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CEM

What Happens When Automated Solvent Extraction and Robust LC-MS/MS are Coupled for Soil Analysis

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What Happens…

When Automated Solvent Extraction and Robust LC-MS/MS are Coupled for Soil Analysis?

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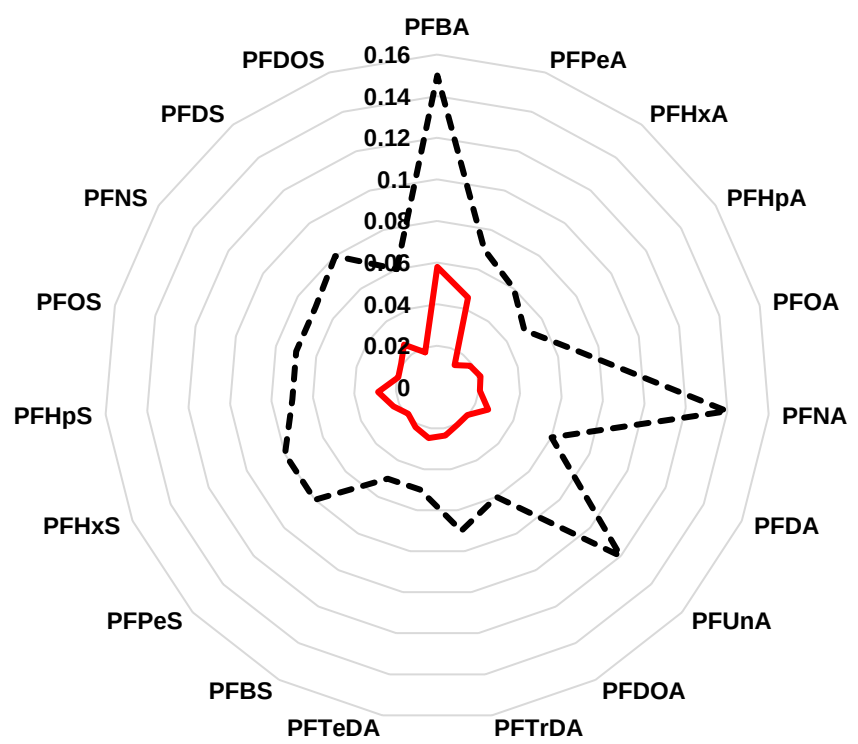
Overall, the calculated MDLs from the workflow are

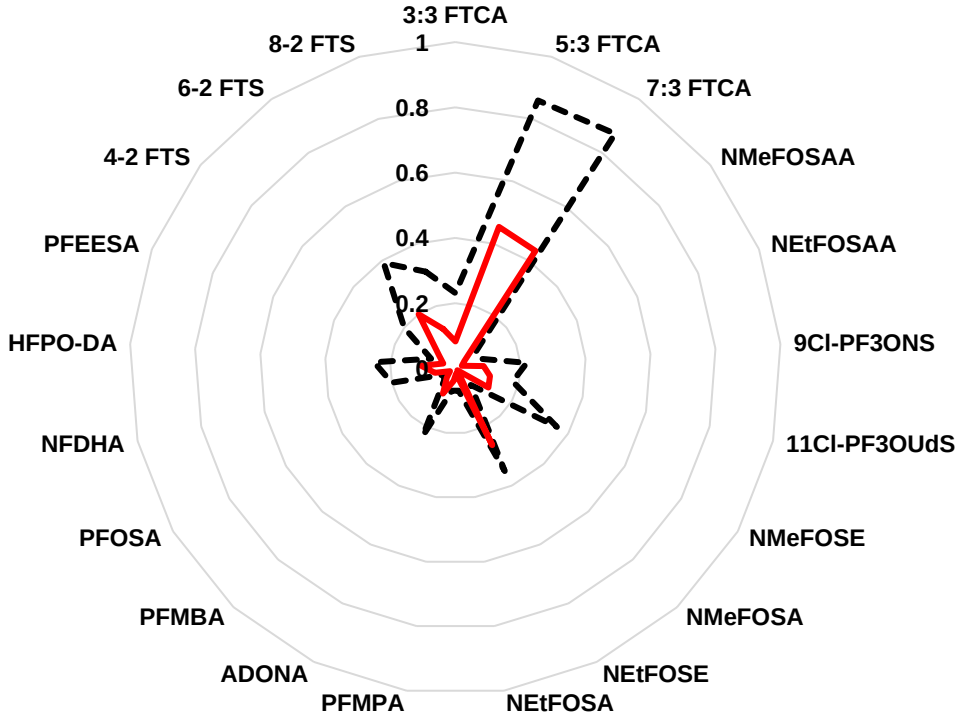
2 times better than those reported in EPA Method 1633 in soils

Summary of MDLs (ng/g)

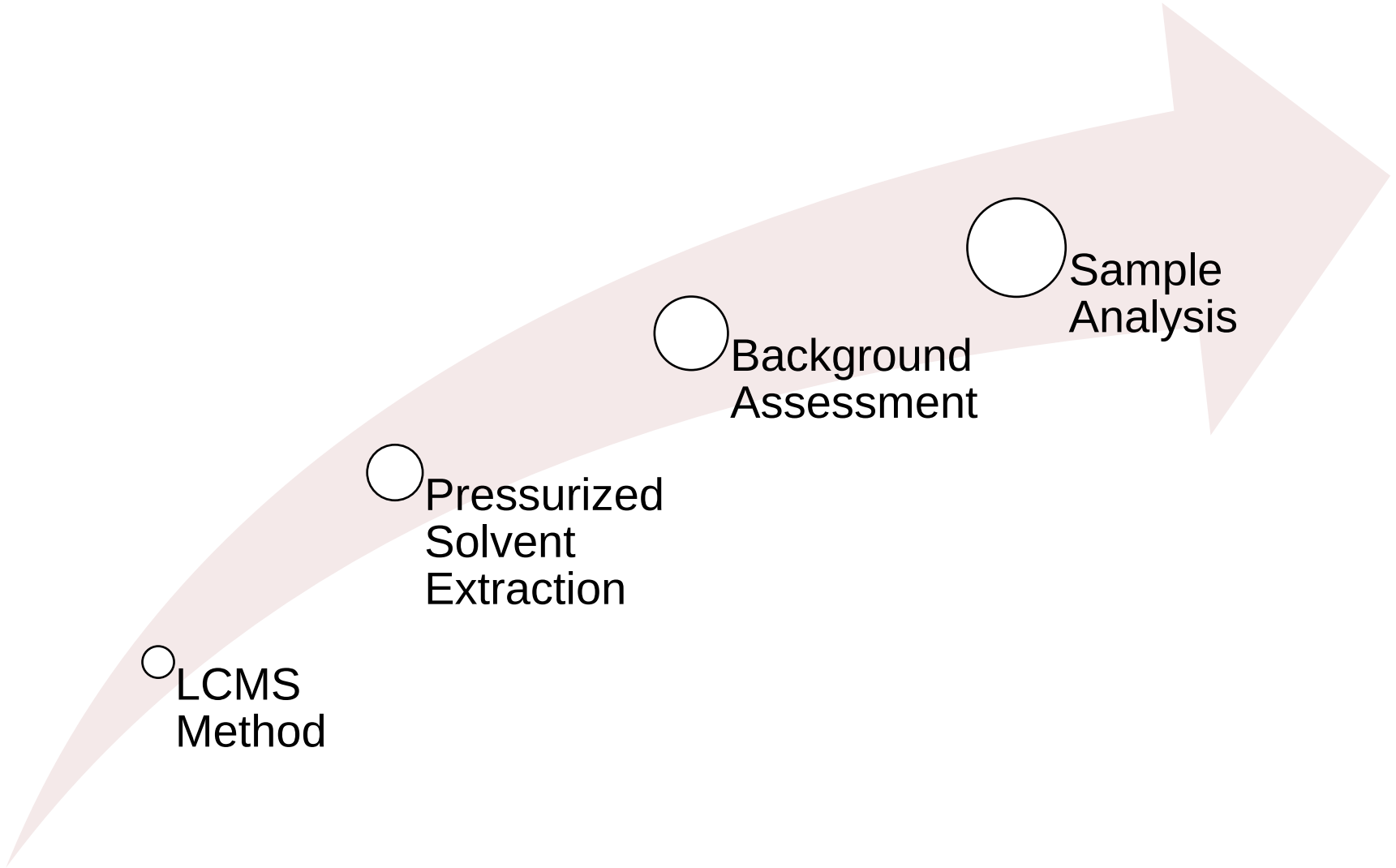
EPA reported MDLs

This work's MDLs





How did we get there?

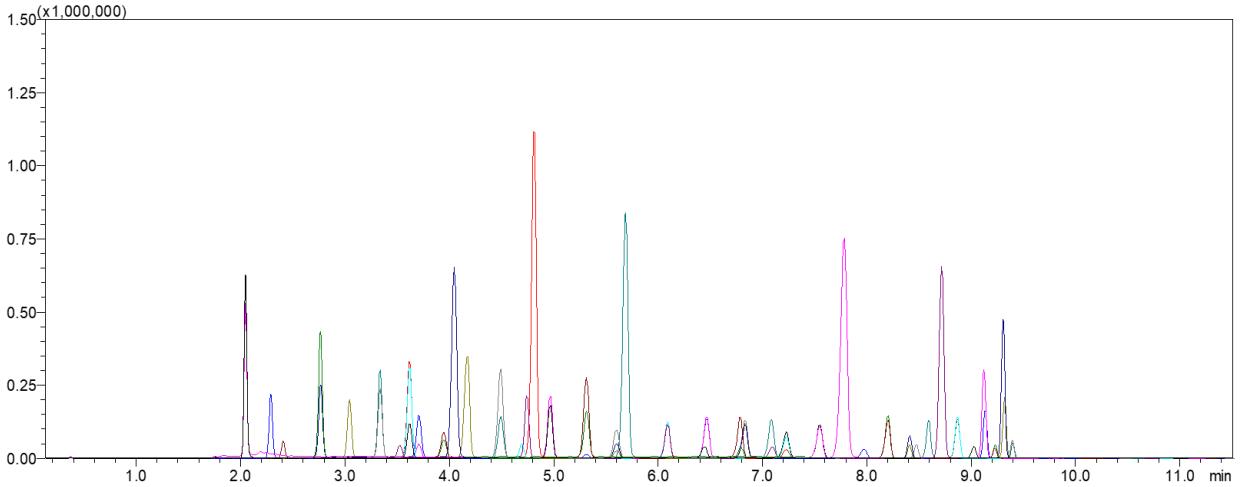


MDLs 2 times better than those reported in EPA Method 1633 in soils

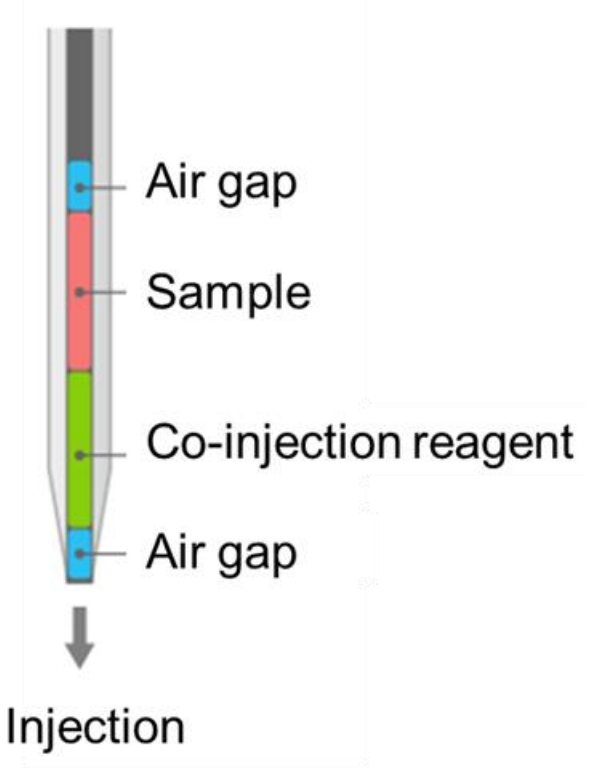
LCMS Method

Parameter	Value
LCMS	Shimadzu LCMS-8060NX
Analytical Column	Shim-pack Scepter C18-120, 3.0 µm, 2.0 x 50mm
Delay Column	Nexcol PFAS Delay Column 5um 3.0 x 50mm
Injection Volume	15 µL
Pretreatment Mode	Co-Injection
Column Oven Temp.	40°C
Mobile Phase	A: 2 mM Ammonium Acetate in LCMS Grade Water
	B: Acetonitrile
Flow Rate	0.4 mL/min
Run Time	14 minutes

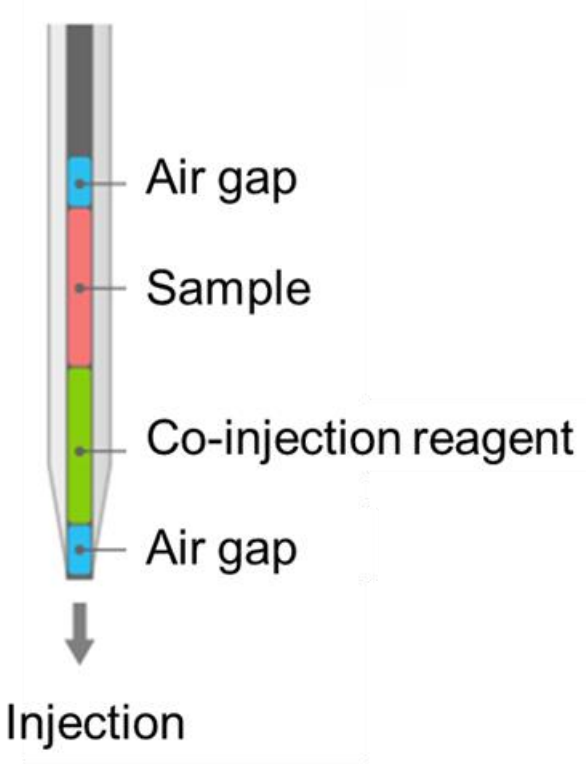
Shimadzu's LCMS-8060NX With Standard Configuration

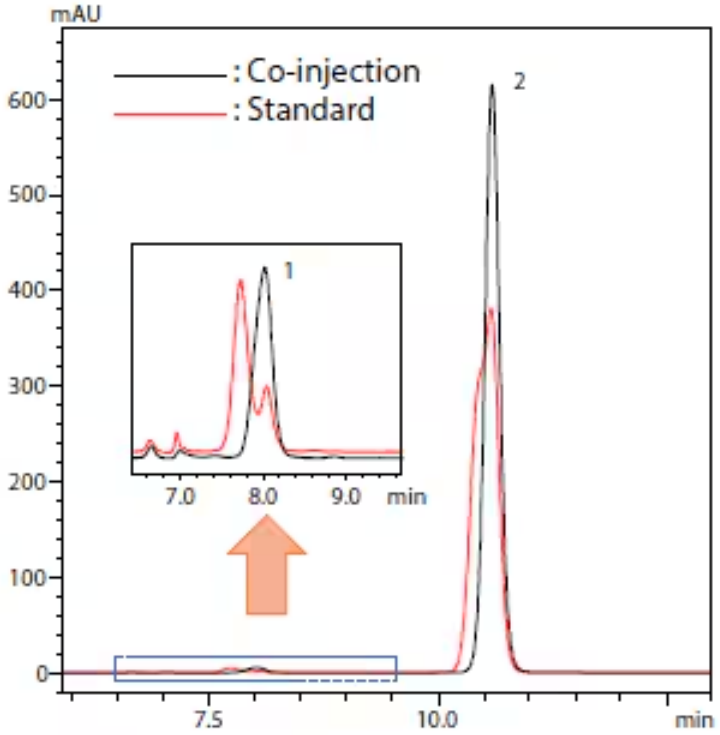


Co-injection – what it is and benefits



Co-injection – what it is and benefits





- Improved peak shape
- Better reproducibility of retention times

Enables good quality larger injection volumes, hence, increases sensitivity

- In-needle derivatization and ion-pairing addition

Co-injection – what it is and benefits

PFPrA
($C_3HF_5O_2$)
m/z 163.00>119.00(-)

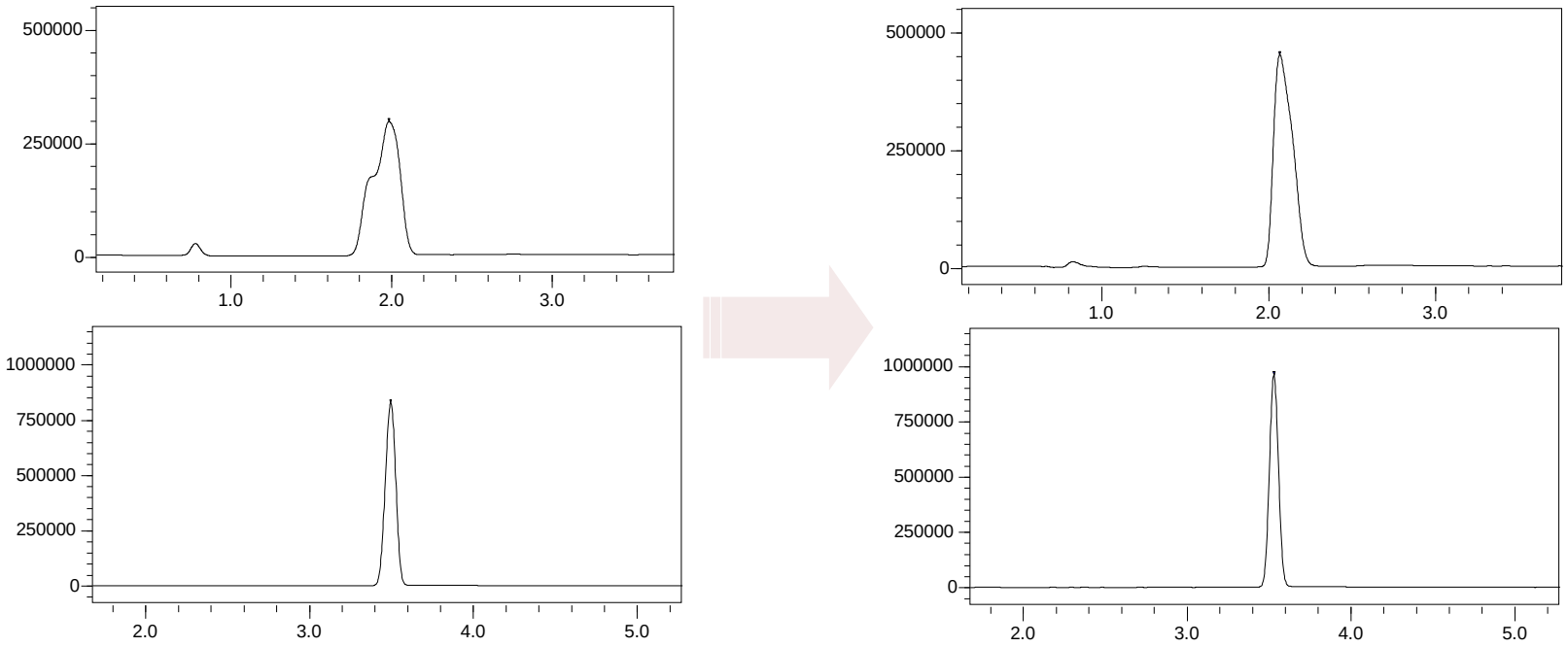
PFBA
($C_4HF_7O_2$)
m/z 213.00>169.00(-)

Standard

25 µL Sample

Co-injection

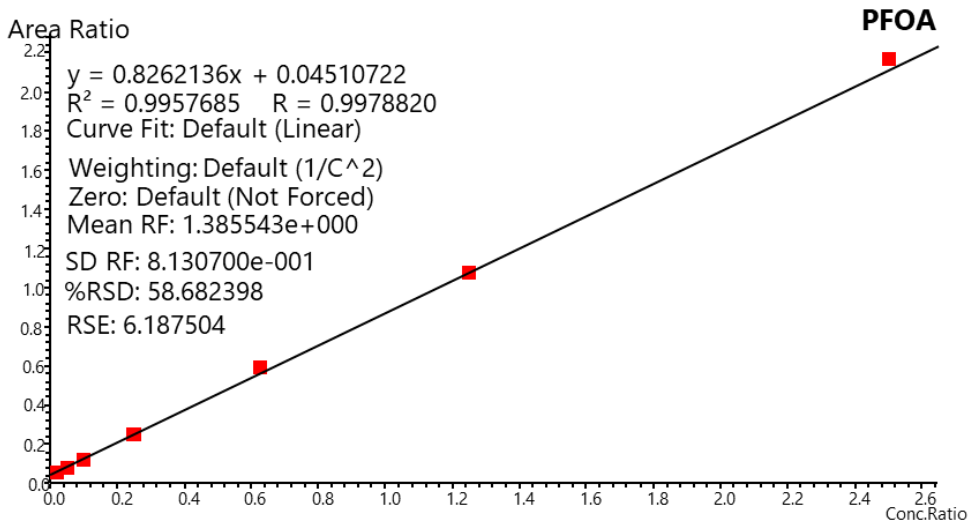
25 µL Sample +
25 µL UPW with 0.1 % AA
(UPA: Ultra pure water, AA: Acetic acid)



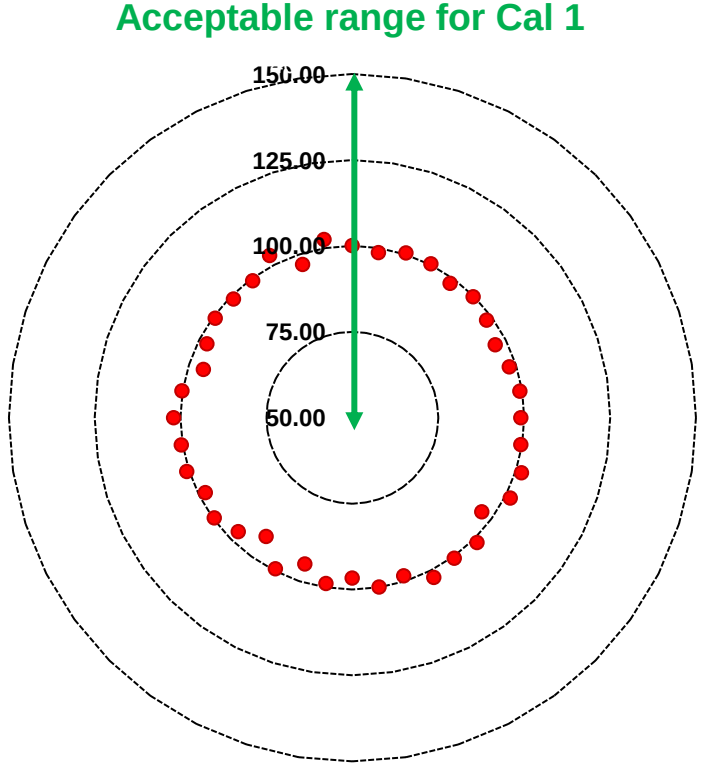
Column: Shim-pack GIST-HP C18, 3.0 mm i.d. x 100 mm L, 3 µm

Calibration curve

- Calibration curve range from 0.02 – 1.25 ng/mL
- Lowest calibration standard 10 times lower than EPA Method 1633 Cal 1 (PFBA: 0.08 ng/mL)



- %RSE values from the calibration curve <18%.
- %Accuracy Cal 1: 93-103%

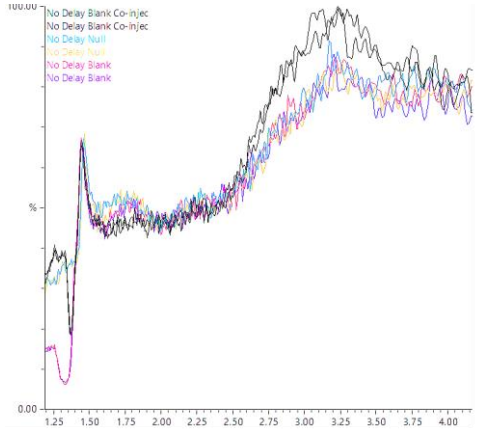


Systematic evaluation of background

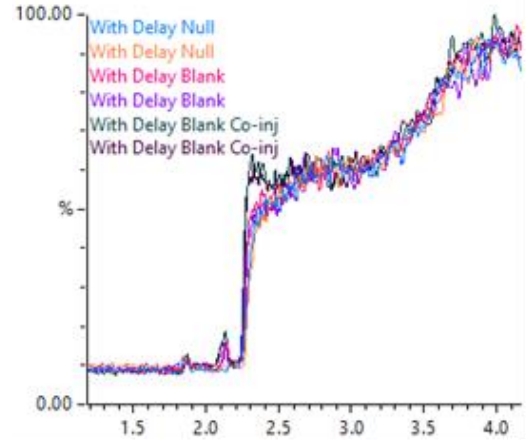
- New Shimadzu LCMS-8060NX
- Standard configuration
  - Degasser in-line
  - Standard fluoropolymer containing tubing
- Data acquired according to EPA 1633
  - Using methods with standard injection and co-injection
- Replicated injections (n=7) of each condition
  - No delay column: NULL, blank, blank co-injection
  - Delay column: NULL, blank, blank co-injection, calibration curves
- Compounds detected in background under at least one condition tested:
  PFBA, PFHxA, 5:3 FTCA, PFPeS, 6-2 FTS, 7:3 FTCA, 9Cl-PF3ONS, PFHpA

Example - PFBA

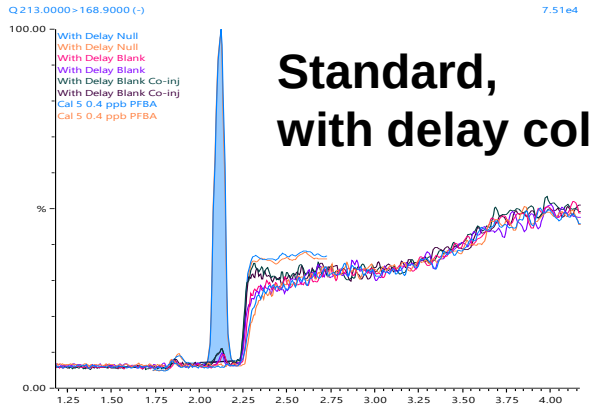
No delay column



With delay column



Standard, with delay column



Data in plot includes only n=2 per condition

Systematic evaluation of background

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More detailed results about this work on Wednesday August 7th at 4:30 pm

Session: Collaborative efforts to improve environmental monitoring

Delay Columns: Additional Impacts to Delaying PFAS Present in the Background

Extraction method

EDGE PFAS: Automated Solvent Extraction

- Pressurized Fluid Extraction
- Sequential – automates 12 samples per rack
- Reusable Q-Cup sample cell
- Side enclosure
- Centrifuge tube collection
- Filtration step included

Extraction method

- PEEK and Polypropylene tubing
- All components tested for PFAS

Extraction method

- PEEK and Polypropylene tubing
- All components tested for PFAS to confirm absence of contamination

Clean filter (Q-Disc):
<LOQs
EPA 1633 by a commercial laboratory
(LOQ = EPA Cal 1)

More info in next slides!

Overall sample preparation

Extraction: EDGE PFAS

Cycle 1
Solvent: 0.05 M KOH in methanol
Top Add: 15 mL
Rinse: 0 mL
Temperature: 65 ℃
Hold Time: 03:00

Cycle 2
Solvent: 0.05 M KOH in methanol
Top Add: 10 mL
Bottom Add: 0 mL
Rinse: 5 mL
Temperature: 65 ℃
Hold Time: 03:00

Wash 1
Solvent: 0.05 M KOH in methanol
Wash Volume: 15 mL
Wash Temperature: 65 ℃
Hold Time: 0:15

Wash 2
Solvent: 0.05 M KOH in methanol
Wash Volume: 15 mL
Wash Temperature: ---
Hold Time: --:--

Clean-up

- Carbon Black
- WAX SPE

MilliporeSigma

Experimental Plan

- Each sample - 5 g of Ottawa sand
- Three spike concentrations tested: ¼ EPA Cal 1, ½ EPA Cal 1, EPA Cal 1
- Each concentration tested:

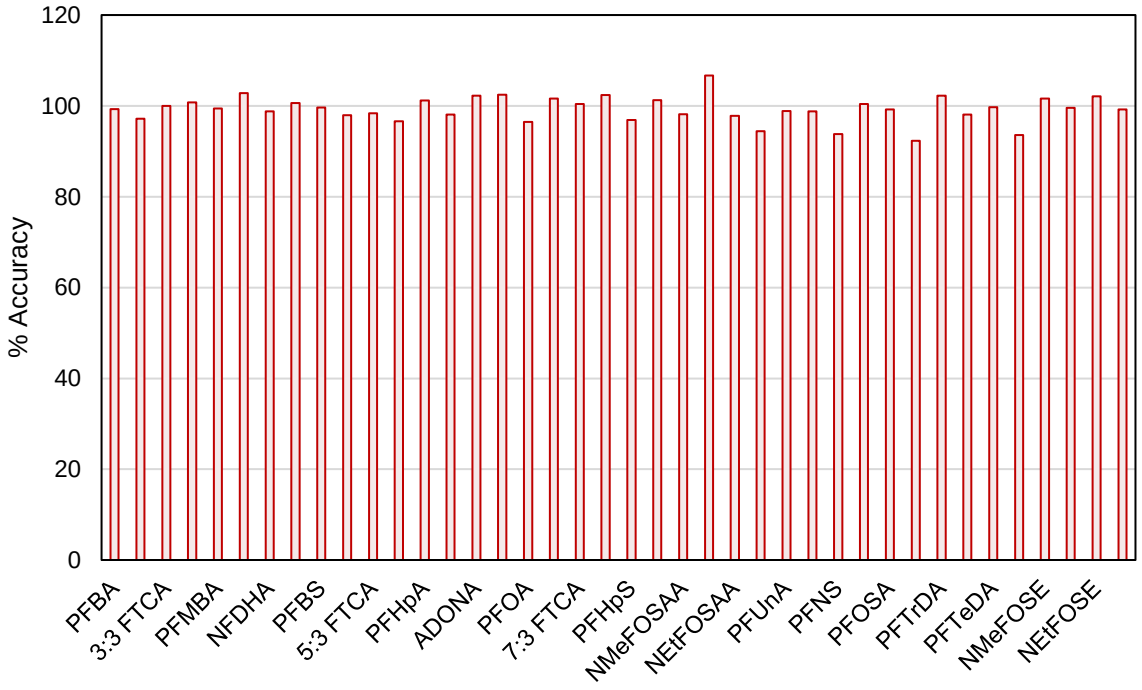
    Extraction batch: spiked samples (n=9), unspiked samples (n=2), blank (n=1)

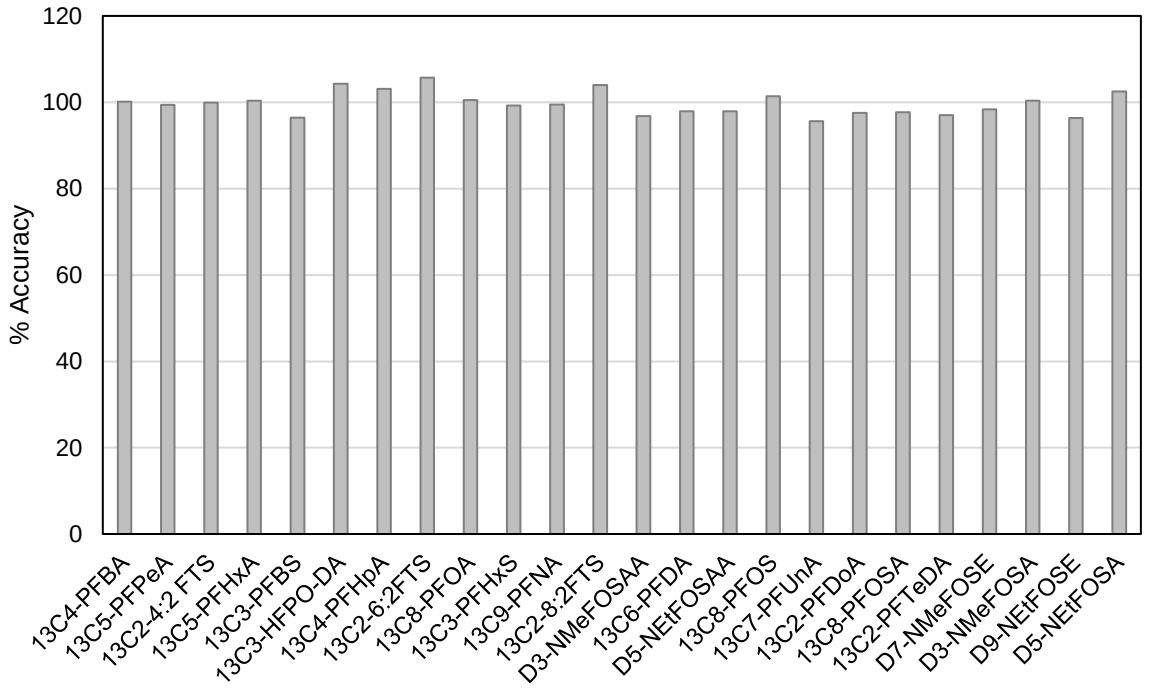
    Randomization of sample position in the extractor

    LCMS Batch analysis according to EPA 1633

Prior work (not included in this presentation): recovery confirmation after spiking samples at each step of the workflow

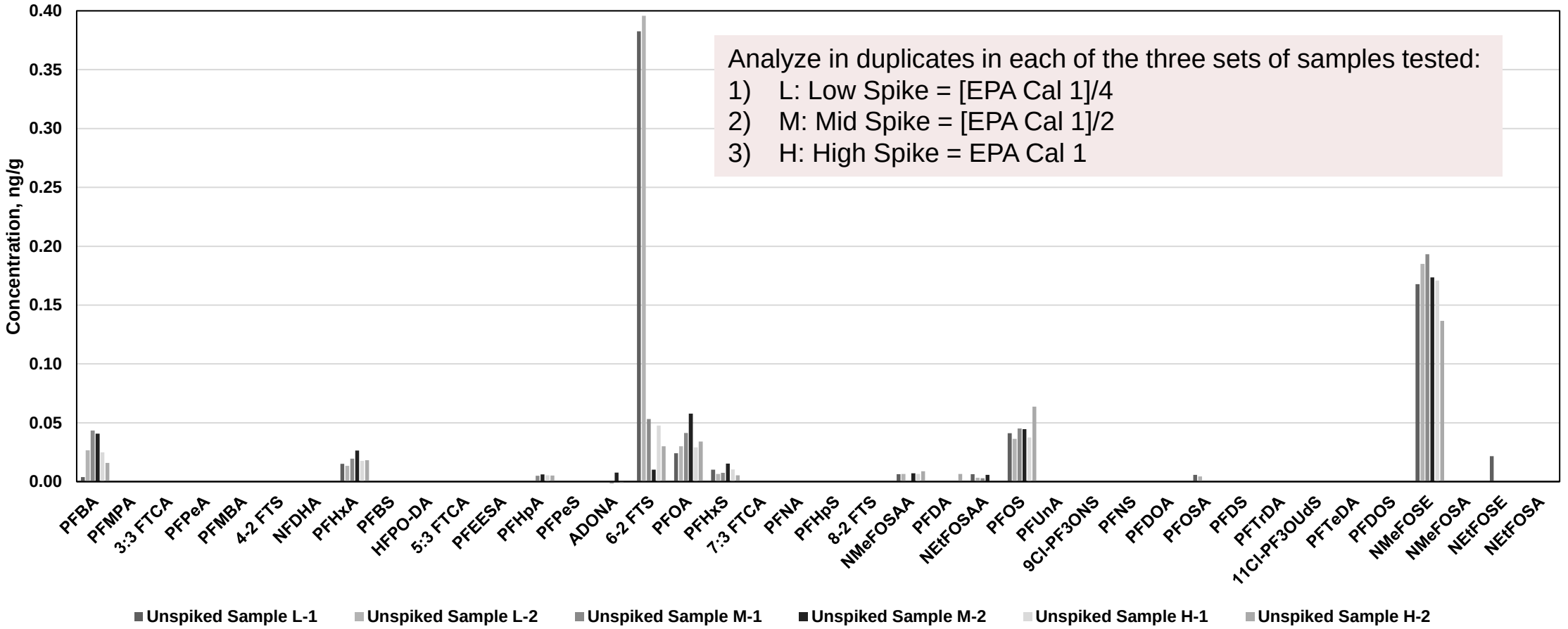
Results – Calibration Verification





- Calibration verification - every 10 sample injections, mid level standard
  - Average %accuracy: Targets - **92 – 107**; EIS – **97 -106**

Results – Unspiked Samples



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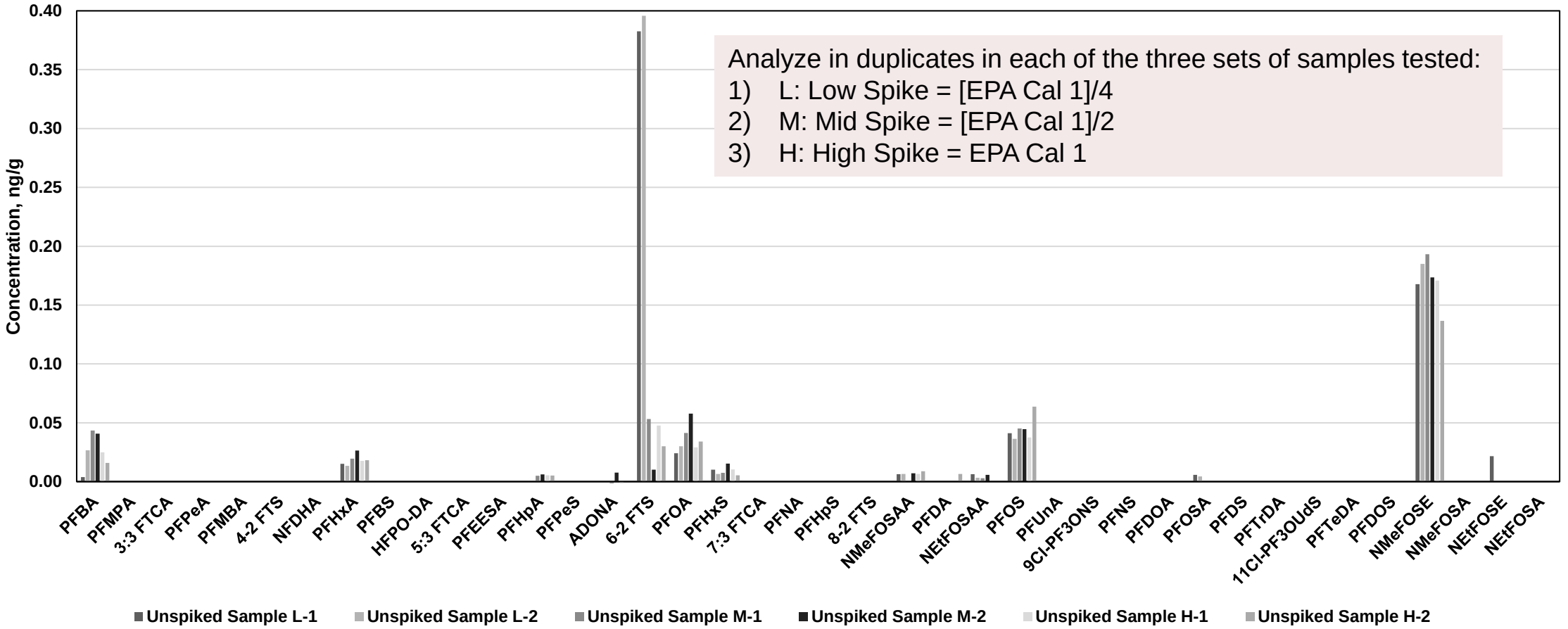
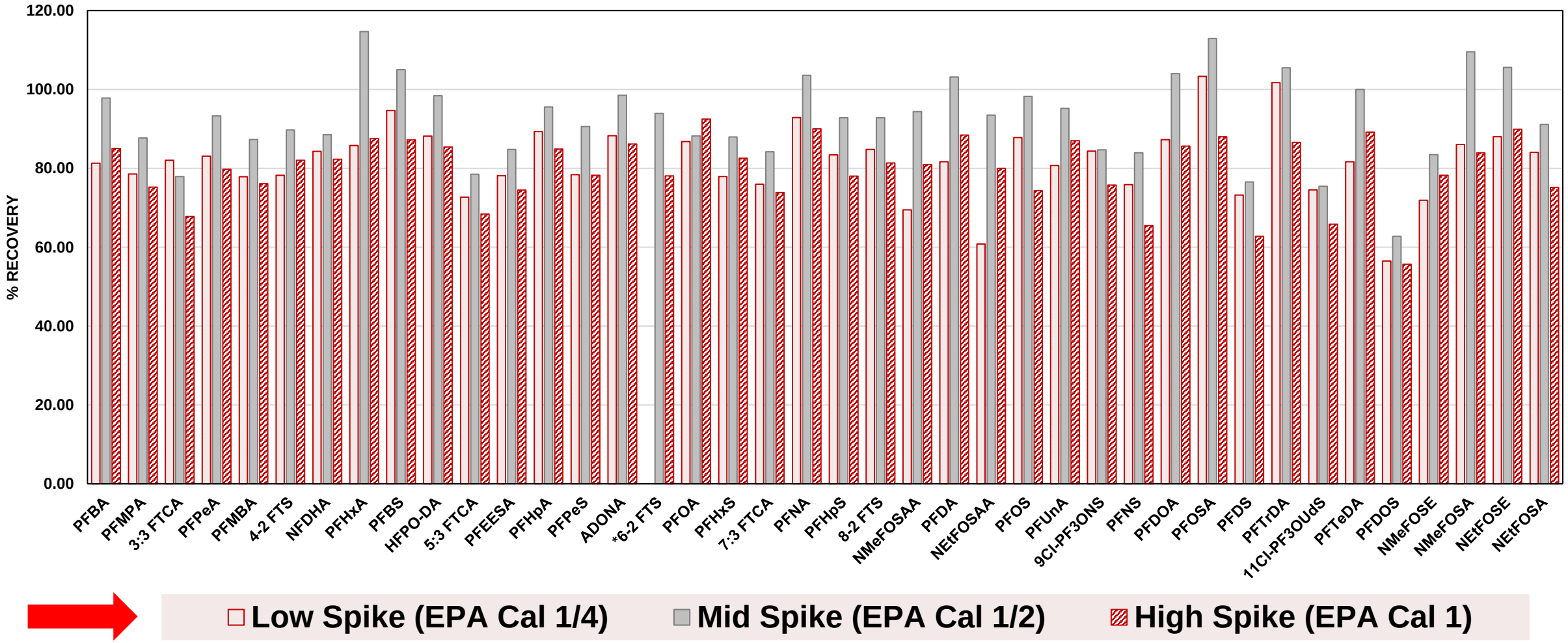


- All results <MDL, except 6-2 FTS in Low batch
- Source of targeted PFAS: Ottawa sand

  Confirmed by absence of detectable peaks in instrument blank (full workflow) and NULL injections (LCMS)

Results – Recoveries Spiked Samples

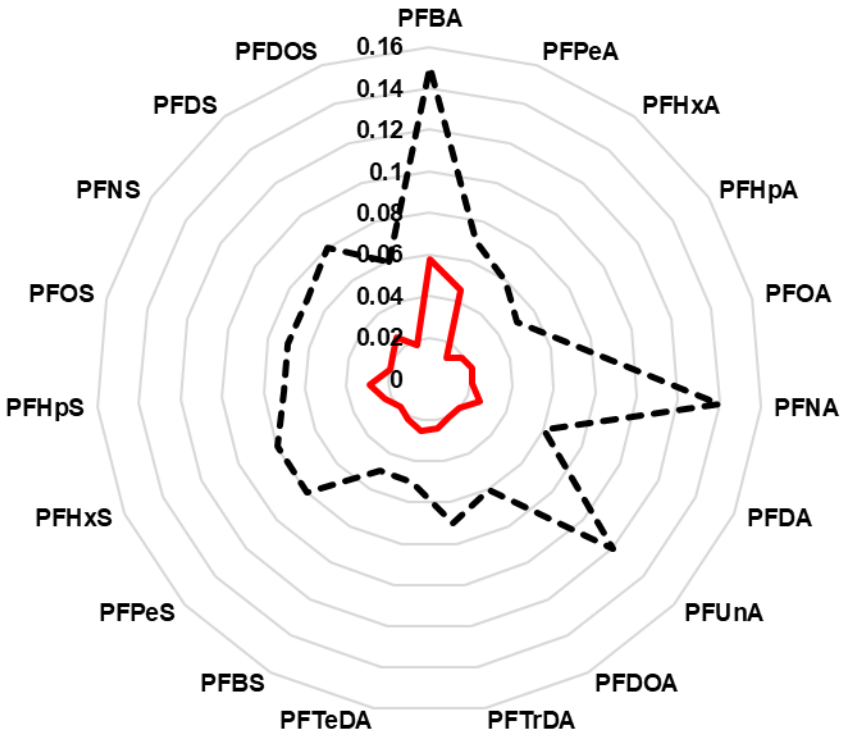


%RSD ranges (n=9): Low – **10 - 25**; Mid – **5 - 27**; High – **6 -14**

6-2 FTS in Low Spike: not reported due to presence of compound in unspiked sample

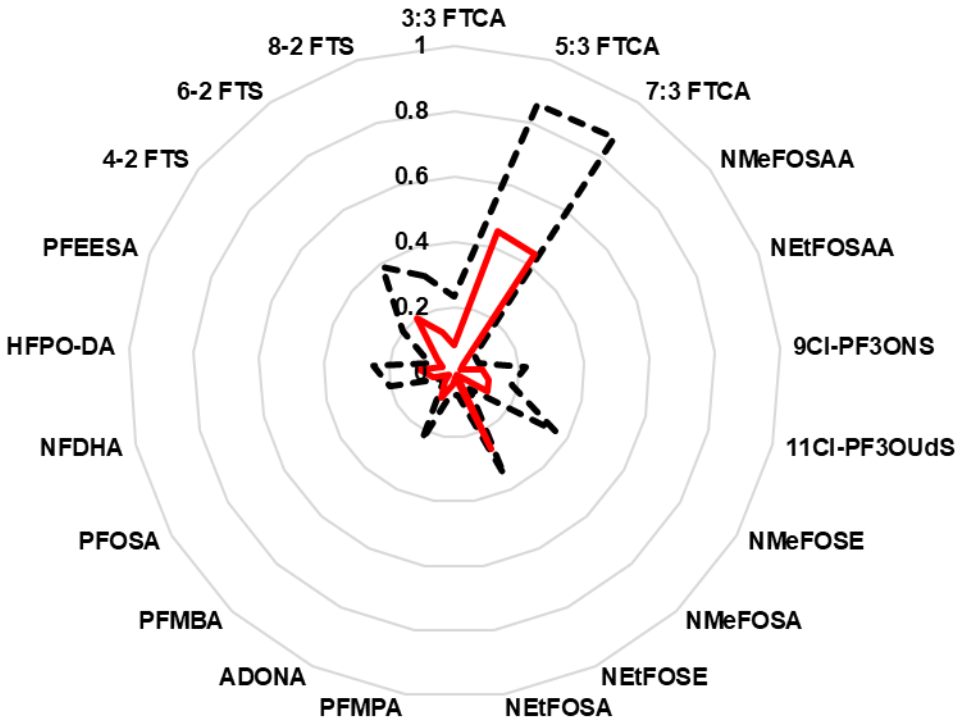
Results – MDLs

EPA reported MDLs



EPA's range: 0.05 – 0.15 ng/g
This work's range: 0.01 – 0.06 ng/g

This work's MDLs



EPA's range: 0.04 – 0.87 ng/g
This work's range: 0.01 – 0.45 ng/g

What Happens…

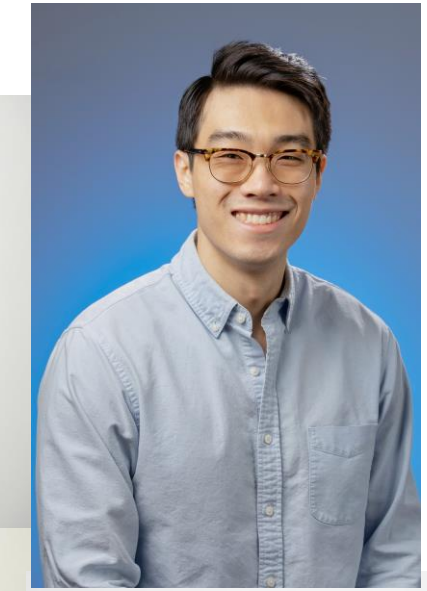
When Automated Solvent Extraction and Robust LC-MS/MS are Coupled for Soil Analysis?

With proper method optimization and thorough evaluation of each component involved in the workflow…

Overall, the calculated MDLs from the workflow using the CEM EDGE PFAS combined with the Shimadzu LCMS8060NX were 2 times better than those reported in EPA Method 1633 in soils

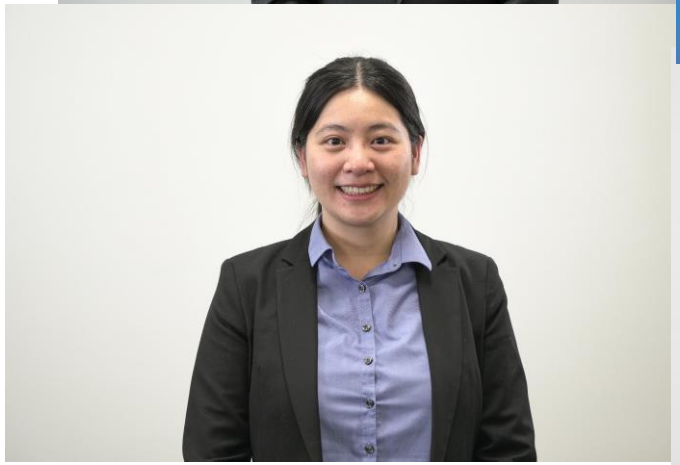
Acknowledgements

Om Shrestha, SSI

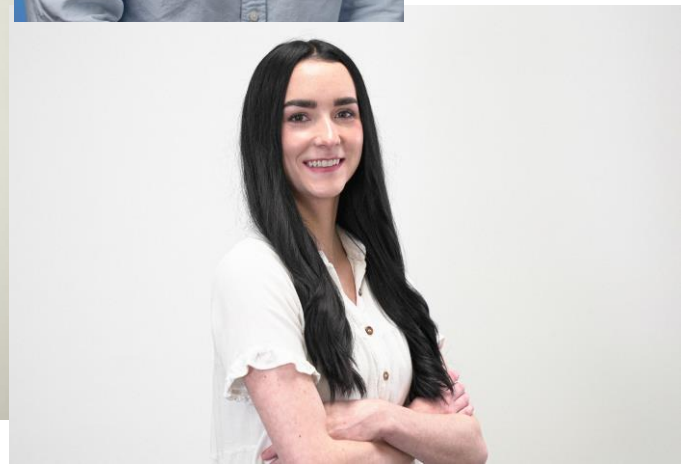


Benedict Liu, CEM

Landon Wiest, SSI



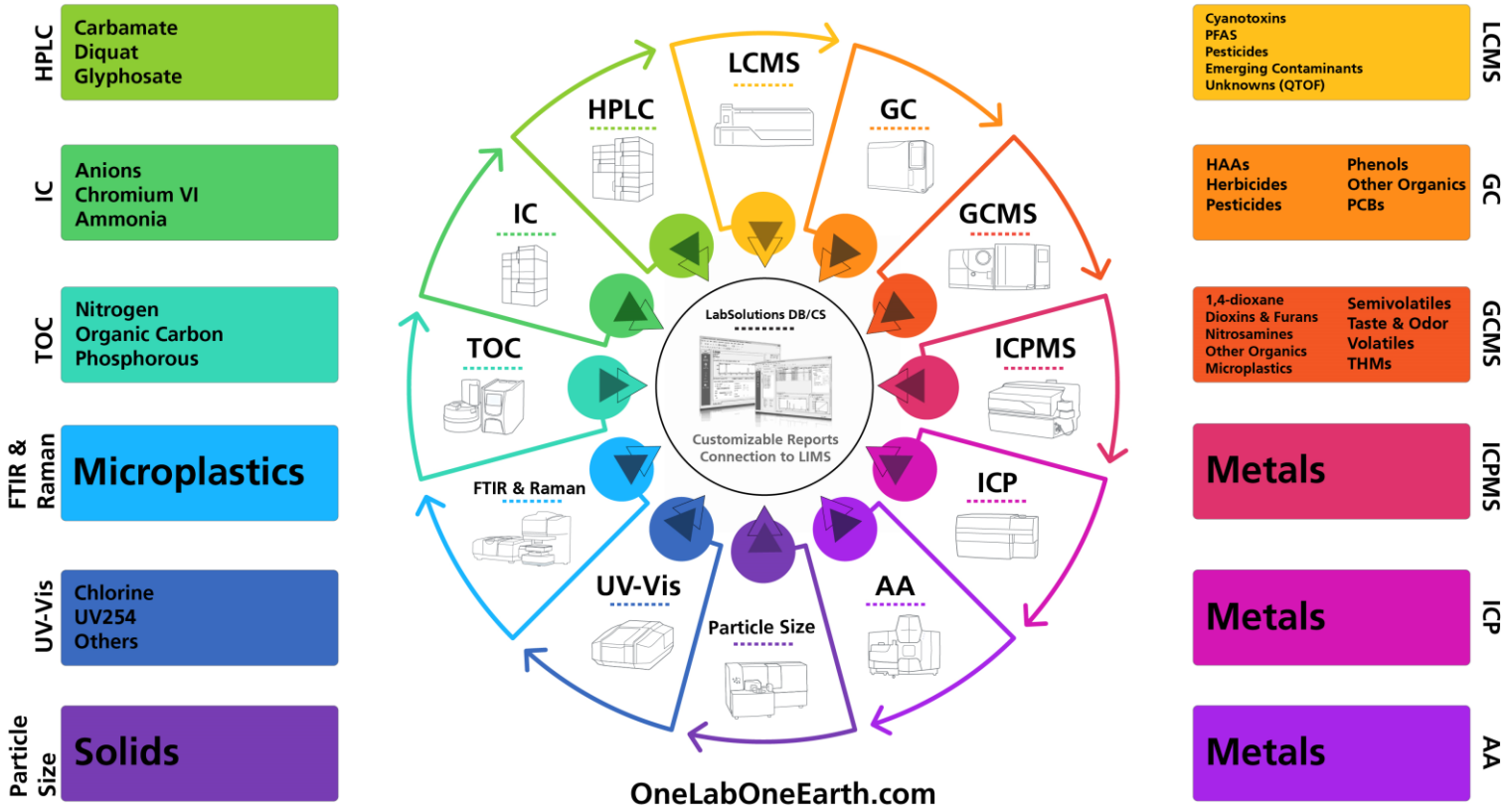
Kathleen Luo, SSI



Megan Davis, SSI

Alicia Stell, CEM

MilliporeSigma



For any questions, contact:

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