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A Direct Injection Approach for Analysis of Legacy and Emerging Perfluoroalkyl Substances in Environmental Water and Soil Samples

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Waters Corporation
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Perfluoroalkylated Substances (PFAS)

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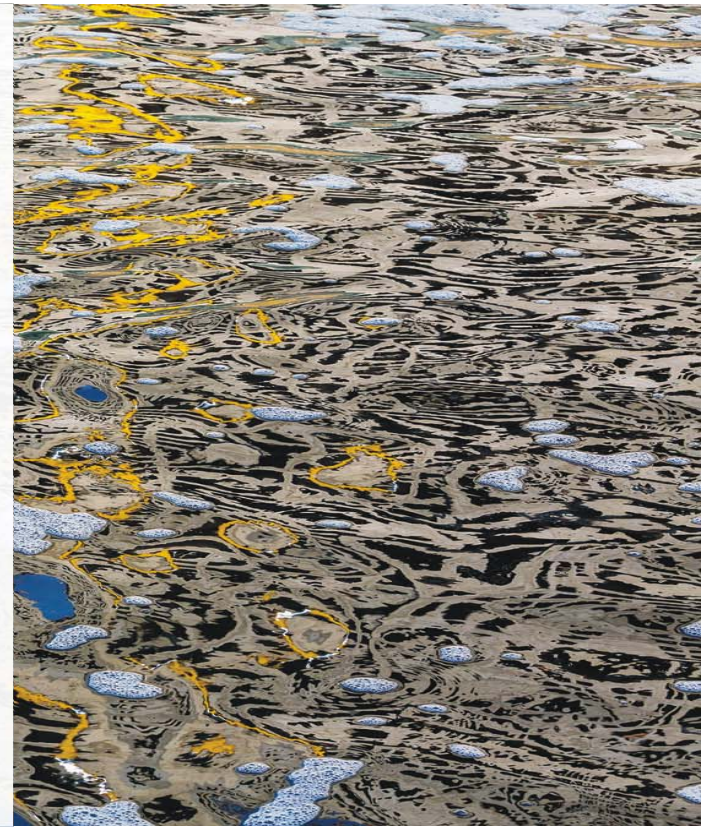
- PFAS = PFC = AFFF
- First **created** in the **1930s**
- **Widespread applications**
  - Non stick **coatings**, **surfactants**, food **packaging**, firefighting **foams**
  - **Polymerization aid** for polytetrafluoroethylene (PTFE) and other fluoropolymers – how PFOS and PFOA became famous
- **Stable** and **persistent** in the environment (POP)
  - Bio-accumulative
- **Identified** in environmental samples **worldwide**
  - Found in arctic **polar bears**
  - Most humans have a range of **PFAS in** their **blood**



Perfluoroalkylated Substances (PFAS)

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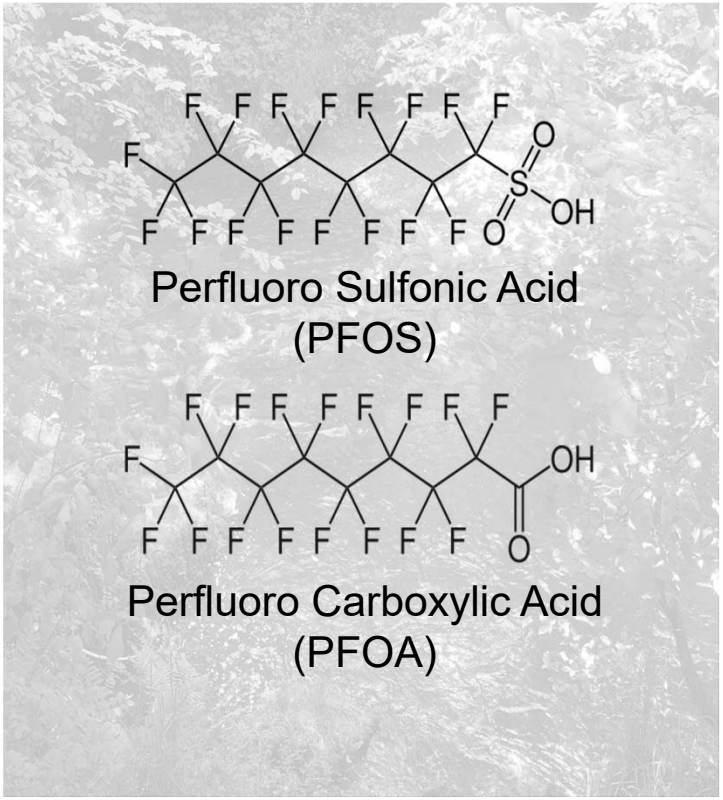
- The **most-studied** PFAS chemicals are PFOA and PFOS.
- Studies in laboratory animals indicate that PFOA and PFOS **can cause effects** in
  - Reproductive and developmental systems
  - Liver and kidney
  - Immune system in laboratory animals
  - Tumors
- But there are **thousands** of **PFAS** that have been created…



Thousands…

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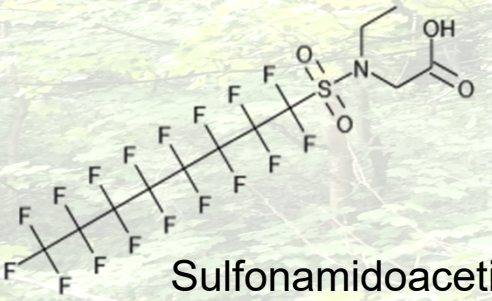
Perfluoro Carboxylic Acid
(PFOA)

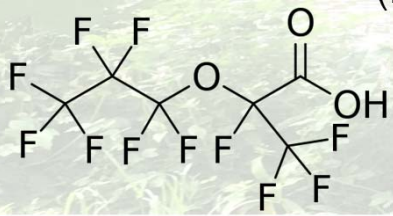
Perfluoro Sulfonic Acid
(PFOS)



Sulfonamidoacetic
acid
(N-EtFOSAA)

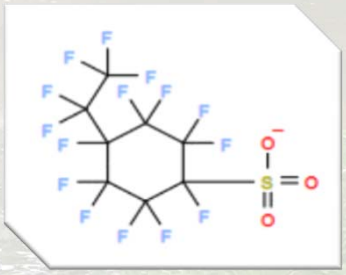
Perfluoro Telomer Acid
(FHEA or 6:2 FTA)

Perfluoro Telomer Sulfonate
(6:2 FTS)



Emerging PFAS
(GenX)

Cyclic
(PFecHS)



How Are People Exposed to PFAS?

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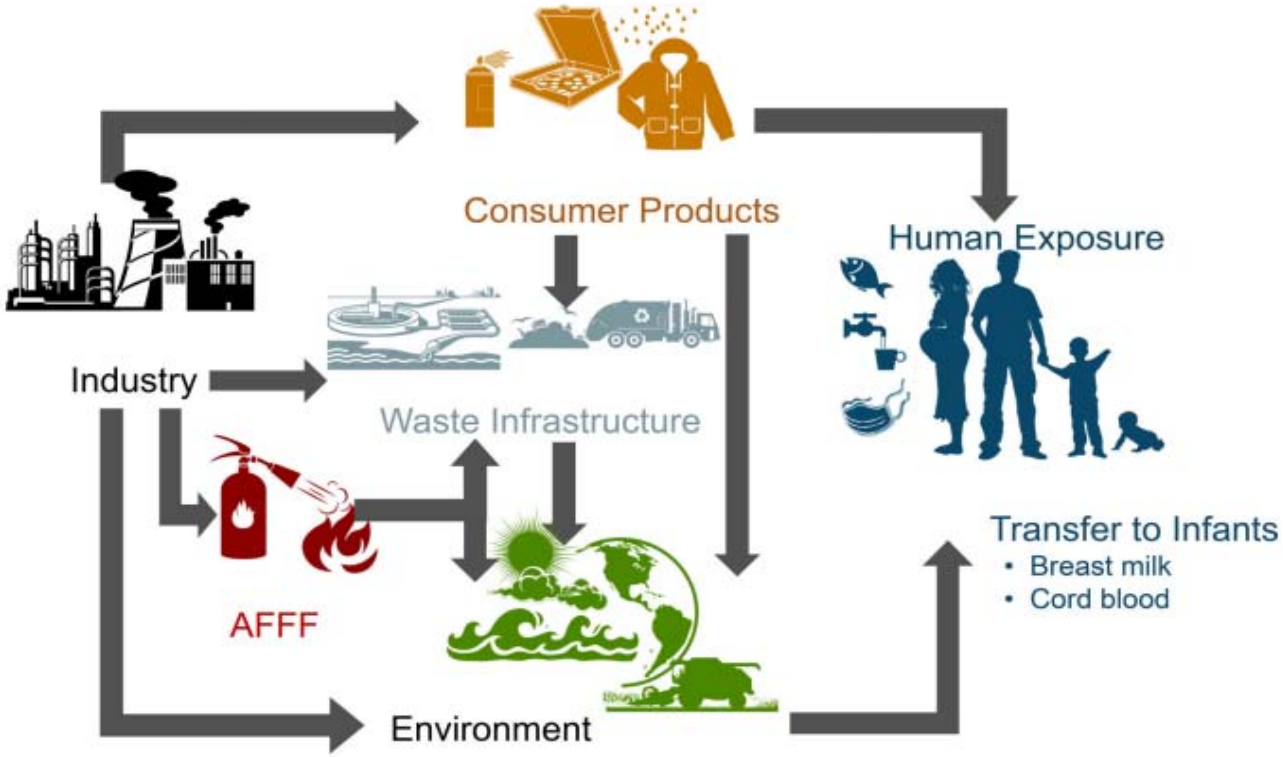

Image from doi: 10.1038/s41370-018-0094-1

A Word on Regulations…

- Currently there are **no federal level regulations** requiring monitoring **for PFAS** (worldwide)
- There are **advisory limits** and established testing methods
  - EPA drinking water series – UCMR 3
  - European water framework directive/drinking water directive
  - ISO and ASTM methods
- EPA advisory limit currently set at **70 ng/L** (ppt) for total PFOA/PFOS
- Individual state proposals and regulations (18 states)
- EPA released **PFAS Action Plan** in early 2019

A Word on Regulations…

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STAY TUNED!

Global Interest in PFAS

NATIONAL QUEENSLAND

Chemicals in Brisbane Airport spill have sparked fears 'worldwide'

Report says incidents of GenX, other PFAS, nearly doubled in last year

White House, EPA headed off chemical pollution study

The intervention by Scott Pruitt's aides came after one White House official warned the findings would cause a 'public relations nightmare.'

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Illustration: The Intercept

NEW TEFLON TOXIN FOUND IN NORTH CAROLINA DRINKING WATER

EU project assesses 'critical' PFAS use in textiles

'New' perfluoroalkyl substances found in fish in China

PFAS costs Europe more than €50 billion a year in health problems

Options for the Analysis of Water Samples

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SPE enrichment prior to injection

- Sample prep allows for use of mid-level sensitivity for mass spectrometer

Xevo TQ-S micro

Large Volume Injection

- High sensitivity mass spectrometer required

Xevo TQ-XS

Comparison of PFAS water analysis methods

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	EPA Method 537*	ISO 25101	ASTM 7979
Sample Prep	SPE (SDVB)	SPE	Dilute and Filter
Injection Volume	1 - 10 µL	1 - 10 µL	30 µL
Instrument sensitivity required	Low to mid	Low to mid	High
Number of compounds	18	2	24

*EPA 537 is for drinking water analysis only

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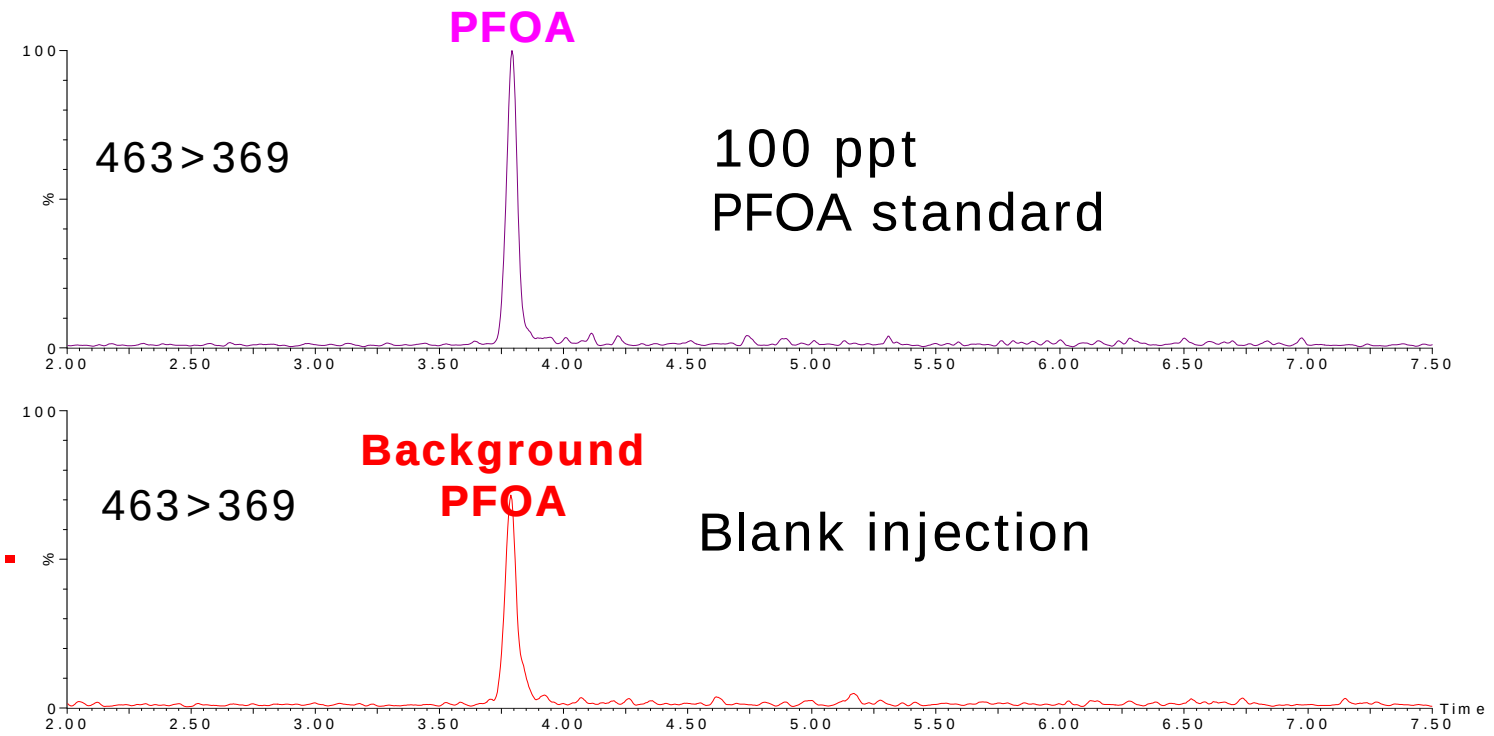
PFAS Contamination

PFAS's Interferences/Contamination



The Waters PFAS Kit

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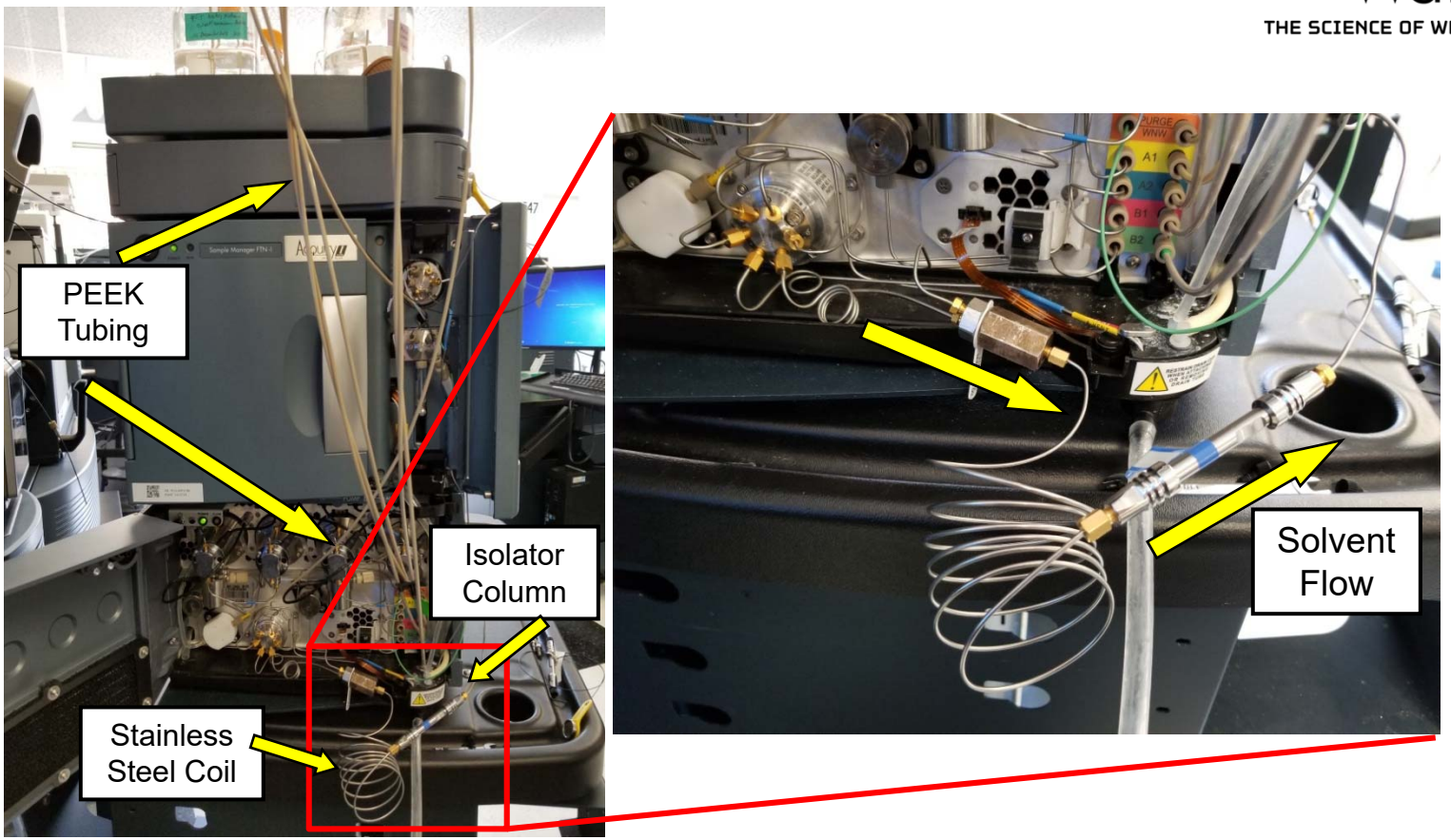

MRM Chromatograms of PFOA With PFAS Kit Installed

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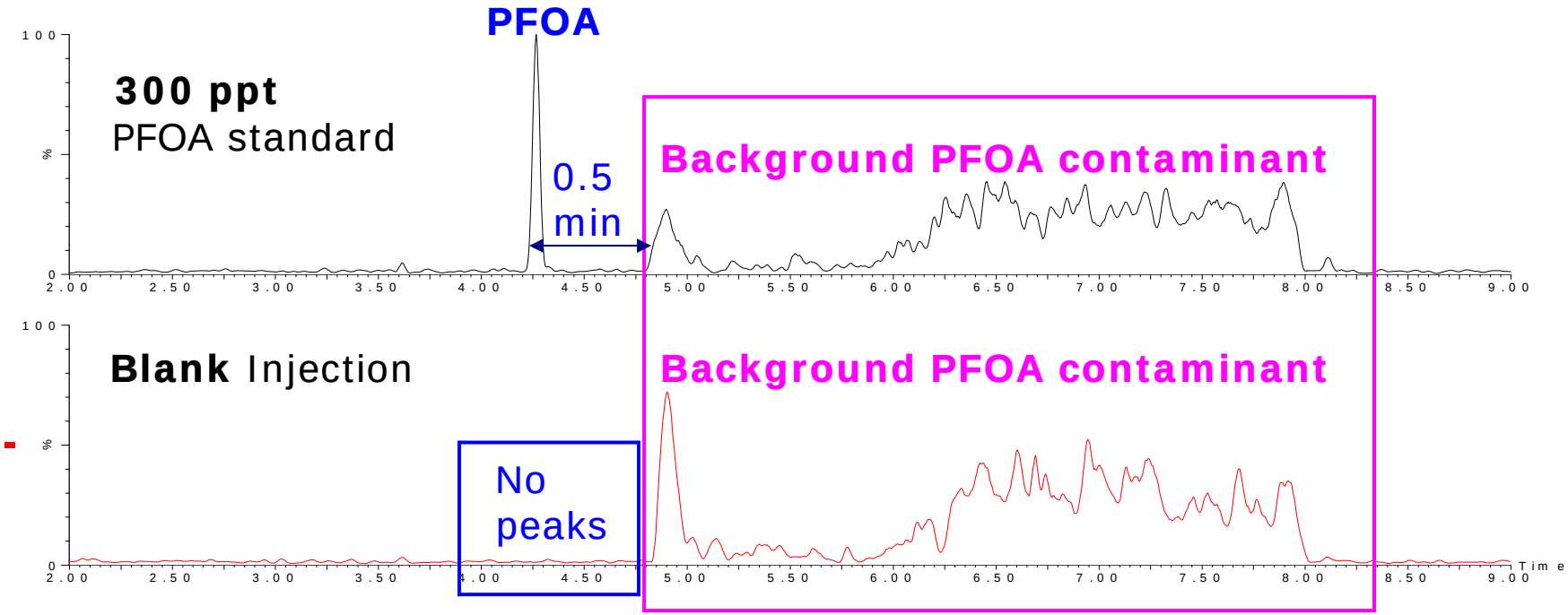

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Direct Large Volume Injection for

Water (ASTM 7979)

and

Soil (ASTM 7968)

Sample Pre-Treatment

WATER

5 mL sample +
5 mL Methanol

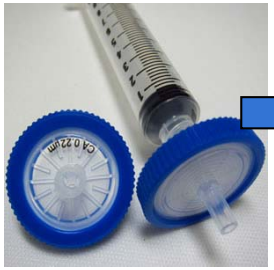
SOIL

2 g sample (soil) + 10 mL 1:1 Water:Methanol
Adjust pH to ~ 9-10
Shake 1 hour

Centrifuge

Water
Surface
Ground
Influent
Effluent

Soils
Sand
Silt
Lean Clay
Fat Clay



Syringe filter entire sample

Acidify and transfer to polypropylene vial

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Instrument Methods

Source Parameters

- Instrument: Xevo TQ-XS
- Ion Mode: ESI-
- Capillary Voltage: 1.0 kV
- Desolvation Temperature: 500° C
- Desolvation Flow: 1100 L/hr
- Cone Flow: 150 L/hr

MS Method

- Developed using QuanOptimize
  - MRMs, CV, CE
- Divert flow to waste from 15 – 21 mins

LC Method

- Instrument: Acquity I Class with PFAS Kit
- Column: CSH Phenyl Hexyl 2.1mm x 100 mm, 1.7 µm
- Mobile Phase A: 95:5 H2O:MeOH + 2 mM ammonium acetate
- Mobile Phase B: MeOH + 2 mM ammonium acetate
- Injection Volume: 30 uL
- Gradient:

Time (min)	Flow (mL/min)	%A	%B
0	0.3	100	0
1	0.3	80	20
6	0.3	55	45
13	0.3	20	80
14	0.4	5	95
17	0.4	5	95
18	0.3	100	0
22	0.3	100	0

Compounds Included in Methods

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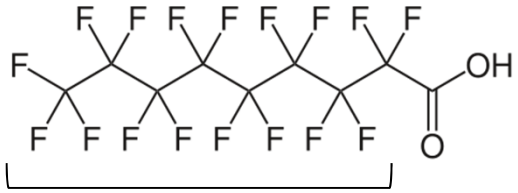
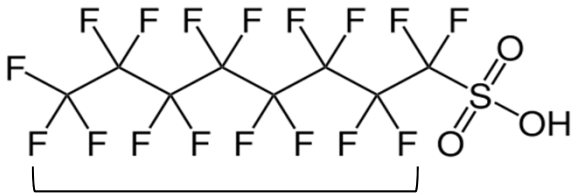
Carboxylates



C4 – C14, C16, C18

Sulfonates



C4 – C10

Emerging

GenX

ADONA

11Cl-PF3OUdS

9Cl-PF3ONS

PFEESA

NFHDA

PFMBA

Others

4:2/6:2/8:2 FTS

FHEA/FOEA/FDEA

FOSA

PFecHS

FHUEA

FHpPA

FOUEA

diPAP

NMeFOSAA/NEtFOSAA

NMeFOSA/NEtFOSA

Overall Method Summary

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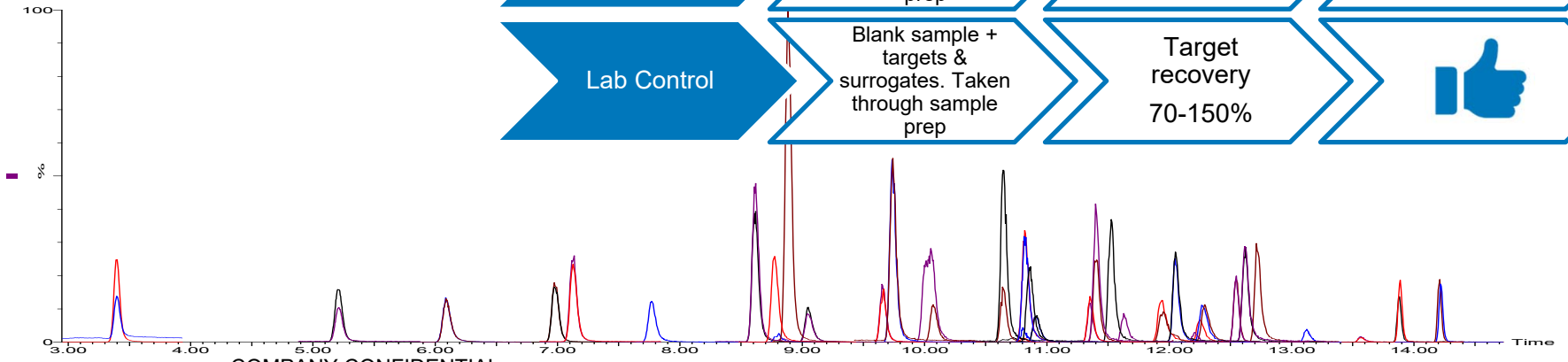
ERA **certified** QC sample injected as **control** throughout analysis

Reagent Blanks	50:50 water : methanol + 0.1% acetic acid	Concentration must be < half reporting limit	
Method Blank	Blank sample + surrogates. Taken through sample prep	Concentration must be < half reporting limit	
Reporting Limit Check	Blank sample + targets & surrogates. Taken through sample prep	Detectable recovery 35-150%	
Lab Control	Blank sample + targets & surrogates. Taken through sample prep	Target recovery 70-150%	



Method Detection Limits (MDL) for Water

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Well **below** the necessary **reporting limits** for the compounds defined **in ASTM 7979**

Compound	Sample spike (ng/L)	MDL (ng/L)	Reporting range (ng/L)*	R^2
PFBA	100	25.20	50–2000	0.993
PFPeA	10	1.04	50–2000	0.999
PFHxA	10	1.33	10–400	0.999
PFHpA	10	0.91	10–400	0.999
PFOA	10	1.42	10–400	0.999
PFNA	10	1.32	10–400	0.999
PFDA	10	0.84	10–400	0.998
PFUnDA	10	2.52	10–400	0.996
PFDoDA	10	1.76	10–400	0.993
PFTriDA	10	2.34	10–400	0.991
PFTreDA	10	1.99	10–400	0.993
PFHxDA	200	25.41	–	0.984
PFOcDA	400	41.99	–	0.983
PFBS	10	1.21	10–400	0.999
PFPeS	10	1.07	10–400	0.999
PFHxS	10	1.41	10–400	0.999
PFHpS	10	1.57	10–400	0.999
PFOS	10	1.61	10–400	0.999
PFNS	10	1.67	10–400	0.999
PFDS	10	1.44	10–400	0.997

Compound	Sample spike (ng/L)	MDL (ng/L)	Reporting range (ng/L)*	R^2
FOSA	10	1.29	10–400	0.999
N-Et-FOSAA	10	1.90	10–400	0.997
N-Me-FOSAA	10	1.59	10–400	0.999
N-Et-FOSA	10	1.45	–	0.997
N-Me-FOSA	10	1.19	–	0.999
FHUEA	10	1.53	10–400	0.999
FOUEA	10	1.36	–	0.999
8:2 diPAP	300	50.16	–	0.988
4:2 FTS	10	1.50	10–400	0.999
6:2 FTS	10	N/A	10–400	0.999
8:2 FTS	10	2.62	10–400	0.997
PFecHS	10	1.17	10–400	0.998
FHEA	200	42.19	300–8000	0.994
FOEA	200	50.38	200–8000	0.997
FDEA	200	79.48	200–8000	0.993
FHpPA	10	1.47	10–400	0.999
ADONA	10	0.82	–	0.999
9Cl-PF3ONS	10	1.06	–	0.999
11Cl-PF3OUdS	10	1.45	–	0.998

Reporting Range is the required range the method must be able to cover as defined in ASTM 7979 method

Lower Limits of Quantitation (LLOQ) for Soil

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Compound	LLOQ (ng/L) In vial	LLOQ (ng/kg) In sample
PFBA	25	125
PFPeA	< 1	< 5
PFHxA	< 1	< 5
PFHpA	< 1	< 5
PFOA	< 1	< 5
PFNA	1	5
PFDA	< 1	< 5
PFUnDA	5	25
PFDoDA	5	25
PFTriDA	5	25
PFTreDA	5	25
PFBS	< 1	< 5
PFPeS	< 1	< 5
PFHxS	1	5
PFHpS	1	5

Compound	LLOQ (ng/L) In vial	LLOQ (ng/kg) In sample
PFOS	1	5
PFNS	5	25
PFDS	5	25
FOSA	< 1	< 5
N-Et-FOSAA	5	25
N-Me-FOSAA	5	25
4:2 FTS	< 1	< 5
6:2 FTS	10	50
8:2 FTS	5	25
ADONA	< 1	< 5
9Cl-PF3ONS	5	25
11Cl-PF3OUdS	5	25
GenX	10	50
PFMBA	< 1	< 5
PFEESA	< 1	< 5

Linearity and Sensitivity

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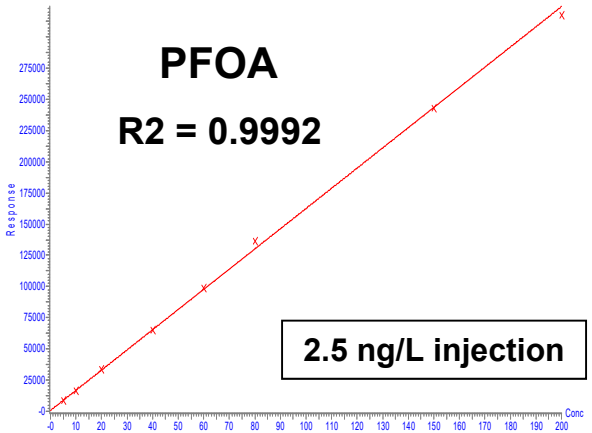
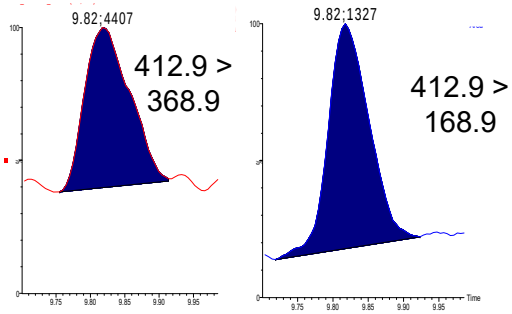
PFOA

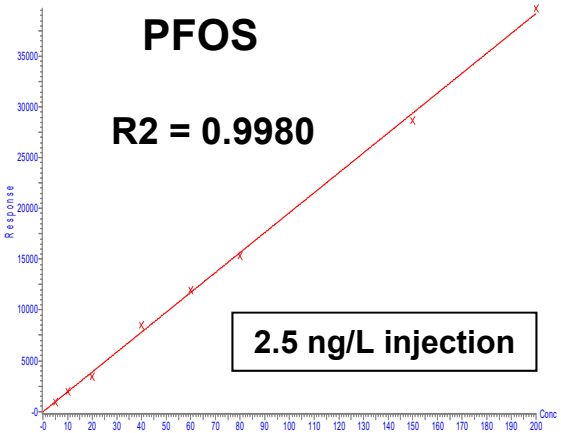
R2 = 0.9992

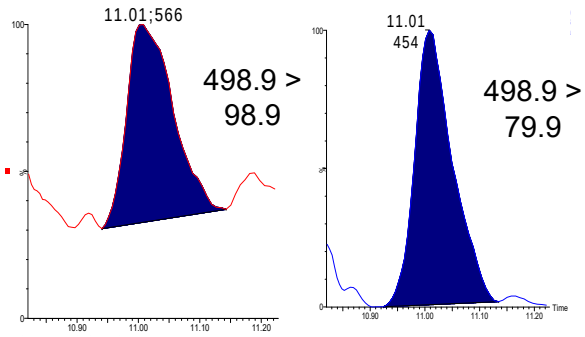




PFOS

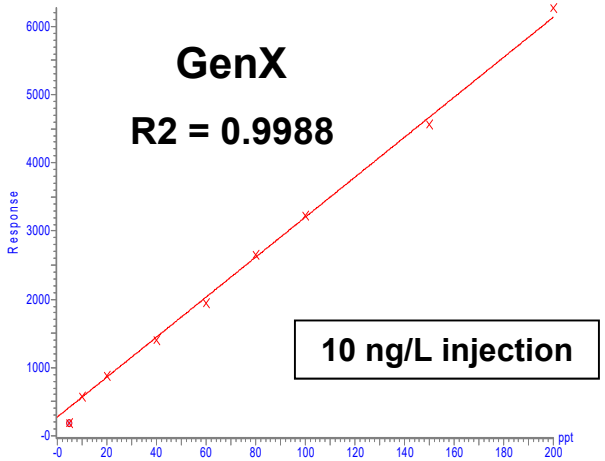
R2 = 0.9980

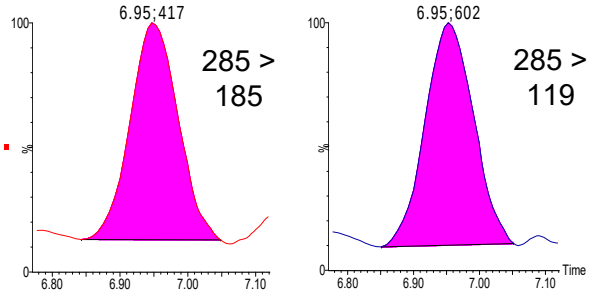




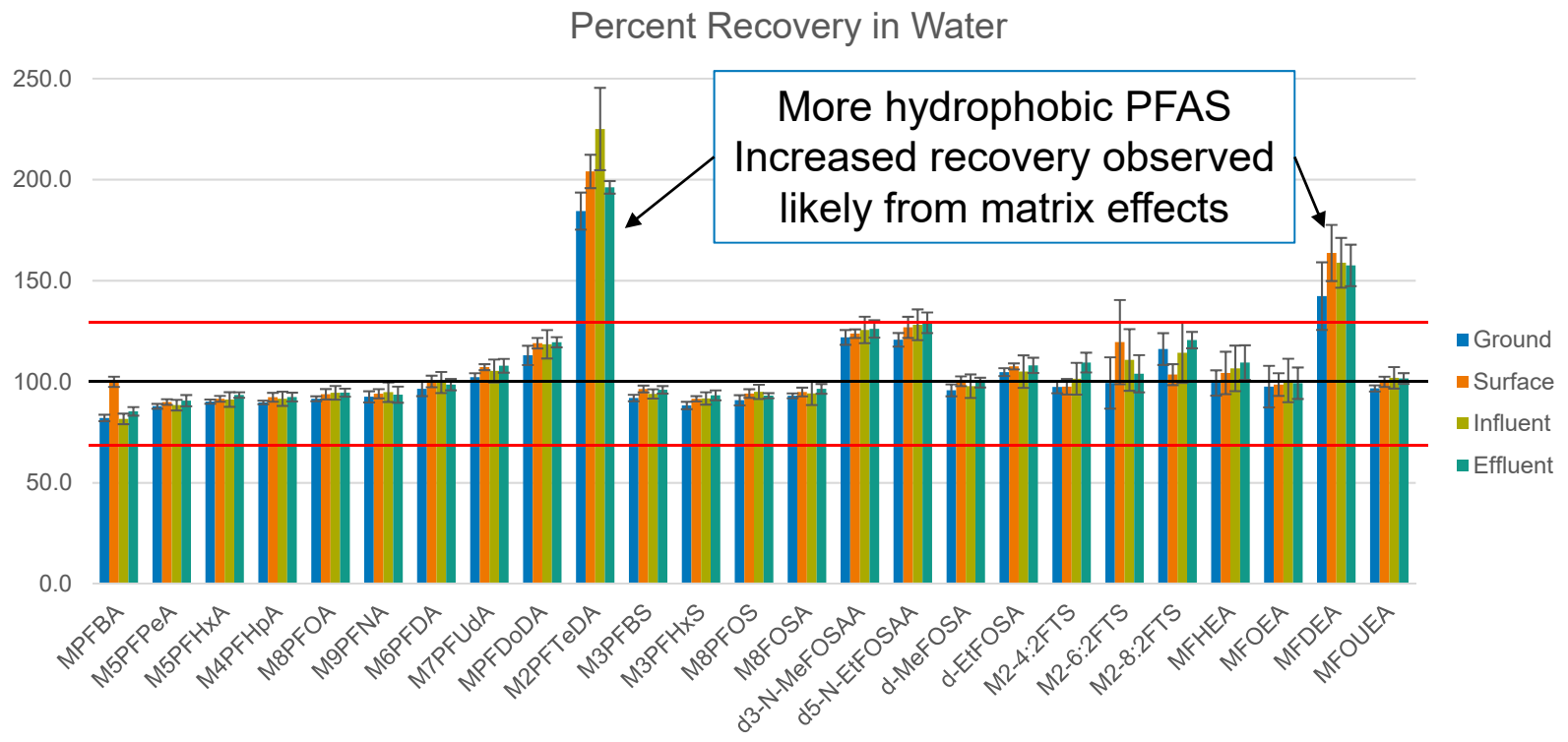
GenX

R2 = 0.9988

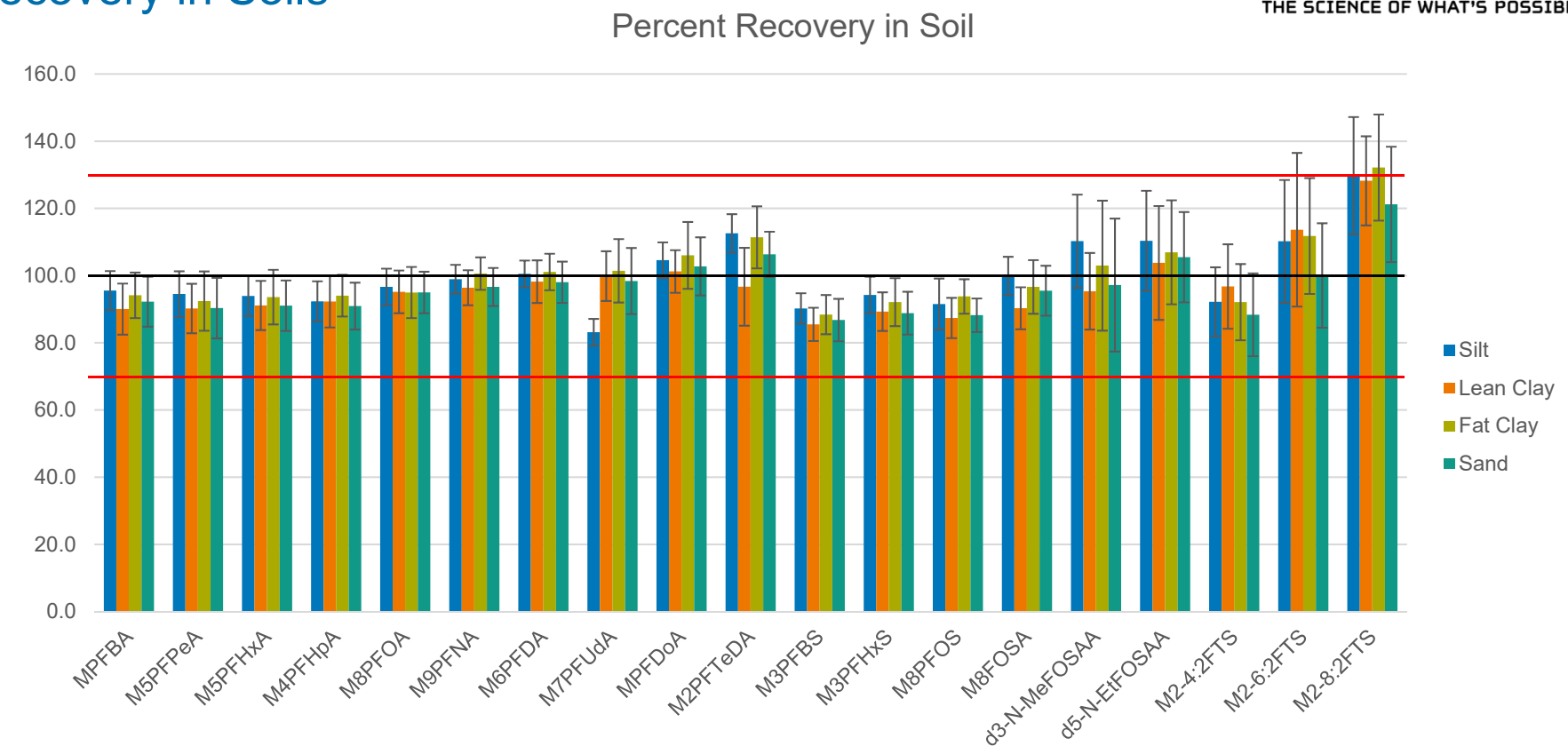




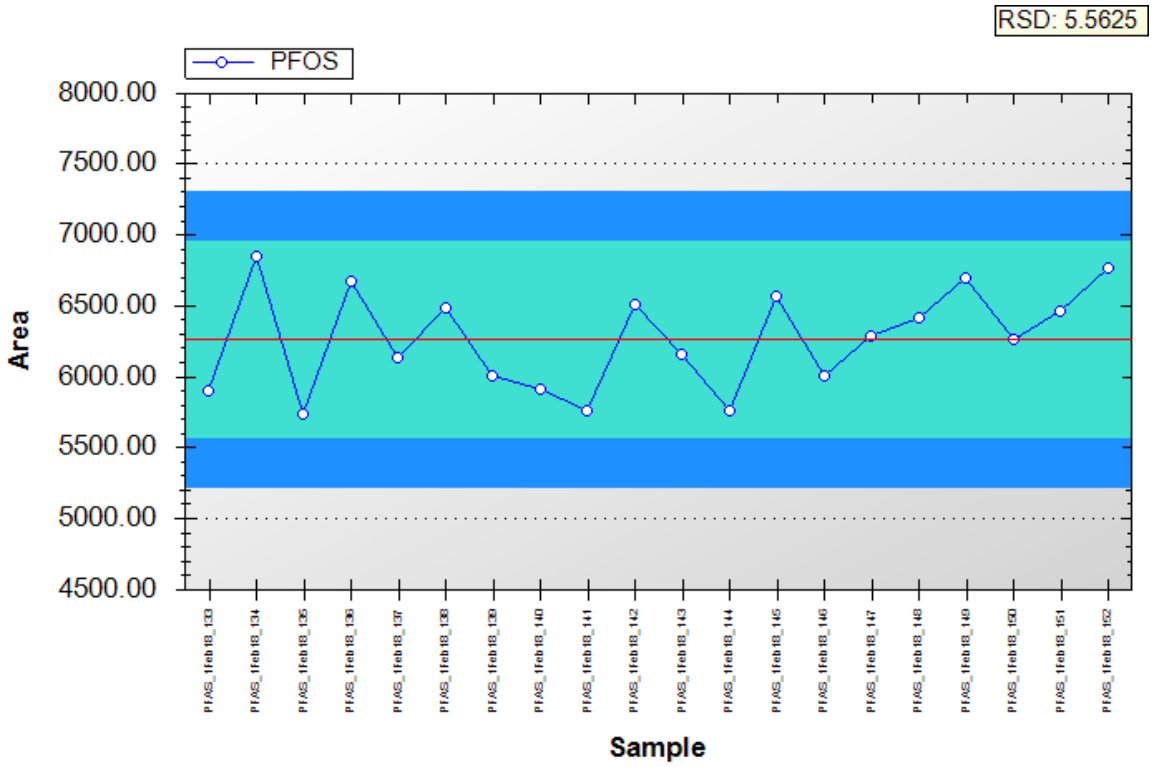
Recovery in Water



Recovery in Soils



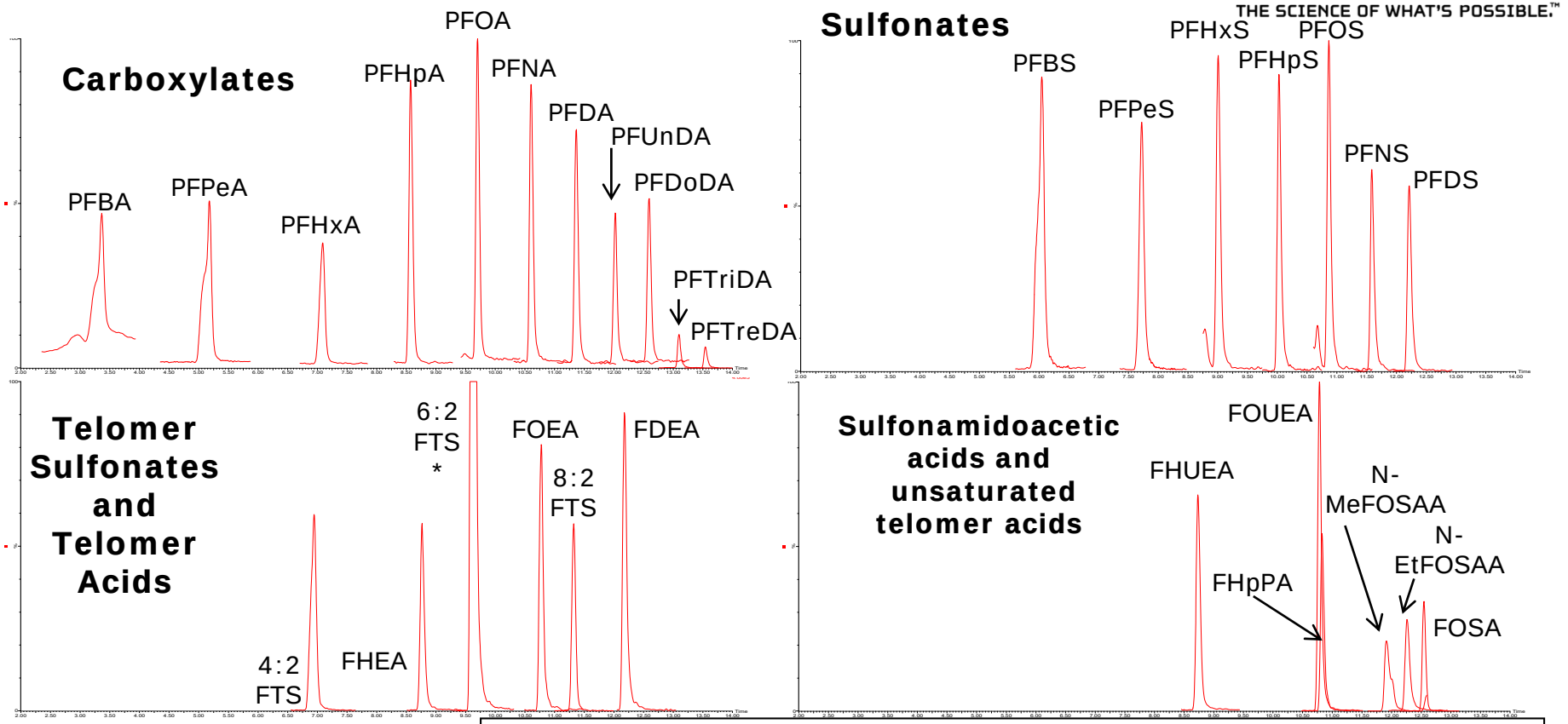
Instrument Robustness



20 injections of surface water sample

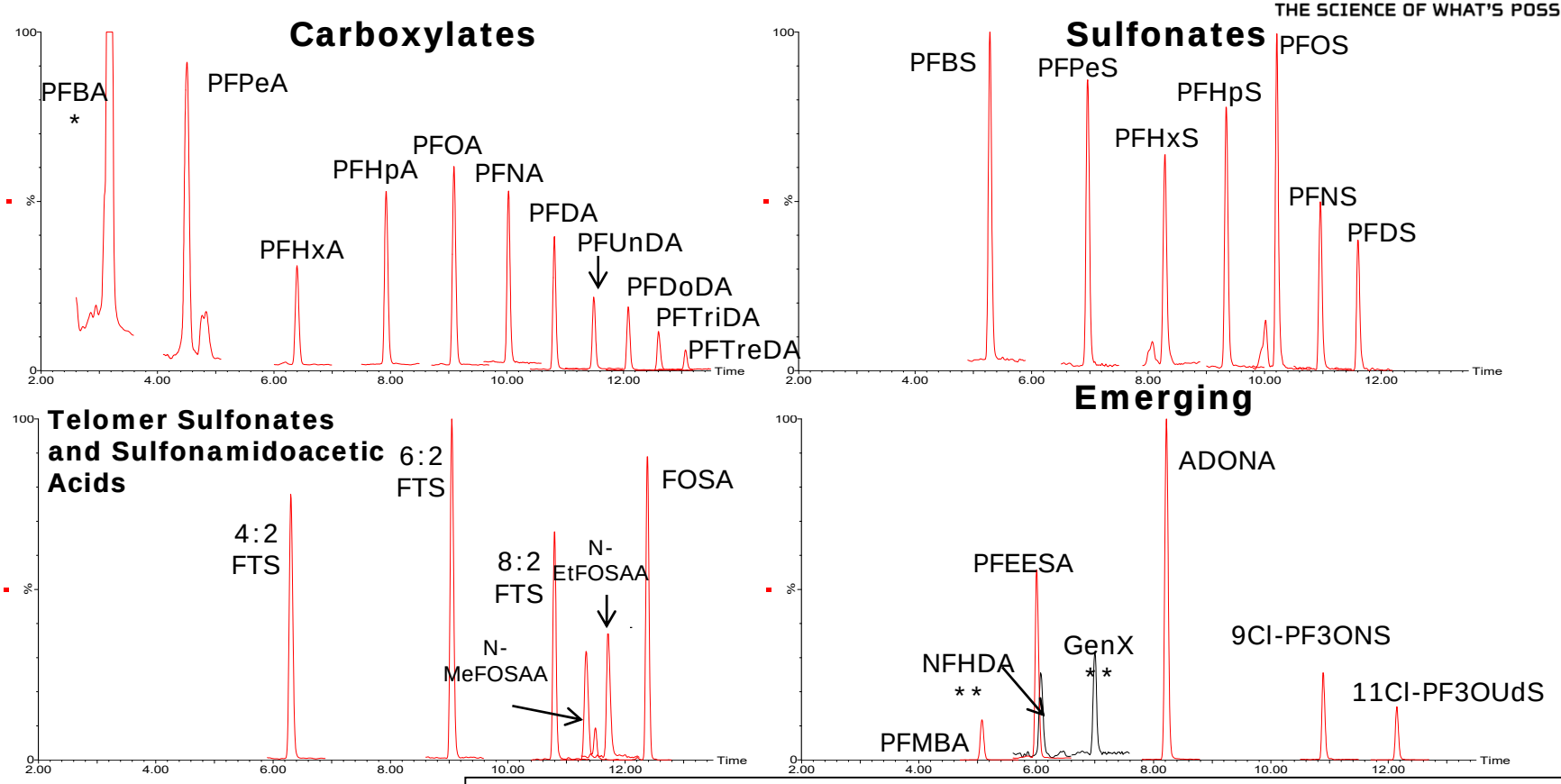
Overall RSD: < 10 %

Spiked Surface Water



PFBA and PFPeA at 300 ng/L; 4:2, 6:2, and 8:2 FTS at 1200 ng/L; all other compounds at 60 ng/L. (*) this compound shown off scale.

Spiked Lean Clay Sample



(*) compound shown off scale (**) compound shown zoomed

Conclusions

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- PFAS are ubiquitous environmental contaminants that are detected around the globe
- Direct Injection approach can be applied to both water and soil samples
- Both ASTM 7979 (water) and ASTM 7968 (soil) are suitable for the basic range of PFAS normally monitored
- Limited sample preparation allows for higher throughput of samples
- New emerging PFAS can easily be incorporated into these methods

Acknowledgements

- EPA
  - Larry Zintek
  - Mark Strynar
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- Waters
  - Ken Rosnack
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