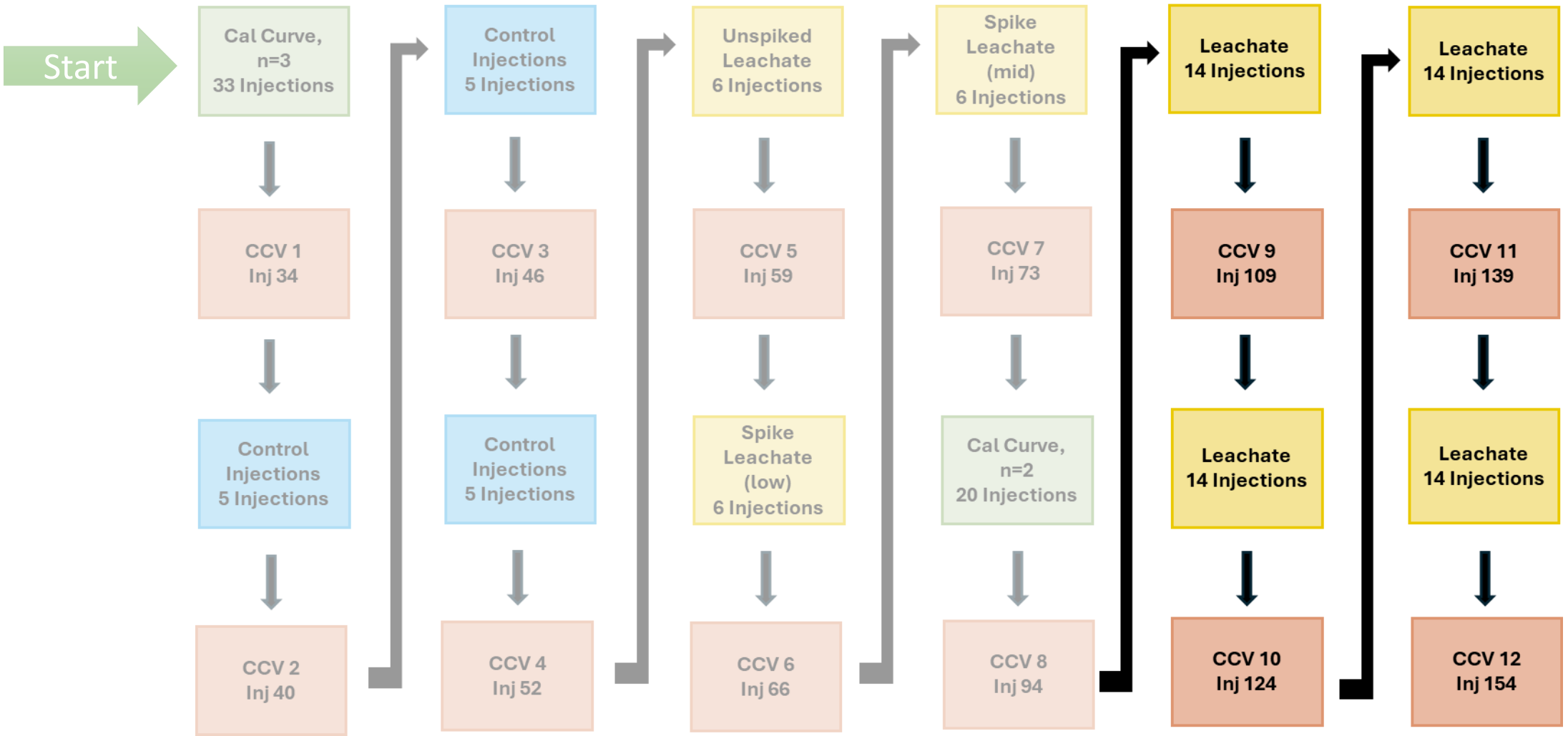
Injection Sequence



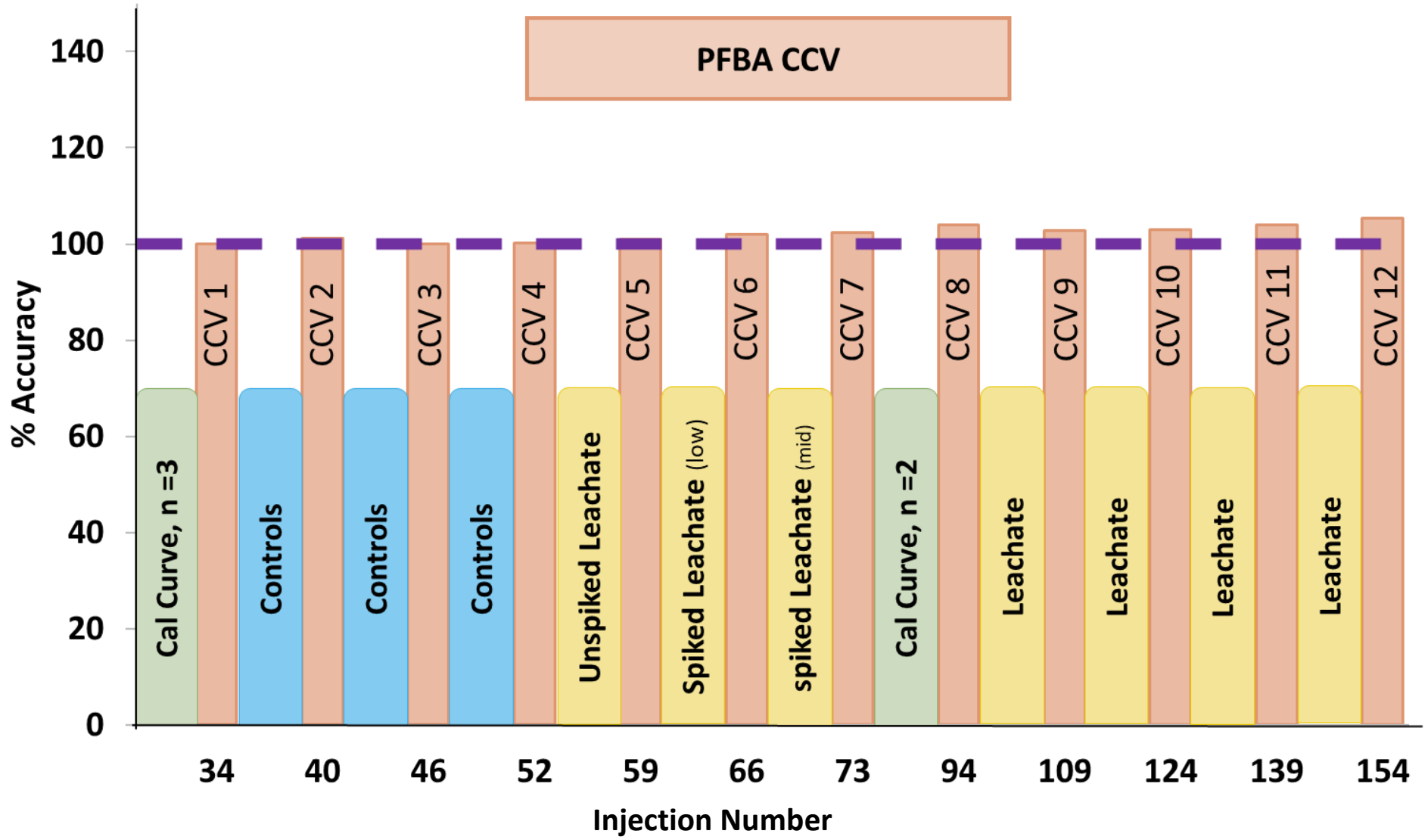
Leachate

- Consisted of
  - Unspiked
  - Spiked Low (Spiked 2x Cal 1)
  - Spiked Mid (Spiked Cal 4)

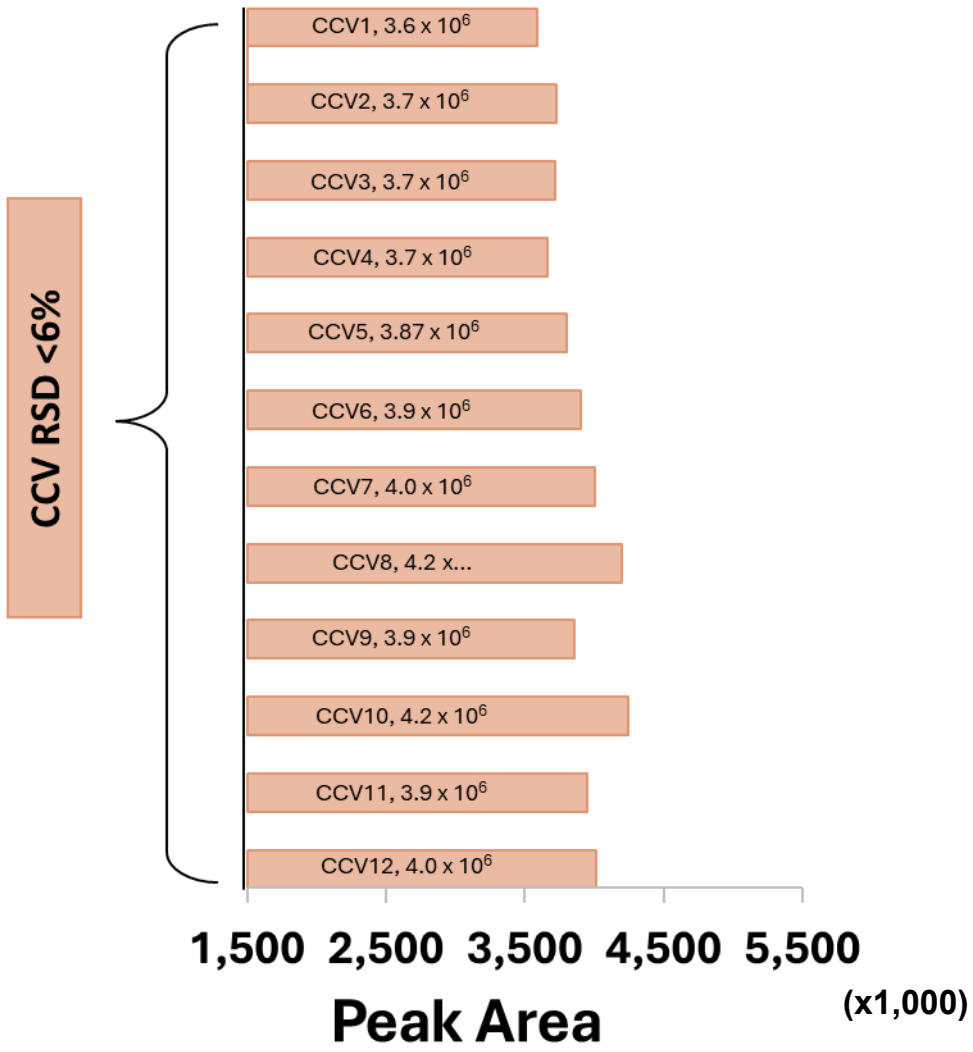
Injection Sequence

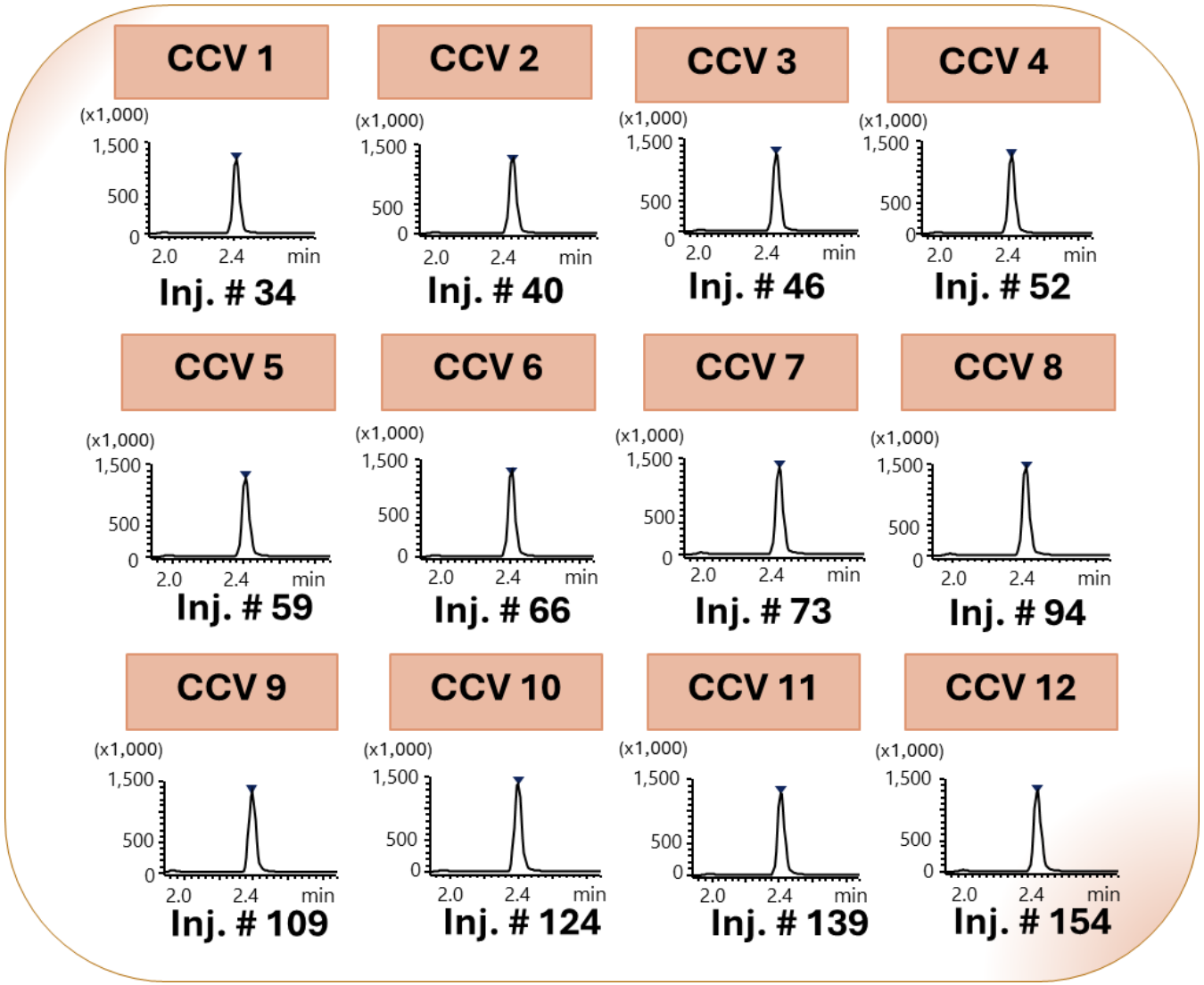


Accuracy-PFBA CCV



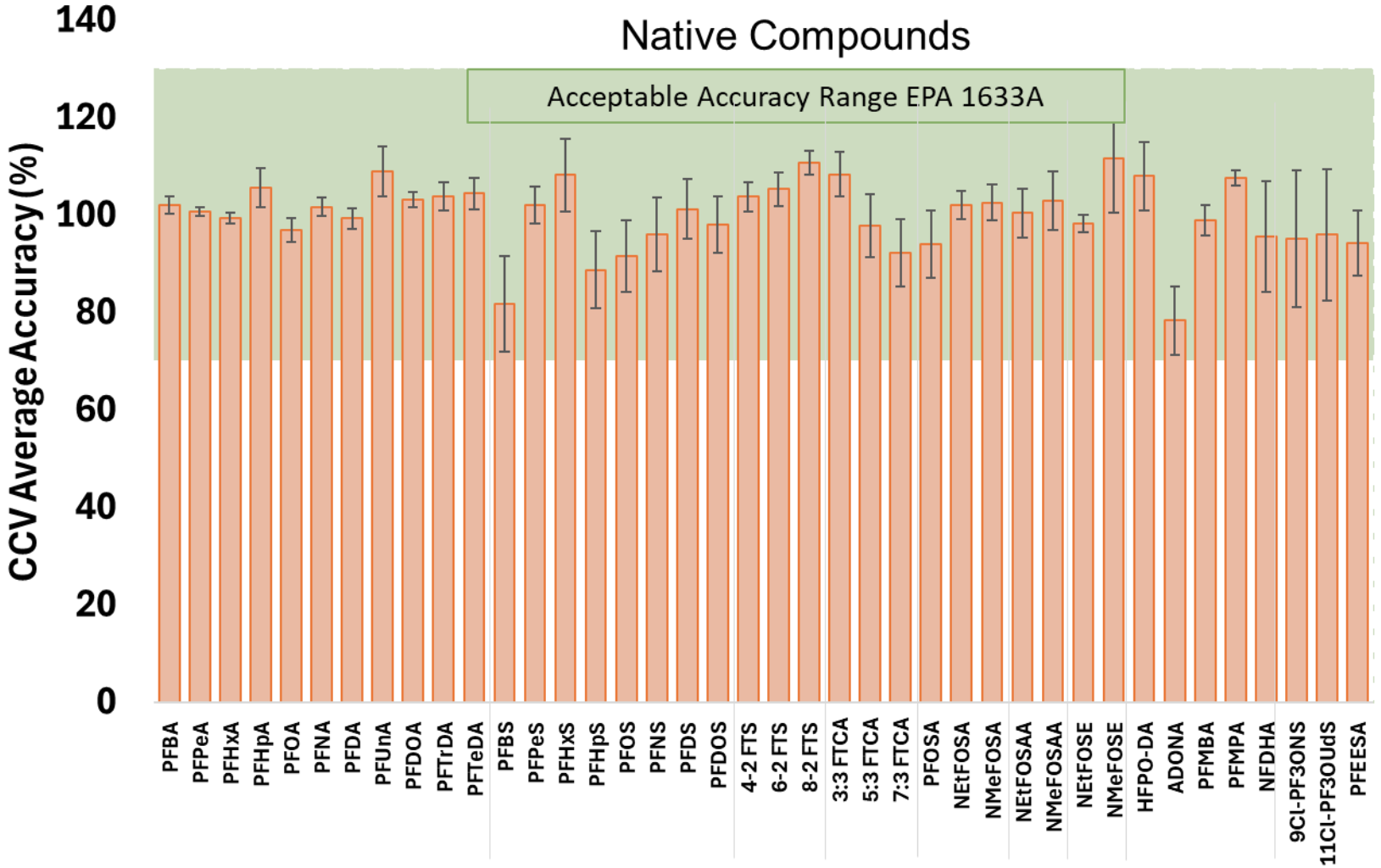
Reproducibility-PFBA





CCV Accuracy

CCV RSD <15% for all native compounds



EPA 1633A Acceptable Limits

United States Environmental Protection Agency

Office of Water

www.epa.gov December 2024

Method 1633, Revision A

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

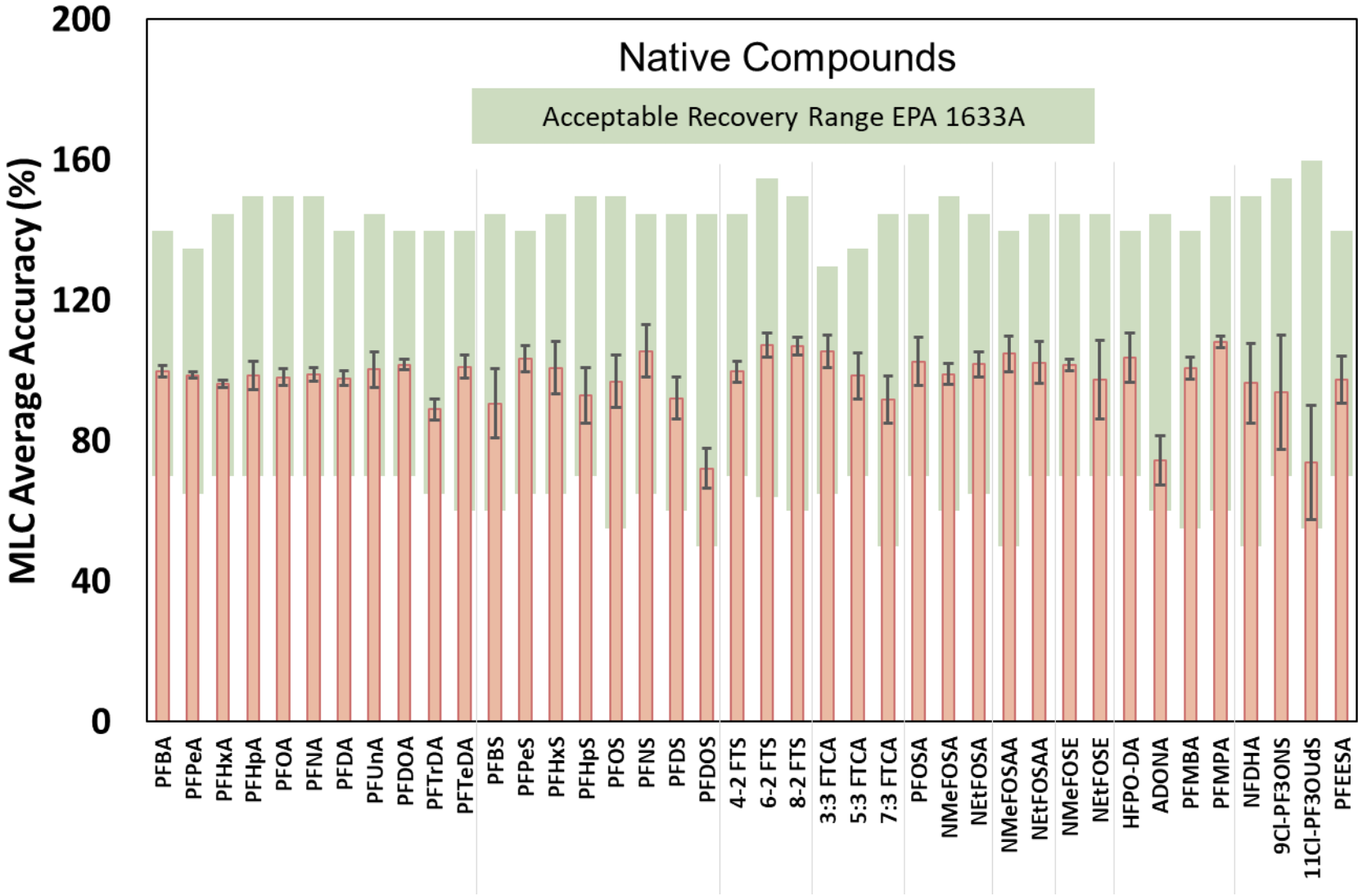
Table 5. IPR/OPR/LLOPR Acceptance Limits for Target Analytes in Aqueous Matrices[1]

Target Analyte	IPR[2] Mean Recovery (%)	IPR[2] RSD (%)	OPR/LLOPR Recovery (%)[2]
PFBA	70 - 135	21	70 - 140
PFPeA	70 - 135	23	65 - 135
PFHxA	70 - 135	24	70 - 145
PFHpA	70 - 135	28	70 - 150
PFOA	65 - 155		
PFNA	70 - 140		
PFDA	65 - 140		
PFUnA	70 - 135		
PFDoA	70 - 130		
PFTrDA	60 - 145		

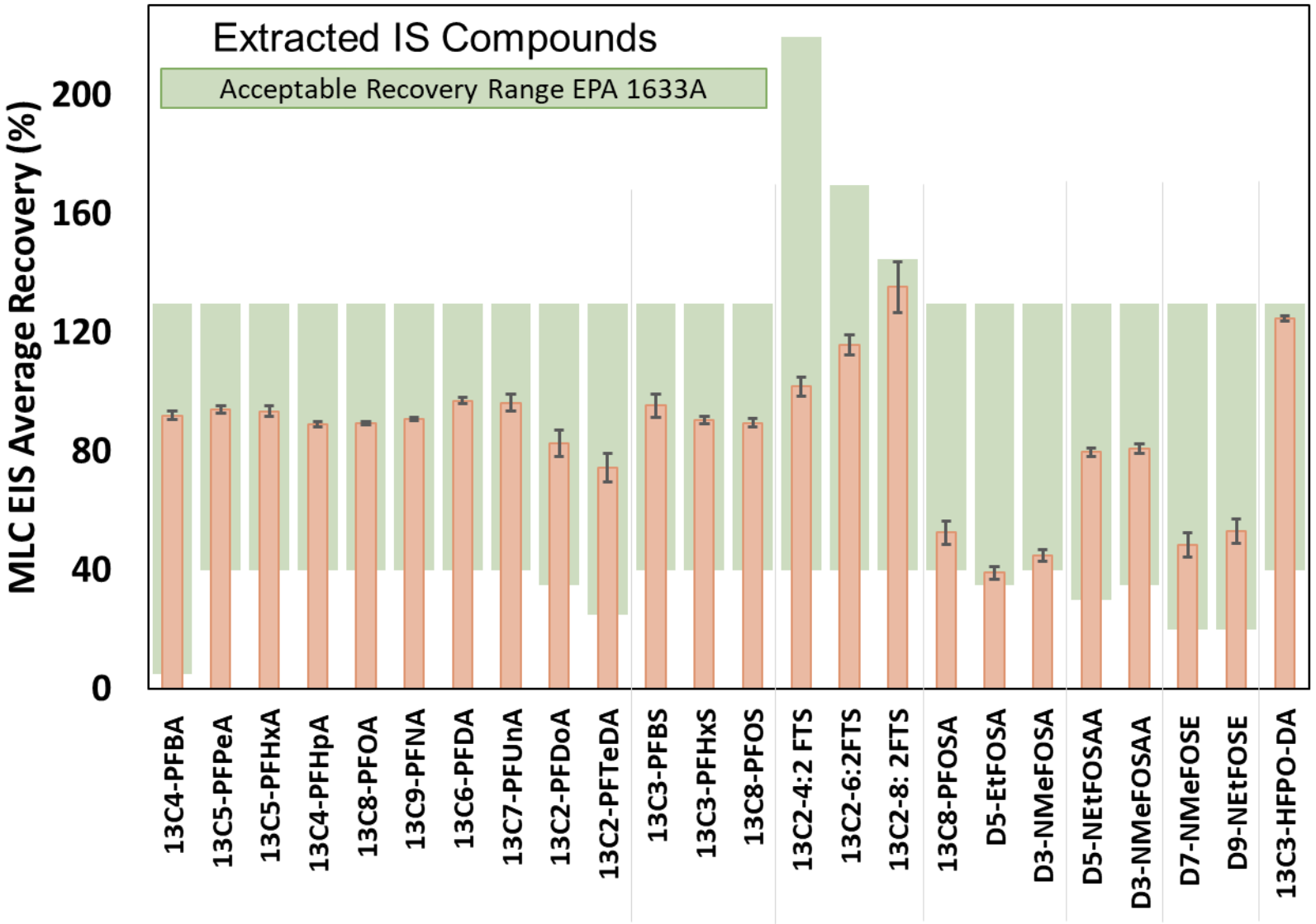
Table 6. Acceptance Limits for EIS and NIS Compounds in All Aqueous Matrices and Associated QC Samples

EIS Compound[1]	Aqueous Matrices Other Than Leachates[2] Recovery (%)	Landfill Leachates[3] Recovery (%)
$^{13}C_4$-PFBA	5[4] - 130	5[4] - 130
$^{13}C_5$-PFPeA	40 - 130	40 - 130
$^{13}C_5$-PFHxA	40 - 130	40 - 130
$^{13}C_4$-PFHpA	40 - 130	40 - 130
$^{13}C_8$-PFOA	40 - 130	40 - 130
$^{13}C_9$-PFNA	40 - 130	40 - 130
$^{13}C_6$-PFDA	40 - 130	40 - 130
$^{13}C_7$-PFUnA	30 - 130	40 - 130
$^{13}C_2$-PFDoA	10 - 130	35 – 130

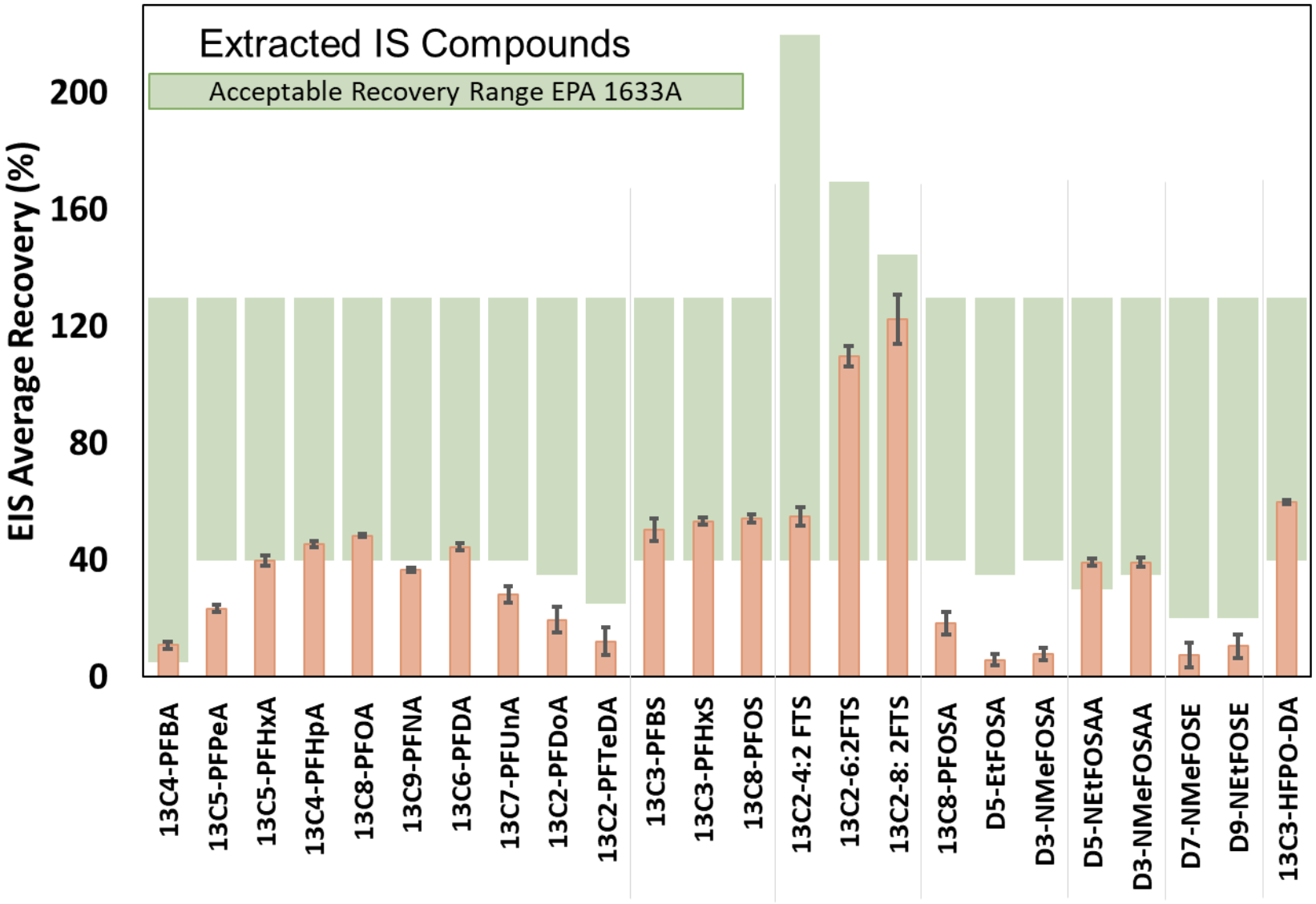
Extracted Lab Controls Native Recovery

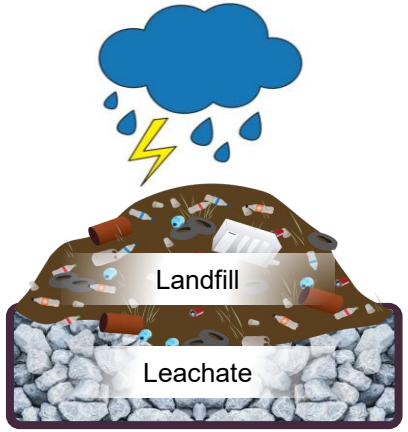


Extracted Lab Controls EIS Recovery

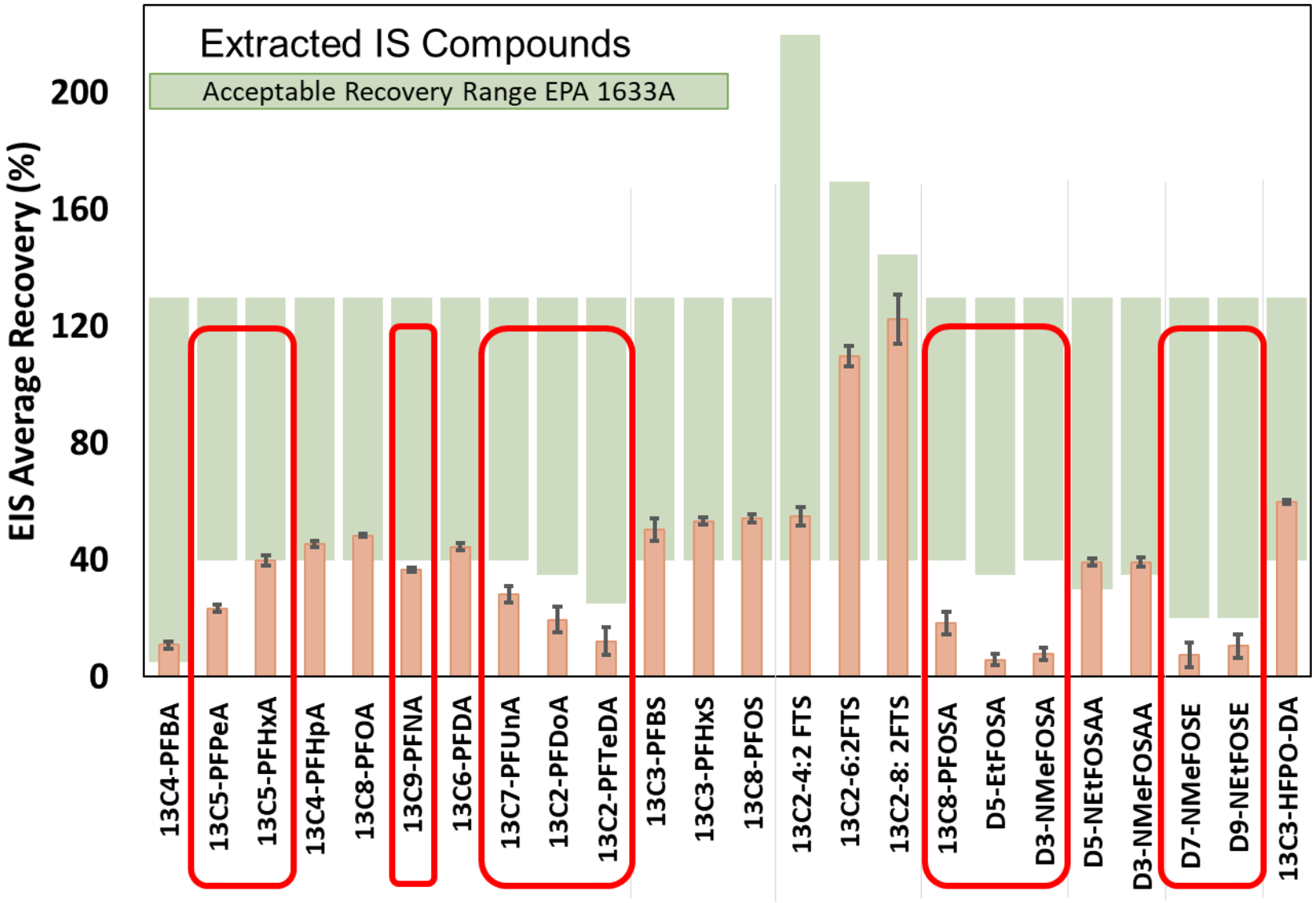


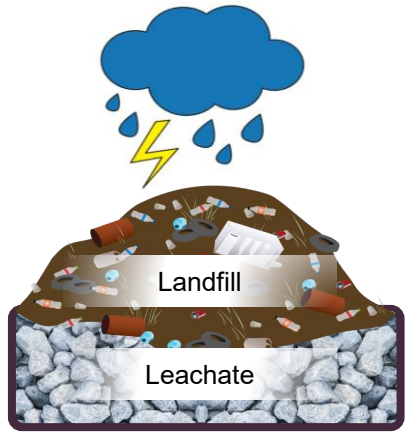
Leachate EIS Recovery





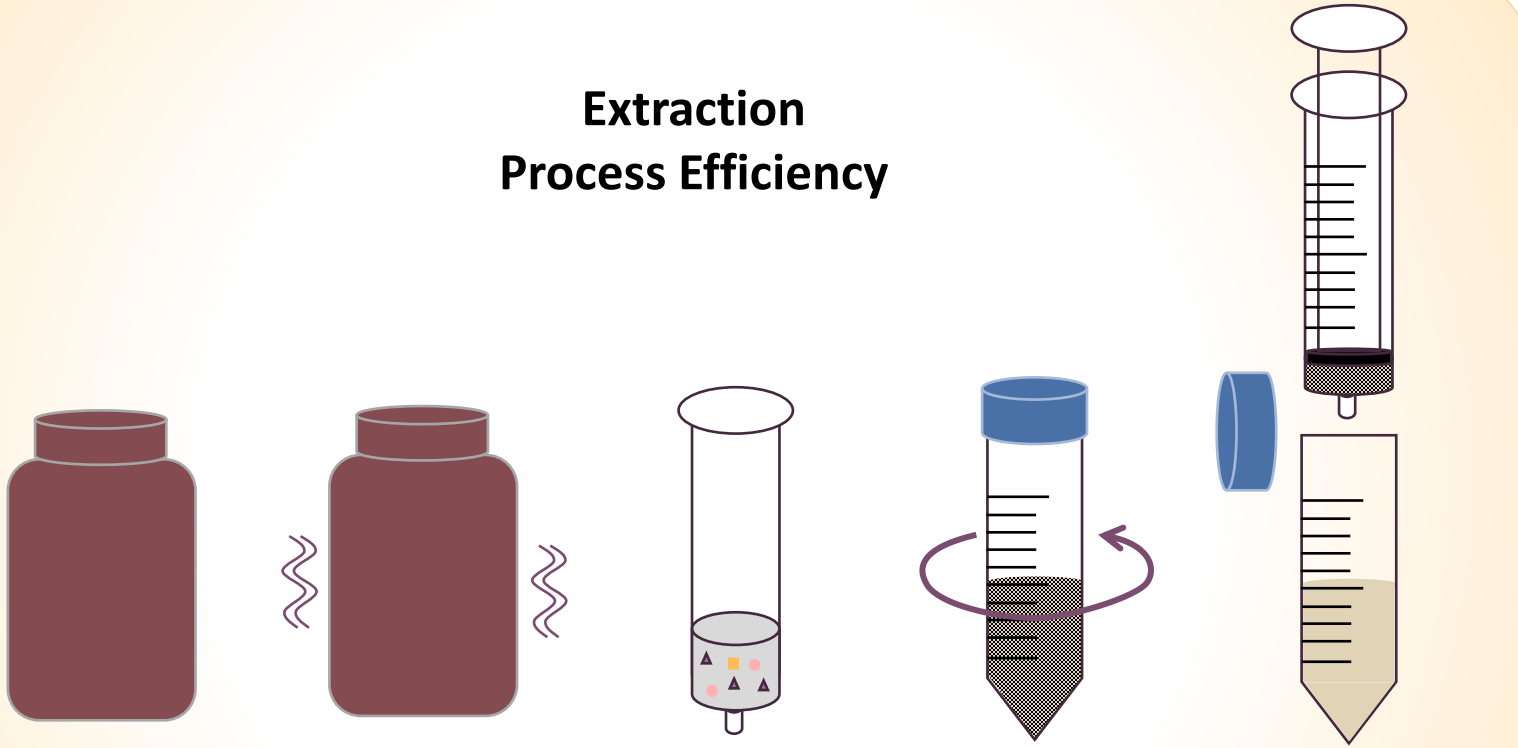
Leachate EIS Recovery





Complex Matrix Challenges

Extraction
Process Efficiency

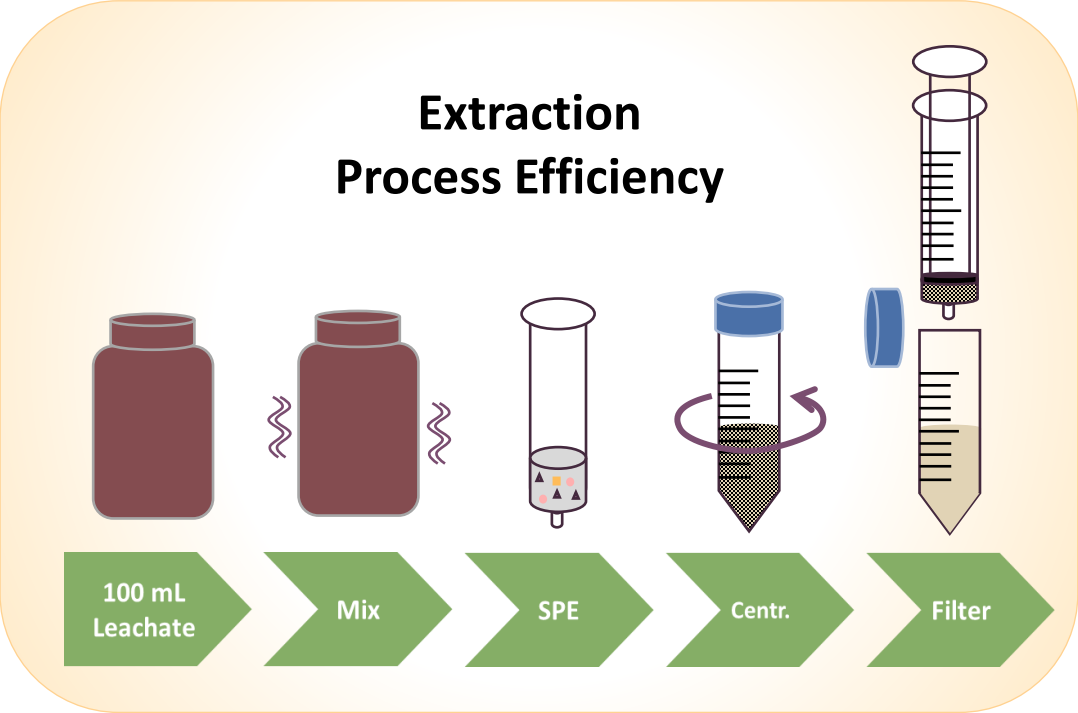


100 mL Leachate → Mix → SPE → Centr. → Filter

Instrument
Matrix Tolerance

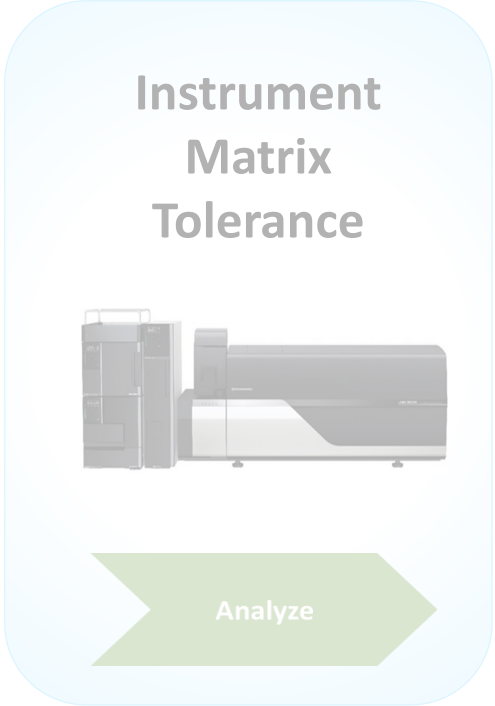
Analyze

Complex Matrix Challenges



Matrix Effects

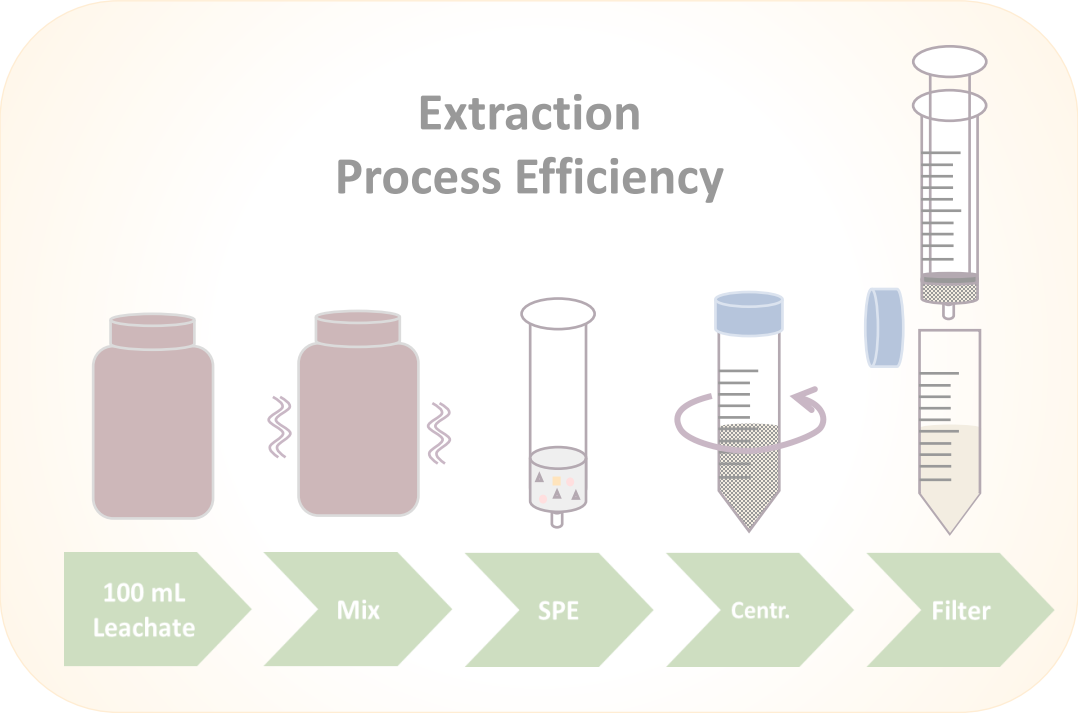
- Co-extraction of interfering compounds
- Sorbent overload or breakthrough
- Incomplete washing



Matrix Effects

- Matrix (Ionization) Robustness/Resilience
- Matrix Compatibility
- Source saturation
  - Ion suppression/enhancement

Complex Matrix Challenges



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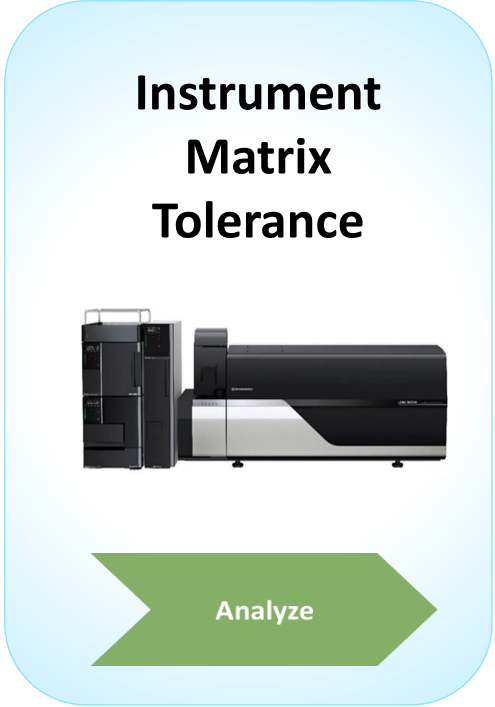

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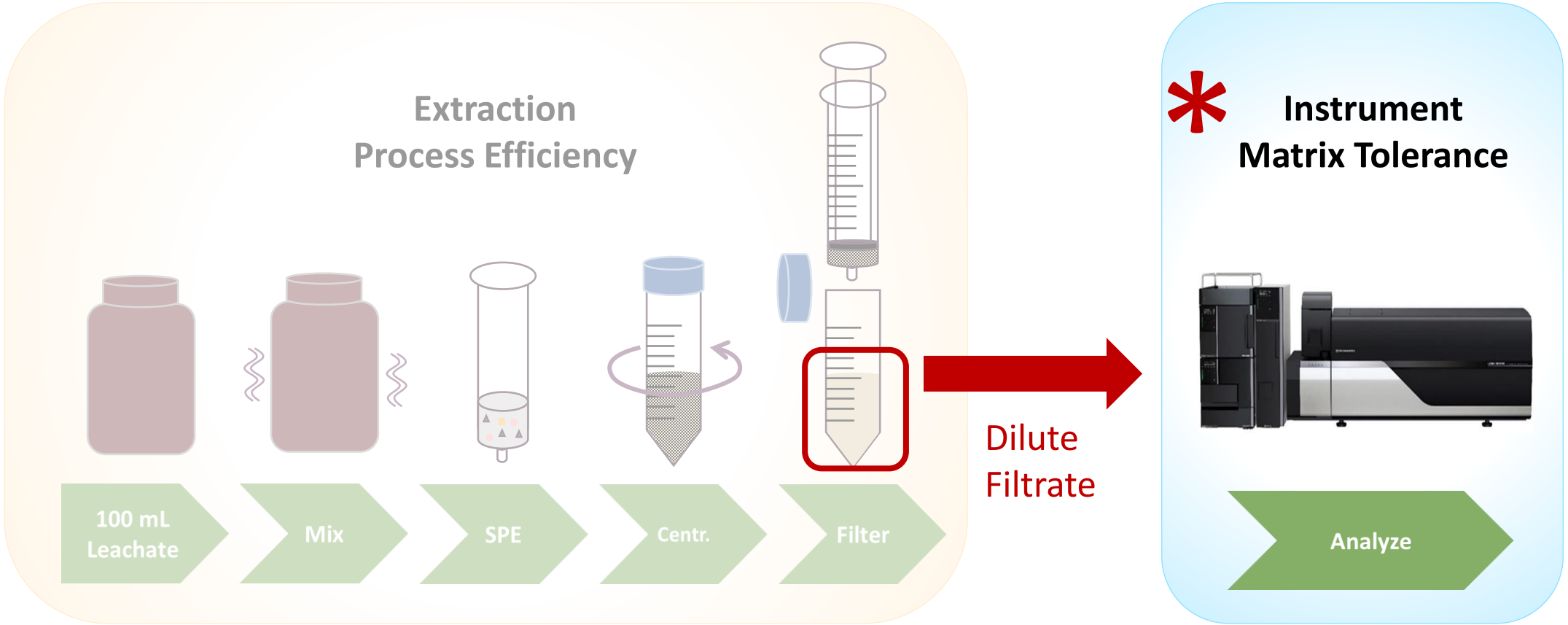
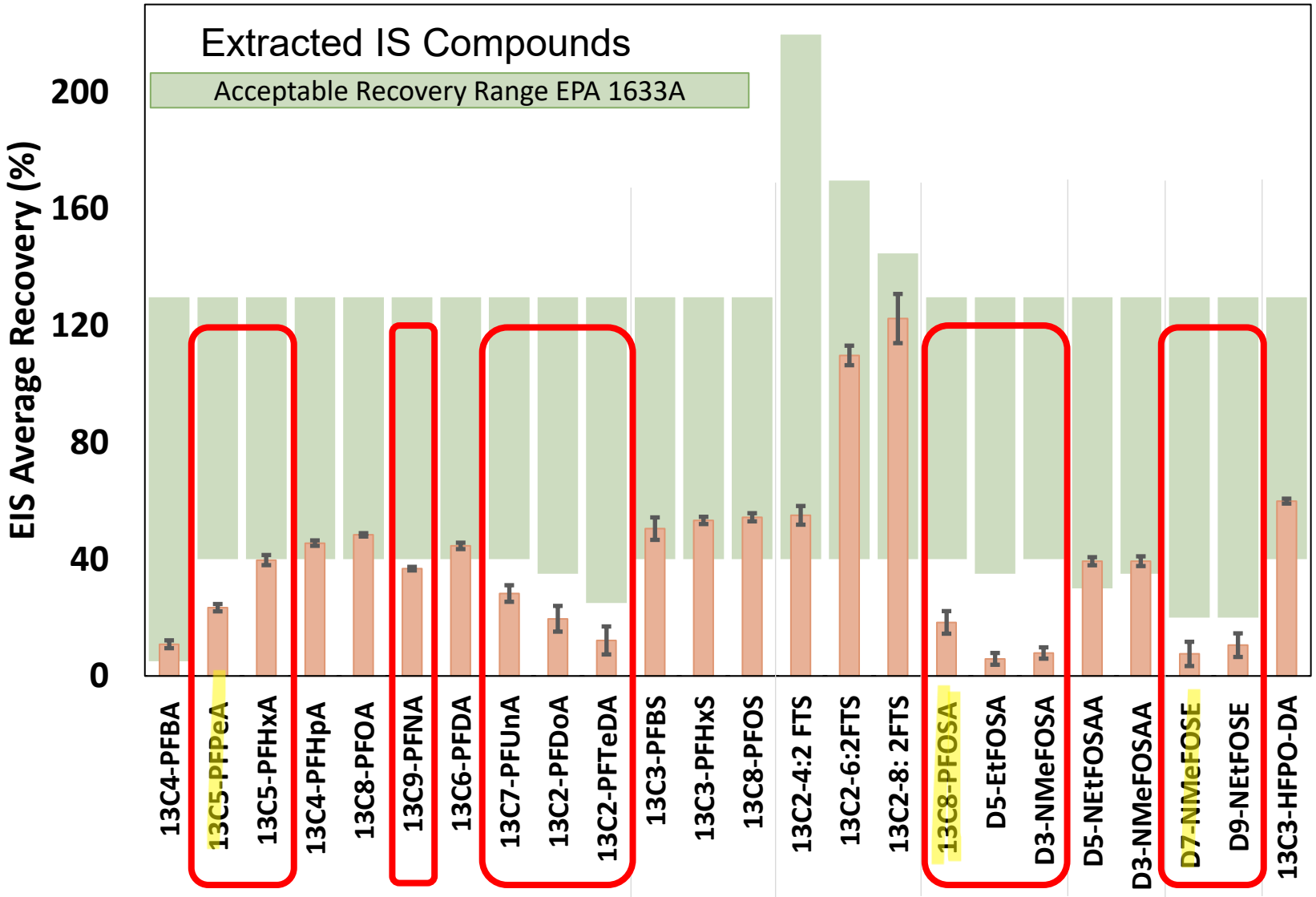
Post-Extraction Dilution Process

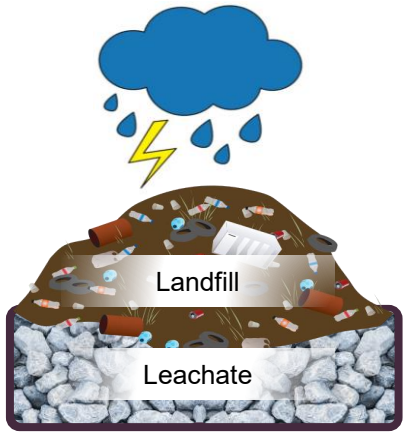


Instrument Matrix Tolerance: Evaluated by dilution of post-extraction filtrate.

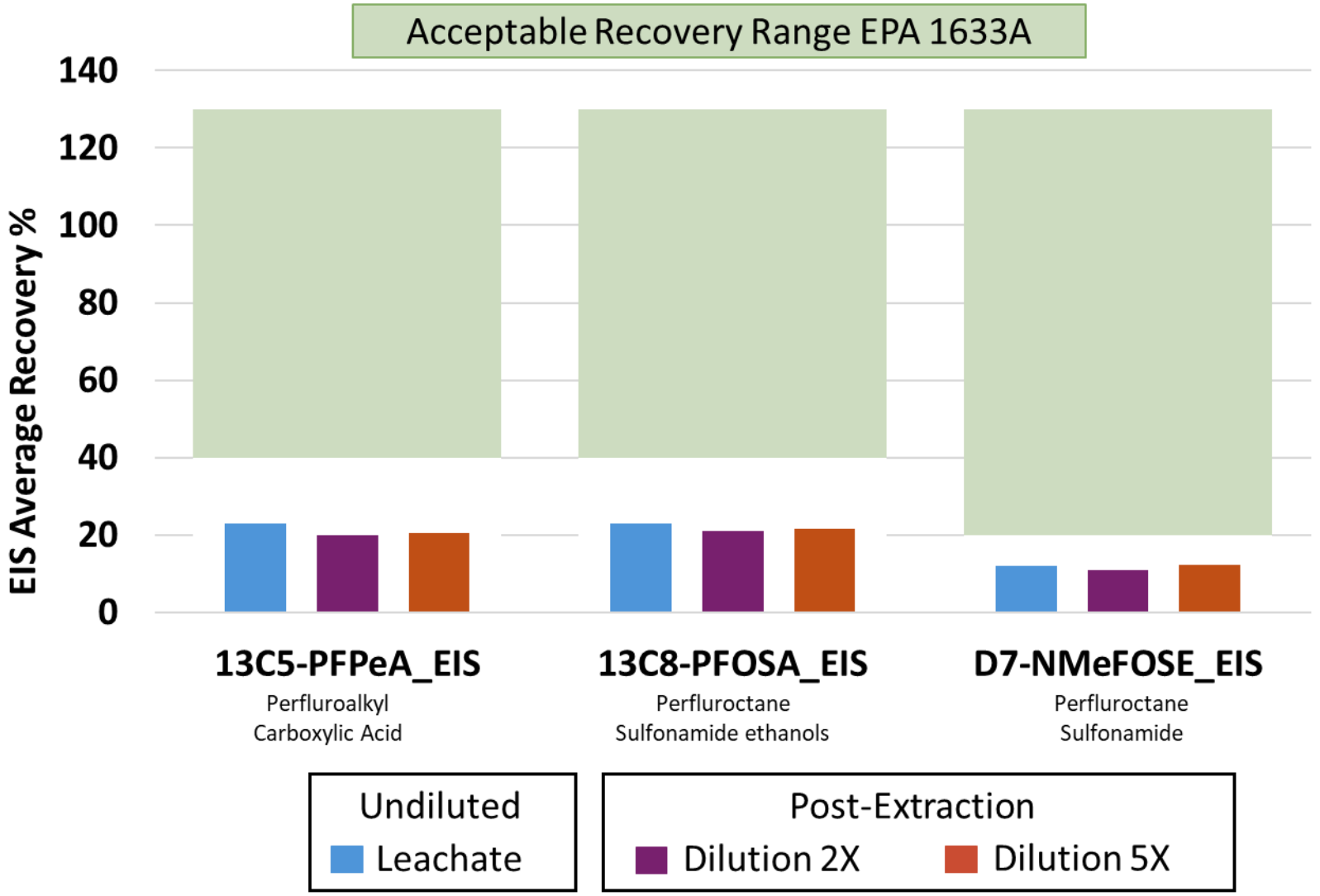
- 2x & 5x dilution

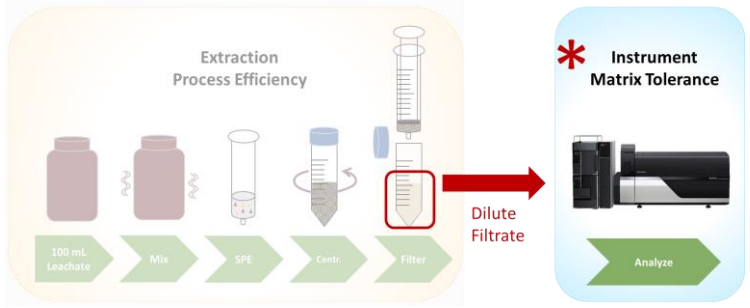
Leachate EIS Recovery





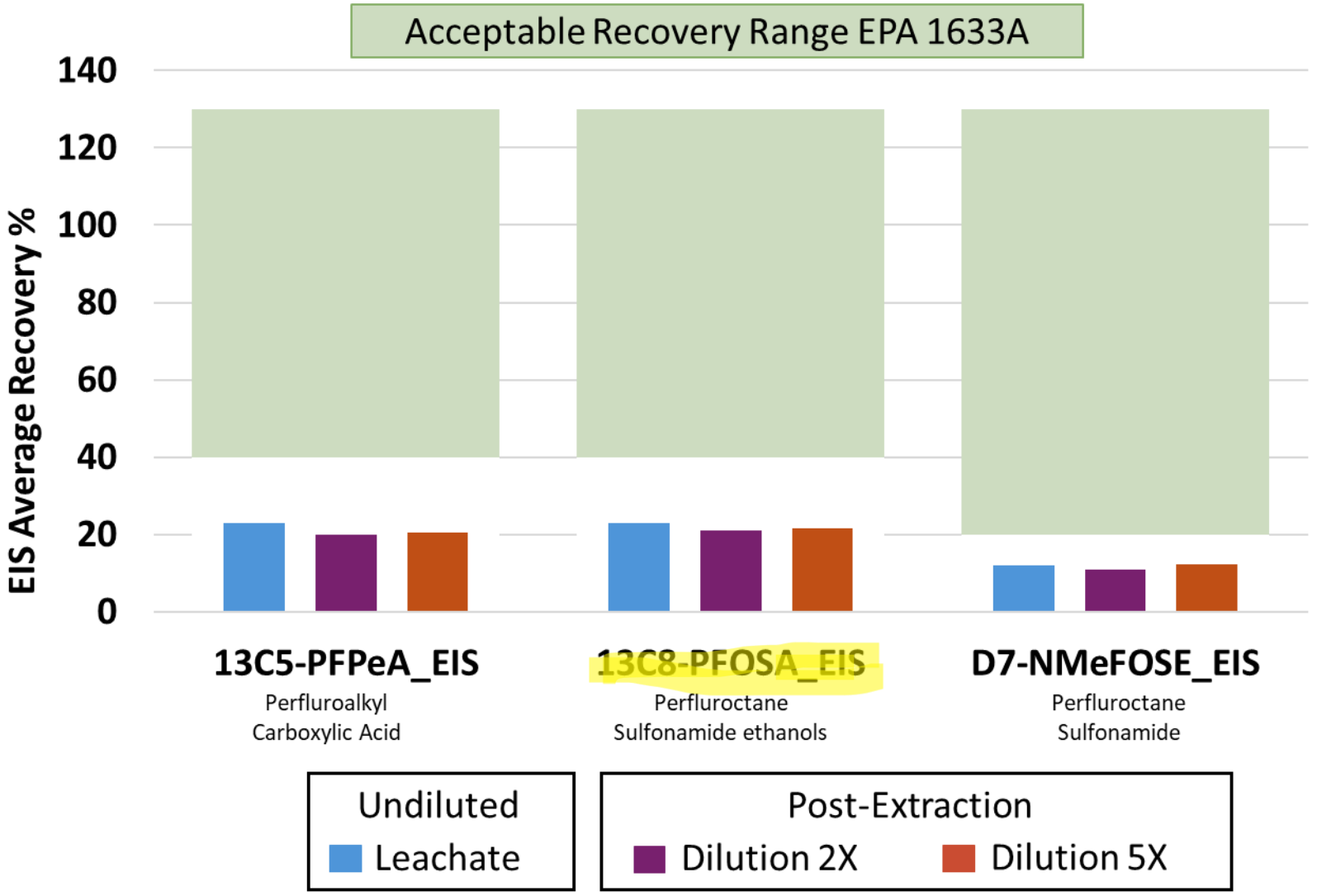
Post-Extraction Dilution EIS Impact

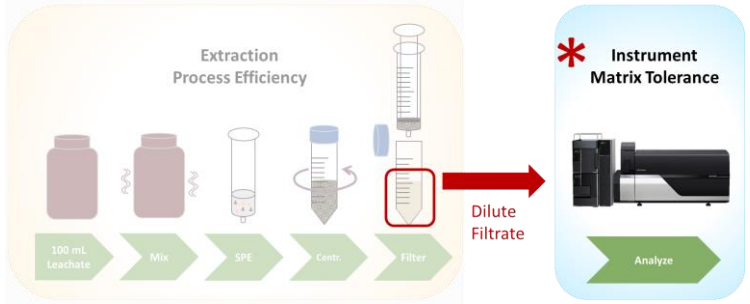




- Instrument Matrix Tolerance is ***not*** the issue.

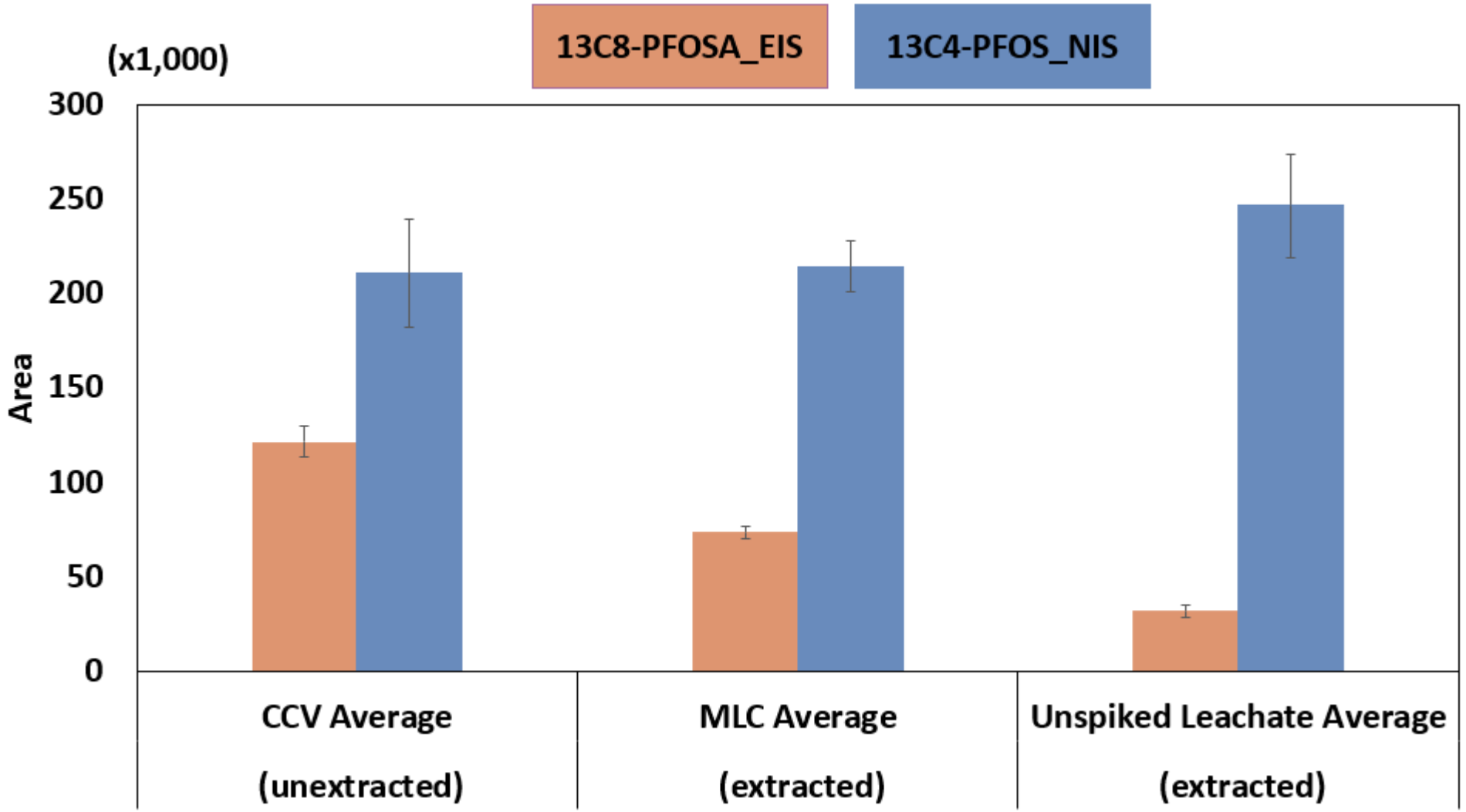
Post-Extraction Dilution EIS Impact





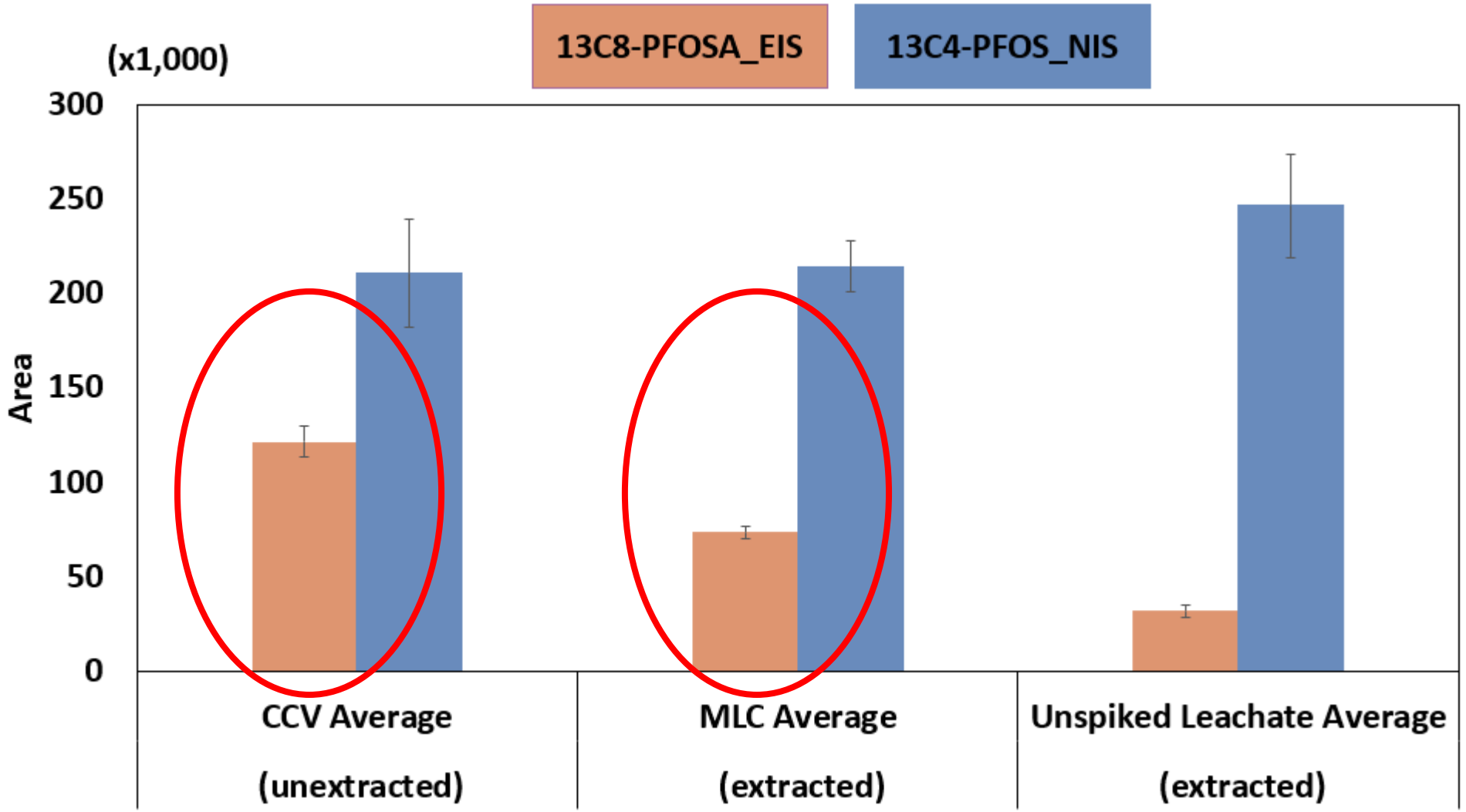
- Instrument Matrix Tolerance is ***not*** the issue.

Area EIS vs NIS



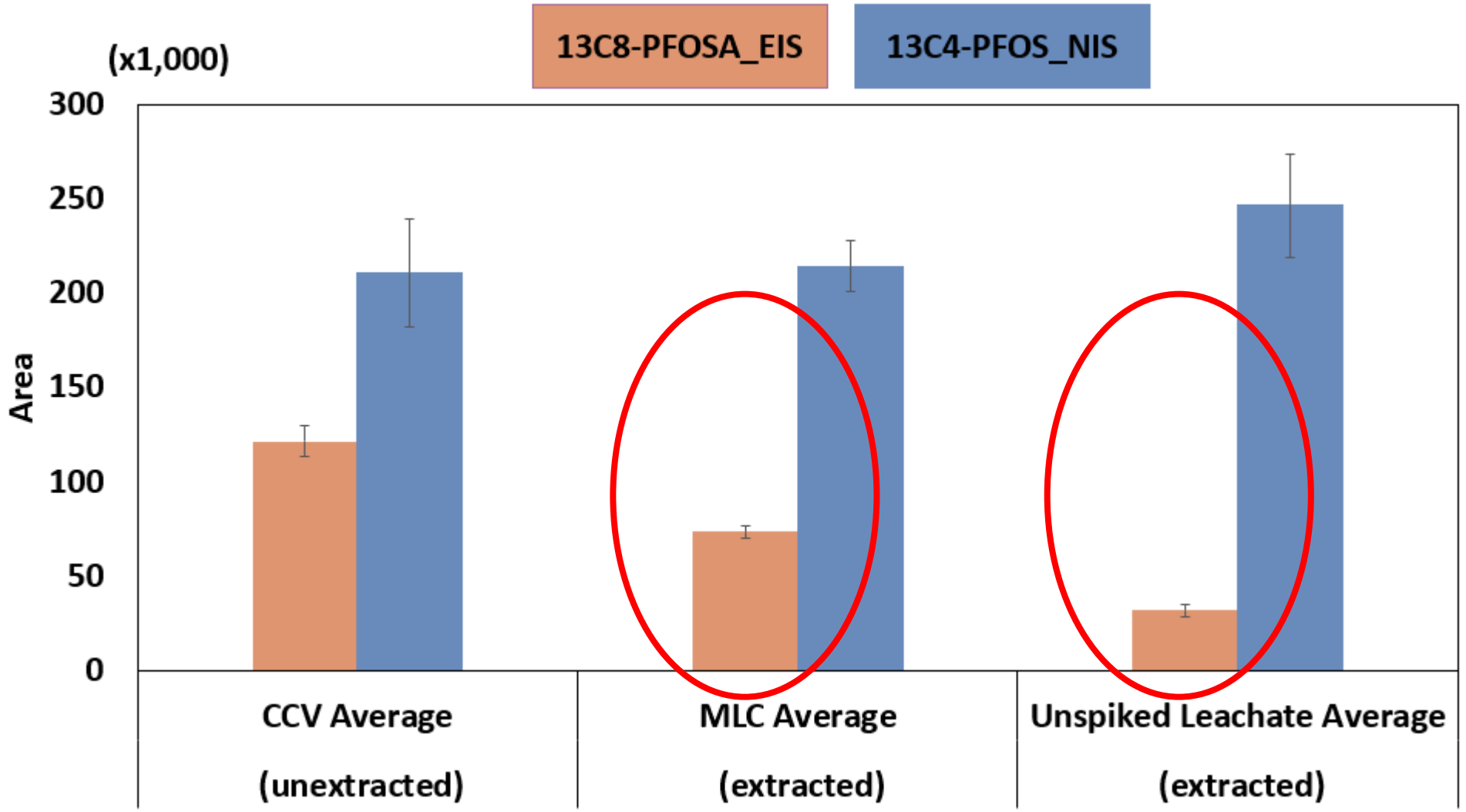
$$\frac{A_{EIS}}{A_{NIS}} = Recovery$$

Area EIS vs NIS



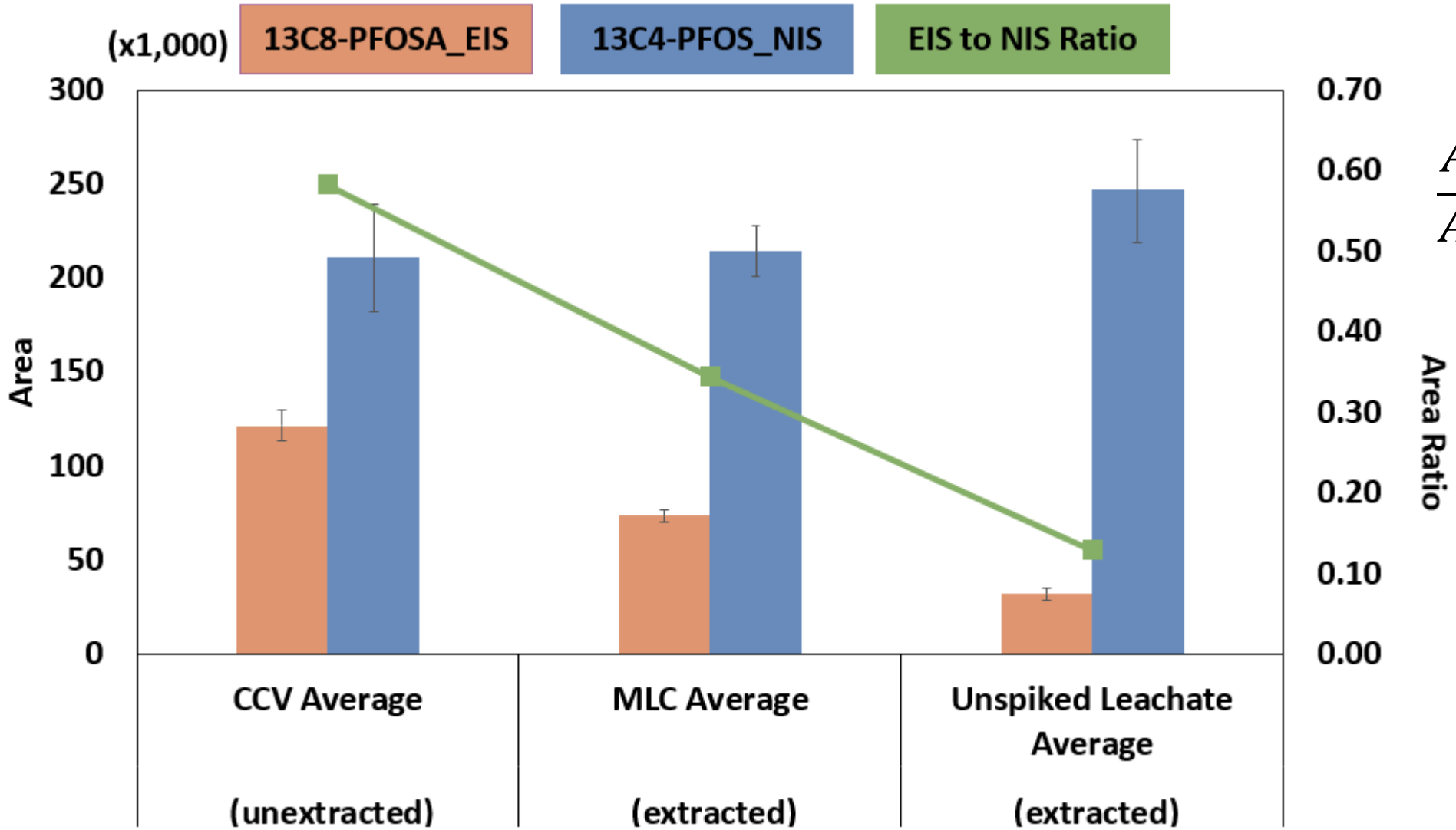
- EIS extraction efficiency < 100% for Lab Control

Area EIS vs NIS



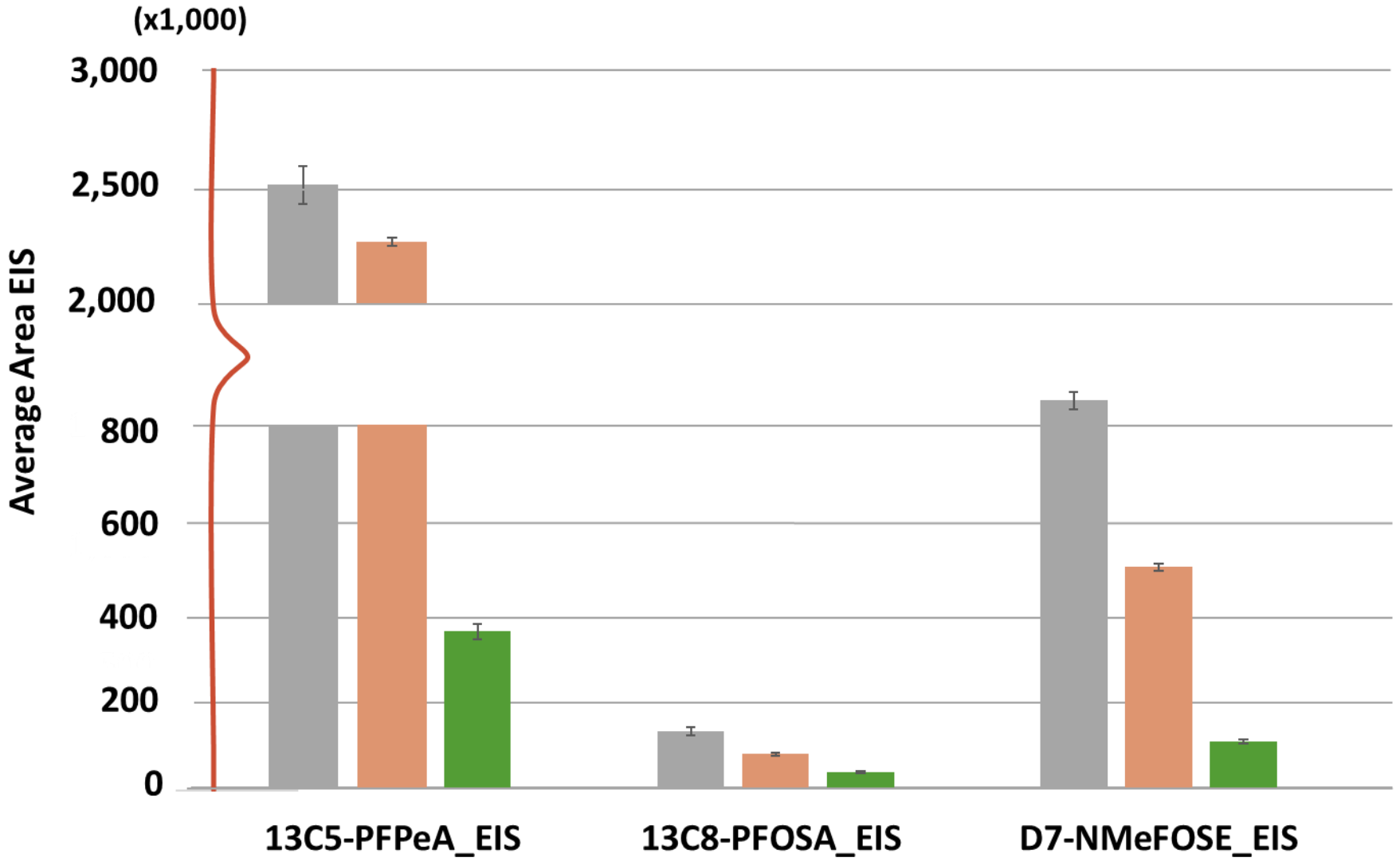
- EIS extraction efficiency < 100% for Lab Control
- EIS extraction efficiency is reduced further in leachate
- NIS is stable

Area EIS & NIS Ratio



$$\frac{A_{EIS}}{A_{NIS}} = Recovery$$

Area of Extracted Internal Standards



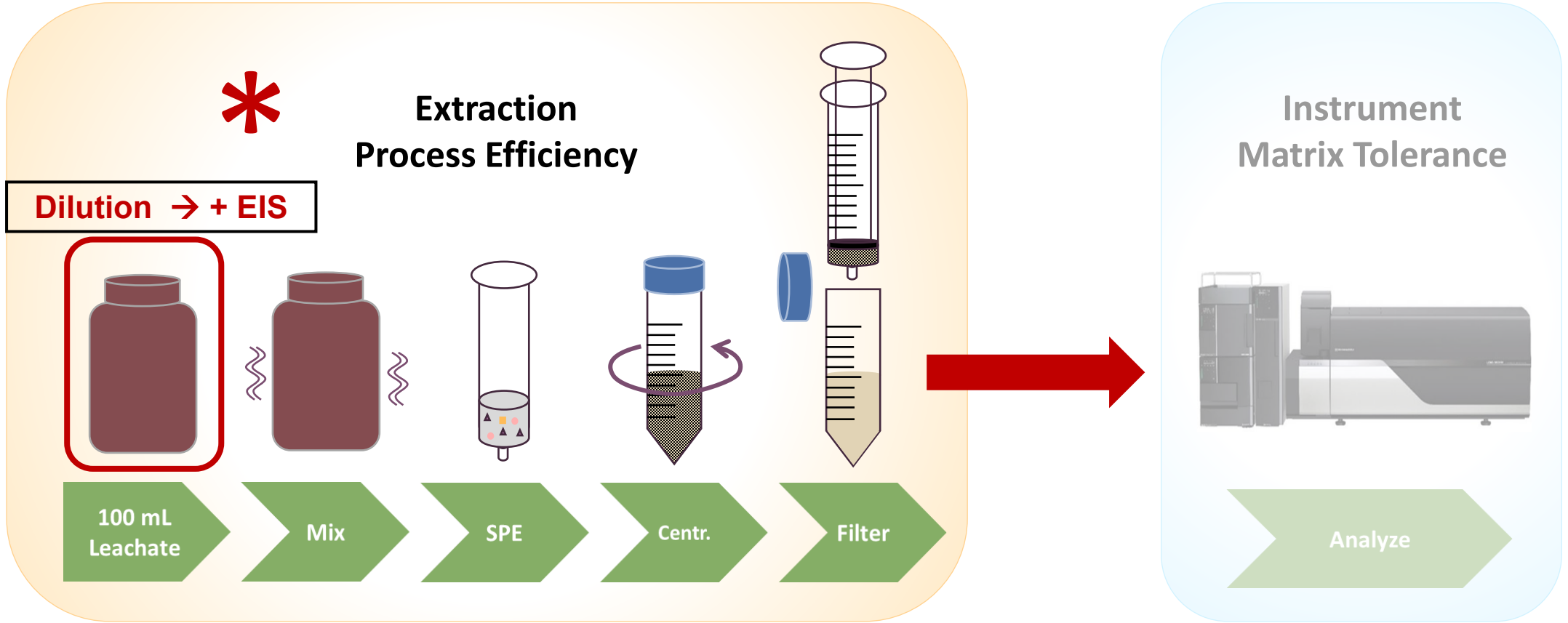
CCV (unextracted)

MLC (extracted)

Leachate (extracted)

Sample Complexity increases: Extraction Efficiency decreases

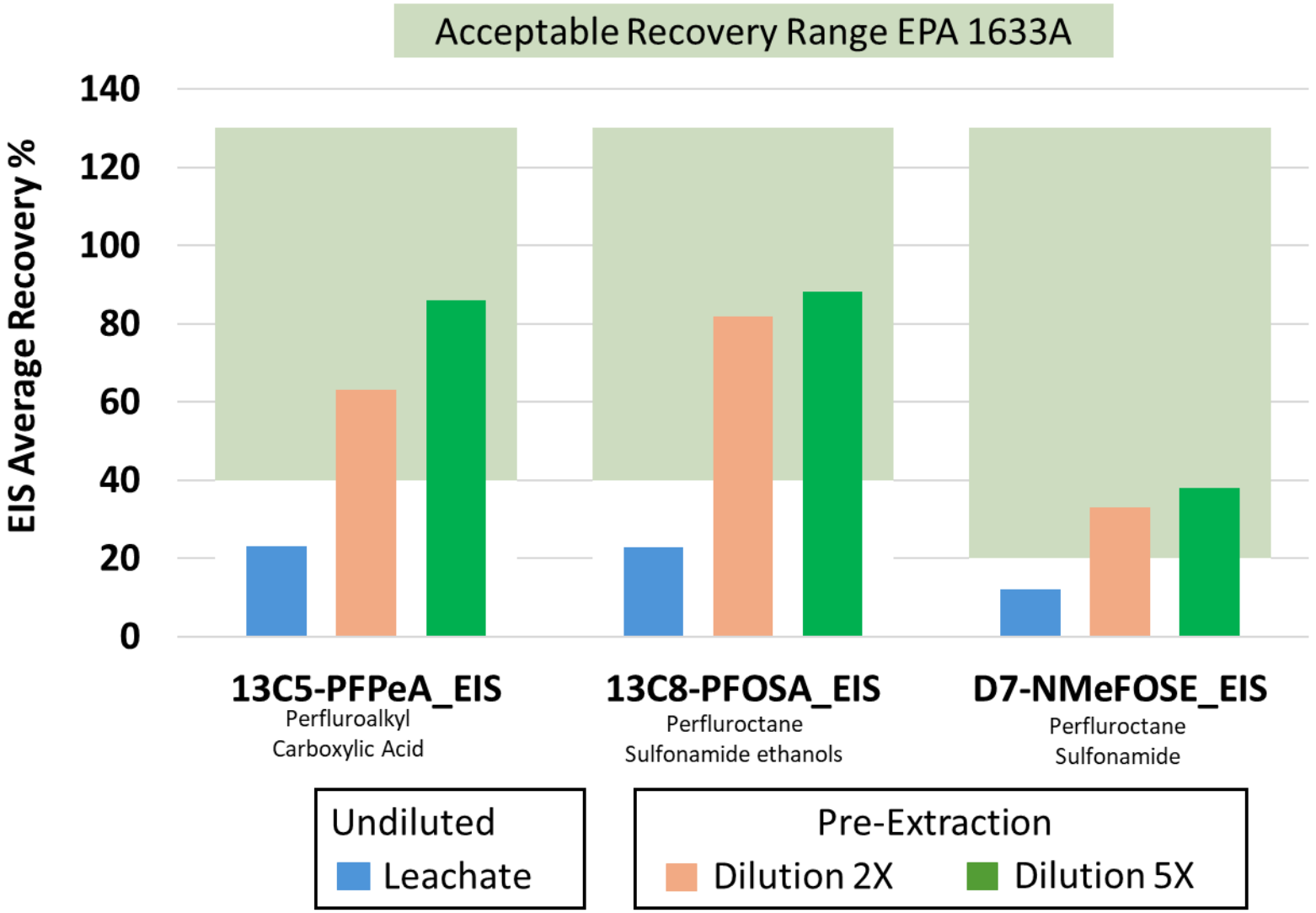
Pre-Extraction Dilution Process

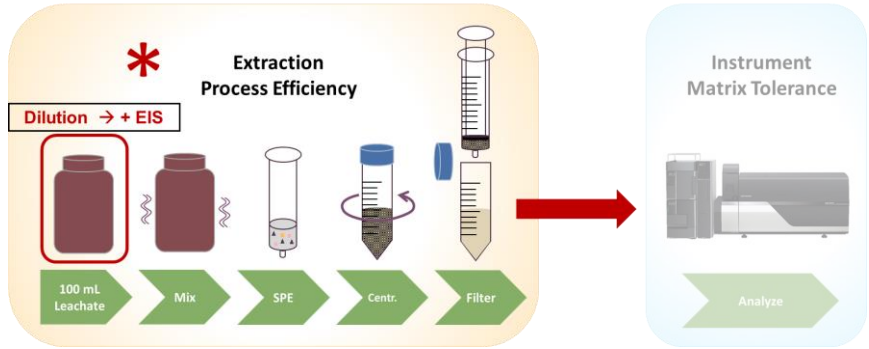


Extraction Process Efficiency: Evaluated by dilution of leachate pre-extraction.

- 2x & 5x dilution

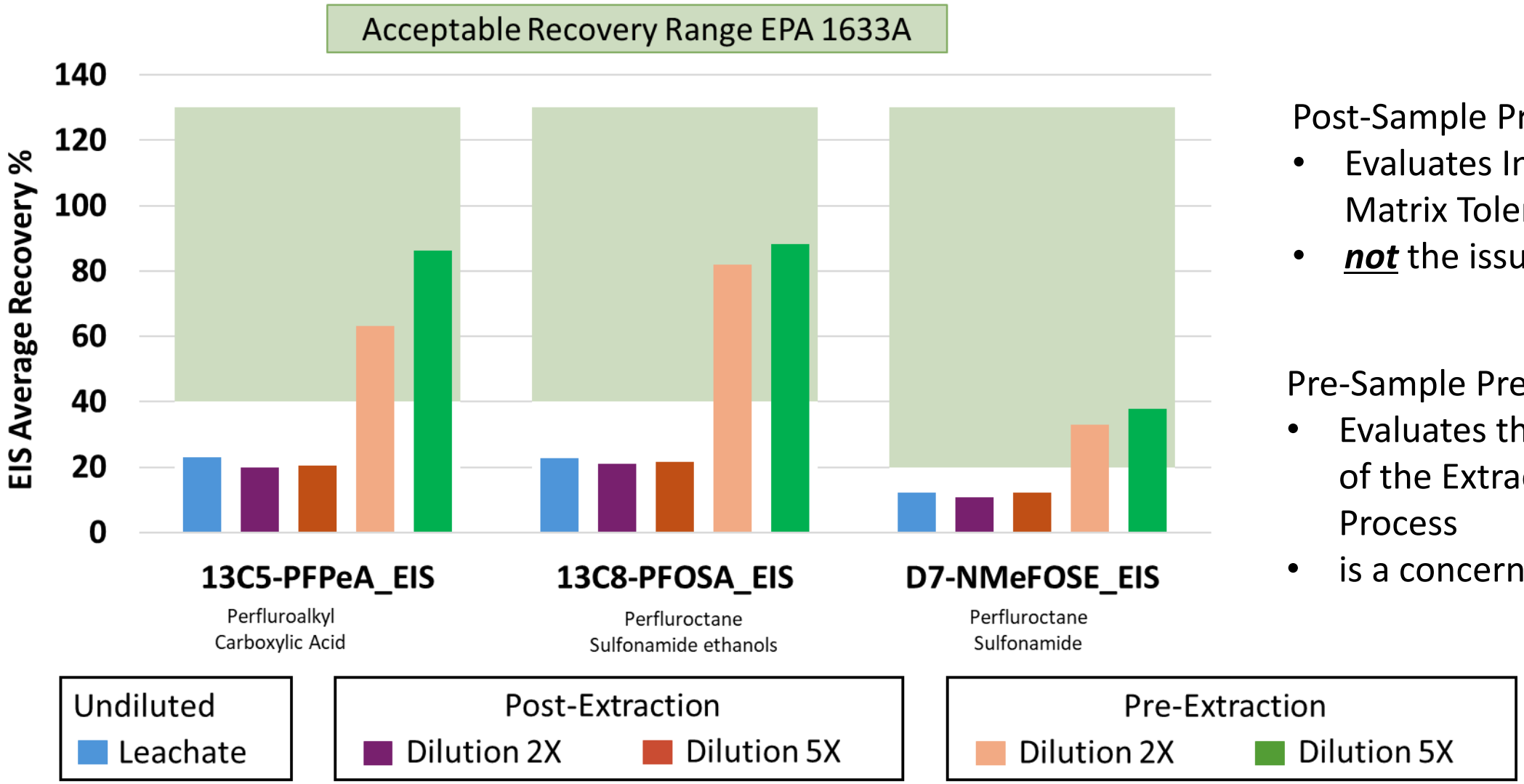
Pre-Extraction Dilutions EIS Impact





- Extraction efficiency is an issue.

Dilutions Comparison: EIS Impact



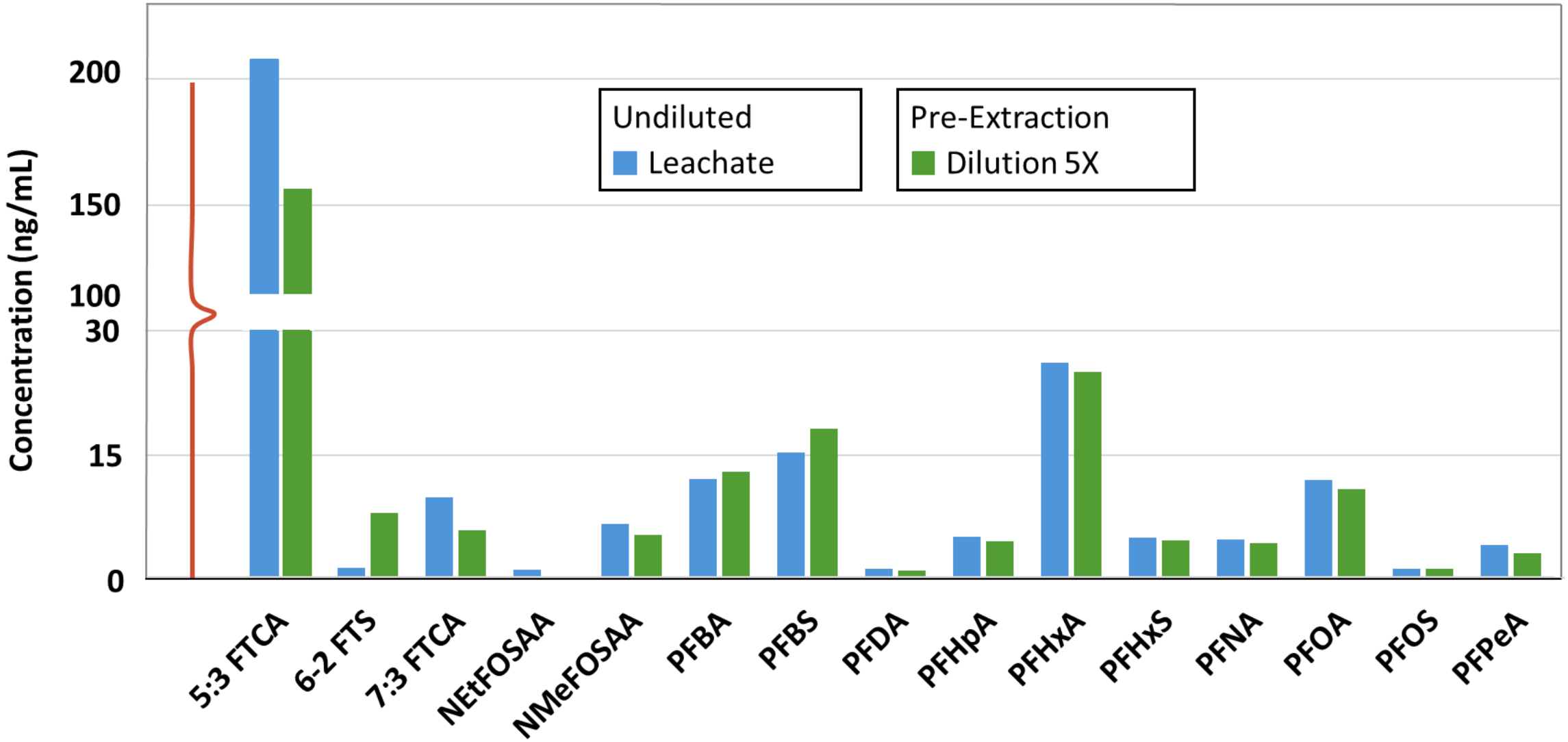
Post-Sample Prep Extraction

- Evaluates Instrument Matrix Tolerance
- ***not*** the issue

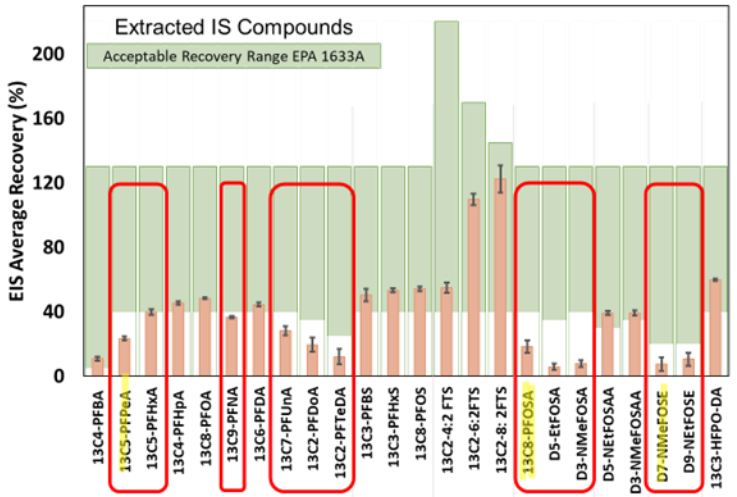
Pre-Sample Prep Extraction

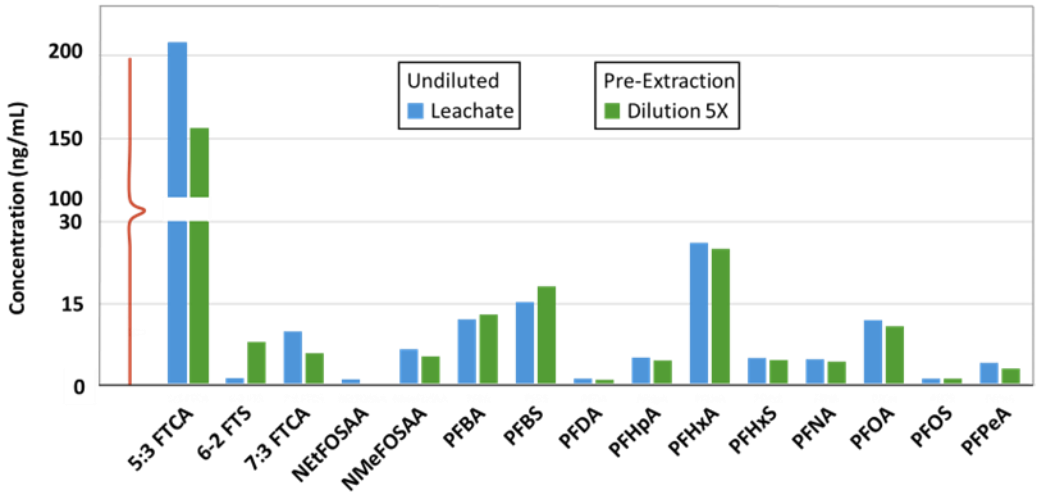
- Evaluates the Efficiency of the Extraction Process
- is a concern

Effects of Dilution on Quantitation of Native PFAS in Leachate Sample



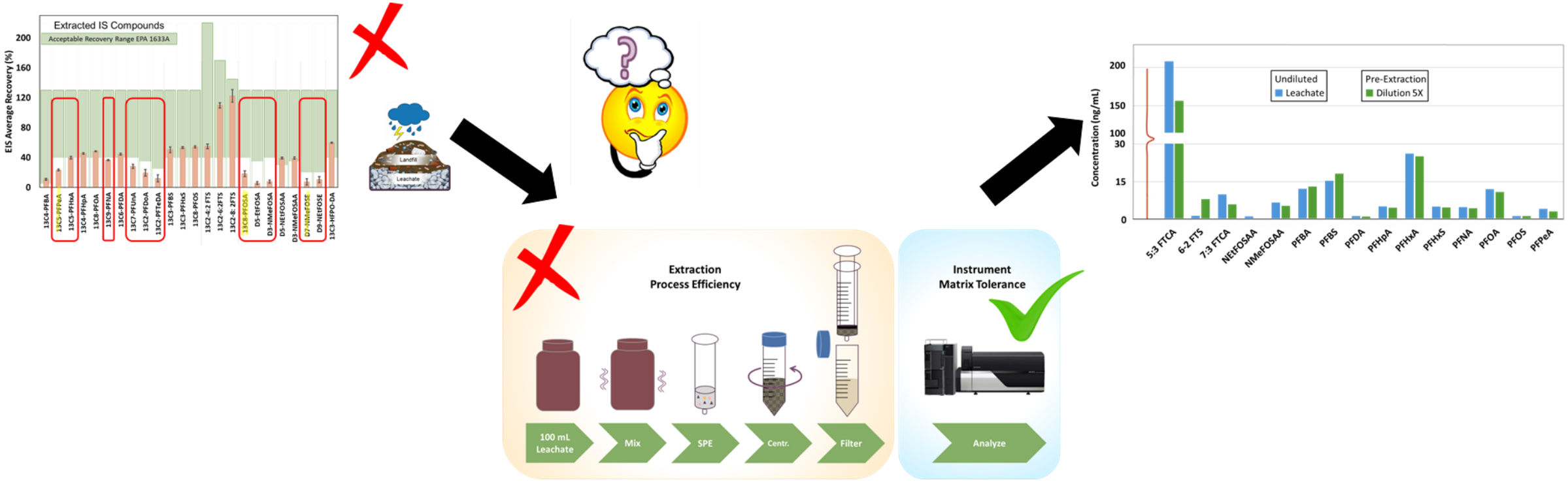
Conclusions





- **Crucial to isolate the reason for bad recovery to ensure accurate results.**

Conclusions



- **Crucial to isolate the reason for bad recovery to ensure accurate results.**
  - Instrument Matrix Tolerance: not an issue.
  - Extraction Process Efficiency: decreases with increased sample matrix complexity

THANK YOU!

Made possible with the support of

- **Ruth Marfil-Vega, PhD**
- **Evelyn Wang, PhD**
- **Toshiya Matsubara, PhD**
- **Robert English, PhD**
- **Kevin Schug, PhD (UTA)**
- **Om Shrestha**

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