LC-MS/MS Analysis of Legacy and Emerging Perfluoroalkyl Substances (PFAS) in Environmental Water Samples Following SPE Enrichment

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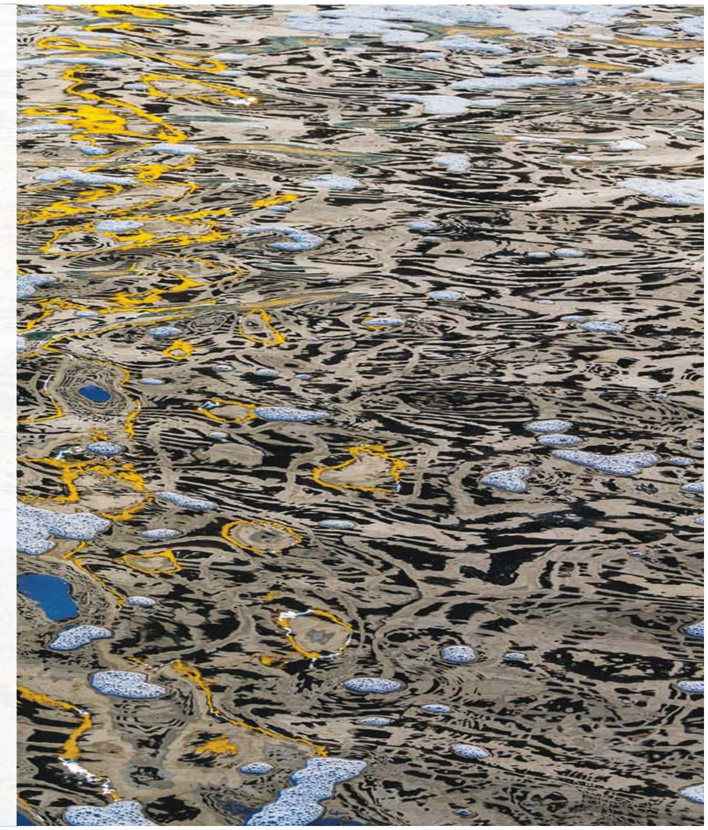
Perfluoroalkylated Substances (PFAS)

- 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**



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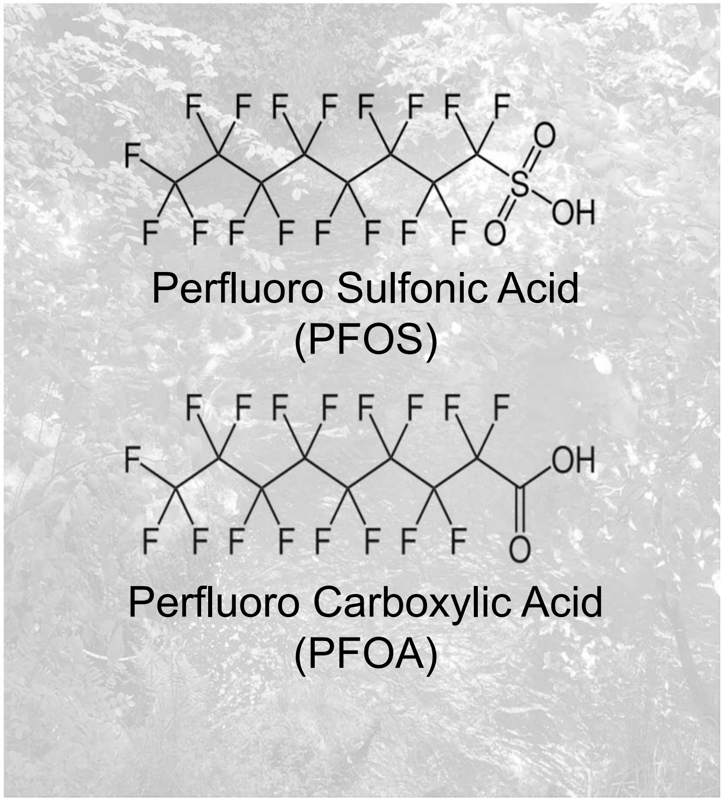
Perfluoroalkylated Substances (PFAS)

- 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…



Perfluoro Sulfonic Acid
(PFOS)

Perfluoro Carboxylic Acid
(PFOA)

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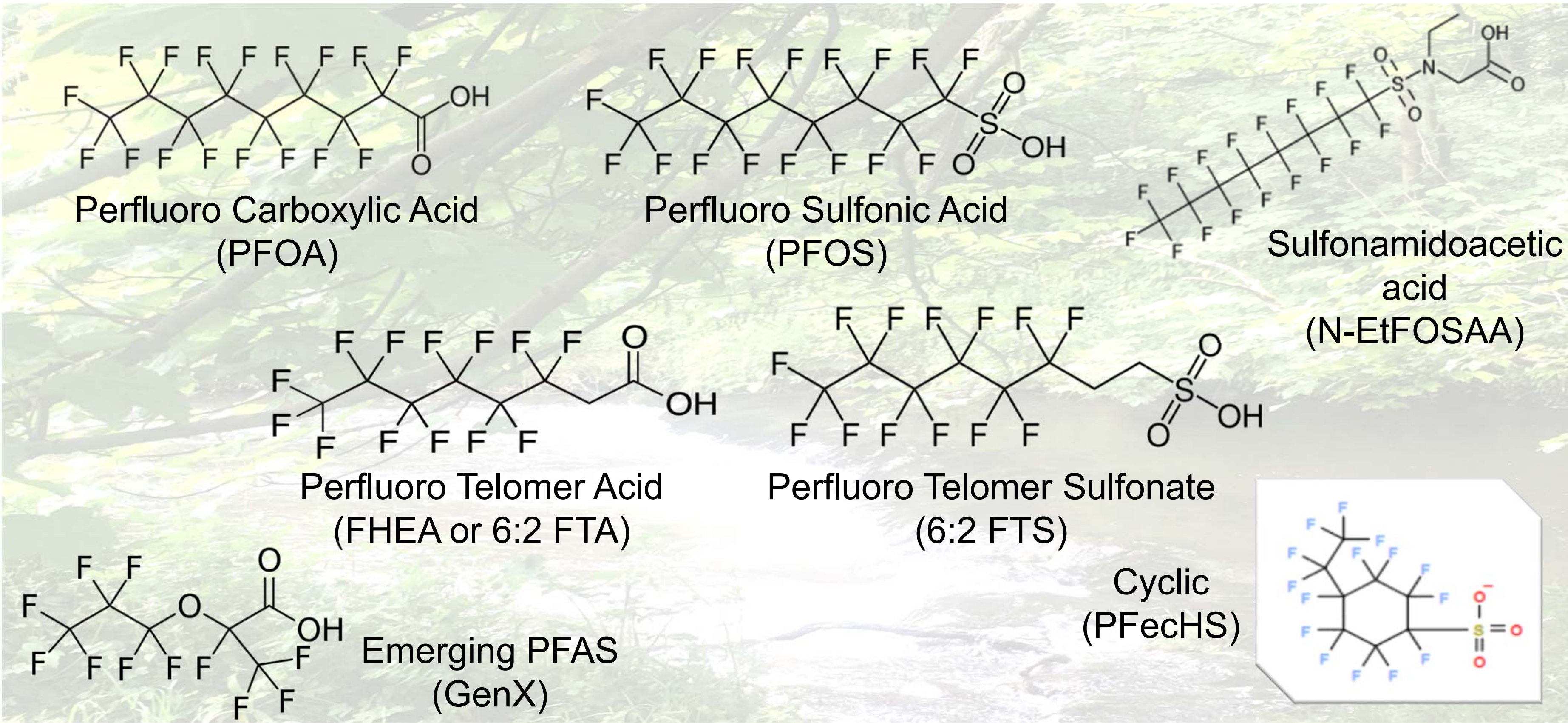
Thousands…



Worldwide 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.'

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

Report: PFAS chemicals found in Chipotle bowls

Posted: 12:51 PM, Aug 07, 2019 **Updated:** 3:13 PM, Aug 07, 2019

By: KOAA News5

The report found that Chipotle bowls all tested positive for PFAS, but it was unclear which specific PFAS the bowls were contaminated with. Chipotle issued the following statement to the New Food Economy in response to the story.

Part of that statement is provided below:

"Chipotle only partners with suppliers who make fluorochemical sciences and food safety a top priority. These suppliers operate under strict guidelines set forth by the FDA, and have provided Chipotle with certification that all raw material and finished pulp products fully meet the FDA regulatory guidelines for the safe use of only approved PFAS."

Options for the Analysis of Water Samples

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

Why do we need SPE for PFAS?

- EPA advisory limit currently set at **70 ng/L** (ppt) for total PFOA/PFOS
- States are creating their own policies for PFAS with stricter limits
  - Some as low as **10 ppt**
- European drinking water directive
  - **proposal** suggesting values of **100 ppt** for individual PFAS and **500 ppt** for total PFAS.
- European water framework directive (non-drinking water)
  - 0.65 ppt PFOS

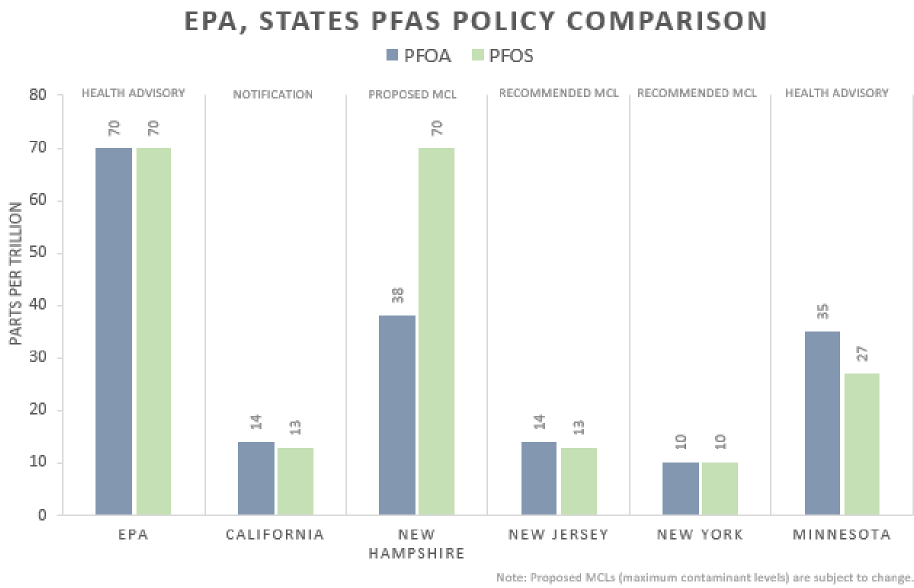


Image sourced from https://www.eenews.net/stories/1060123043

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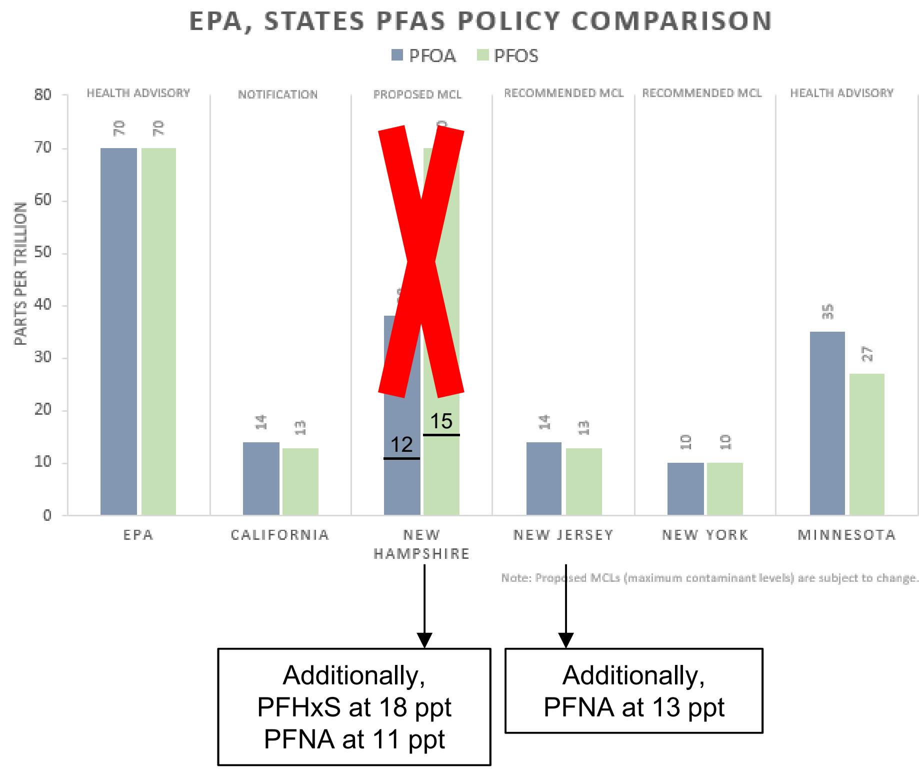

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Why do we need SPE for PFAS?

MATRIX!

Photo credit https://www.thisiscolossal.com/2017/06/polluted-water-popsicles/

SPE Enrichment for PFAS

Adapted from ISO 25101

ISO 21675 in development

Sample Preparation based on ISO 25101

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Prep Samples

Spike with surrogates

PH **adjust** to < 3

Filter with **glass fiber filters**

Condition

4 mL 0.5% ammonia/methanol

4 mL methanol

4 mL water

Load Sample

Rinse – 4 mL of 25 mM acetate buffer

Elute

4 mL methanol – waste

8 mL 0.5% ammonia/methanol → Dry to 0.5 mL

Dilute 1:1 with 2mM ammonium acetate

OASIS® SAMPLE EXTRACTION PRODUCTS

Oasis WAX cartridge
6 cc
150 mg

250x enrichment

Instrument Methods

Source Parameters

- Instrument: Xevo TQ-S micro
- Ion Mode: ESI-
- Capillary Voltage: 0.5 kV
- Desolvation Temperature: 350° C
- Desolvation Flow: 900 L/hr
- Cone Flow: 100 L/hr

MS Method

- Developed using QuanOptimize
  - MRMs, CV, CE
- Divert flow to waste from 16 – 21.5 mins

LC Method

- Instrument: Acquity I Class PLUS with **PFAS Kit**
- Column: ACQUITY BEH C_{18} 2.1mm x 100 mm, 1.7 µm
- Mobile Phase A: 95:5 H_2O:MeOH + 2 mM ammonium acetate
- Mobile Phase B: MeOH + 2 mM ammonium acetate
- Injection Volume: 10 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

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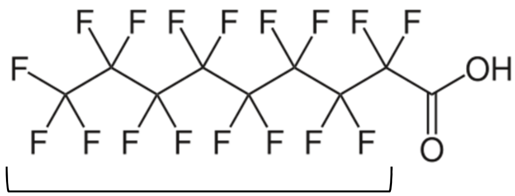
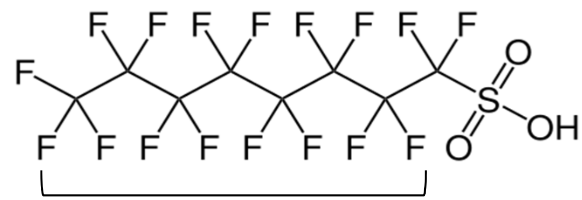
Carboxylates



C4 – C14

Sulfonates



C4 – C10

Emerging

GenX
ADONA
11Cl-PF3OUdS
9Cl-PF3ONS
PFEESA
NFHDA
PFMBA

Others

4:2/6:2/8:2 FTS
FHEA/FOEA/FDEA
FHUEA
FHpPA
FOUEA
PFecHS
diPAP
NMeFOSAA/NEtFOSAA

Detection Limits

Compound	DL vial (ng/L)	DL sample (ng/L)	R^2
PFBA	10	0.04	0.999
PFPeA	10	0.04	0.999
PFHxA	10	0.04	0.999
PFHpA	5	0.02	0.999
PFOA	< 2	< 0.01	0.999
PFNA	10	0.04	0.999
PFDA	10	0.04	0.999
PFUnDA	10	0.04	0.999
PFDoDA	10	0.04	0.999
PFTriDA	10	0.04	0.993
PFTreDA	10	0.04	0.999
PFHxDA	500	2.00	0.994
PFOcDA	2000	8.00	0.988
PFBS	4.4	0.02	0.999
PFPeS	4.7	0.02	0.999
PFHxS	3.7	0.01	0.999
PFHpS	9.5	0.04	0.999
PFOS	3.65	0.01	0.999
PFNS	4.8	0.02	0.999
PFDS	9.6	0.04	0.999

Compound	DL vial (ng/L)	DL sample (ng/L)	R^2
N-EtFOSAA	10	0.04	0.999
N-MeFOSAA	5	0.02	0.999
FHUEA	5	0.02	0.999
FOUEA	5	0.02	0.999
8:2 diPAP	500	4.00	0.997
4:2 FTS	23.4	0.09	0.999
6:2 FTS*	< 95	< 0.38	0.999
8:2 FTS	9.6	0.04	1.000
PFecHS	9.2	0.04	0.999
FHEA	20	0.08	0.999
FOEA	8	0.03	0.999
FDEA	20	0.08	0.999
FHpPA	5	0.02	0.999
GenX	20	0.08	0.999
ADONA	< 2	< 0.01	0.999
9Cl-PF3ONS	< 1.9	< 0.01	0.999
11Cl-PF3OUdS	9.42	0.04	0.996
NFHDA	5	0.02	0.999
PFEESA	< 2	< 0.01	0.999
PFMBA	< 2	< 0.01	0.999

Linearity and Sensitivity

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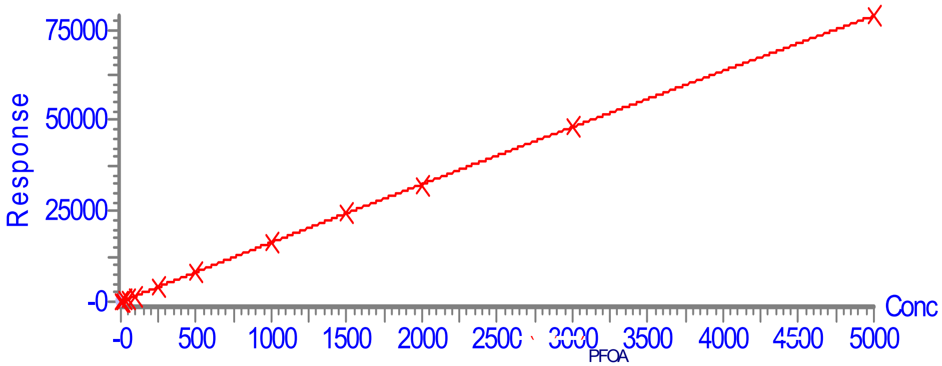
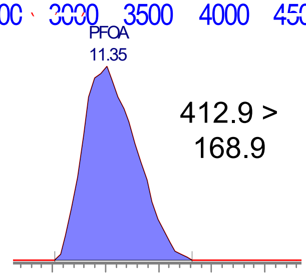
PFOA

R^2 = 0.9999
2 – 5000 ng/L (vial)
0.008 – 20 ng/L (sample)



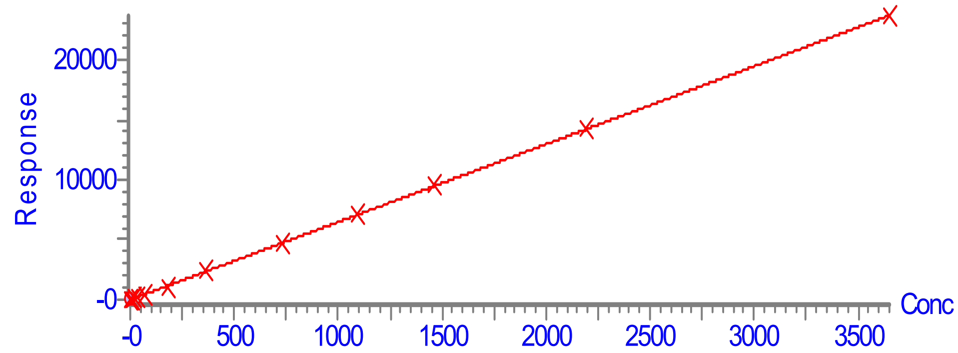
0.008 ng/L (sample)
2.0 ng/L (vial)



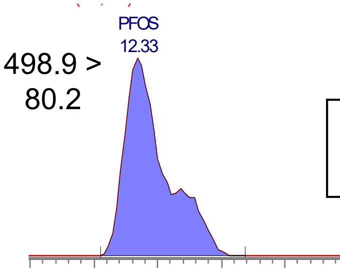
412.9 > 168.9

PFOS

R^2 = 0.9998
3.65 – 3650 ng/L (vial)
0.015 – 14.6 ng/L (sample)



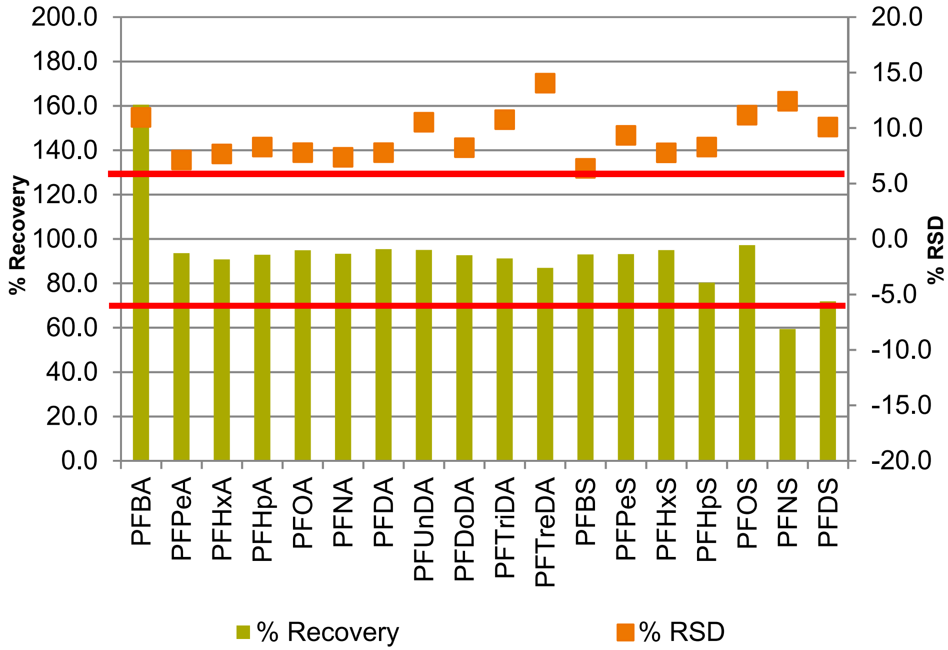
498.9 > 80.2



0.015 ng/L (sample)
3.65 ng/L (vial)

Recovery and Method Repeatability

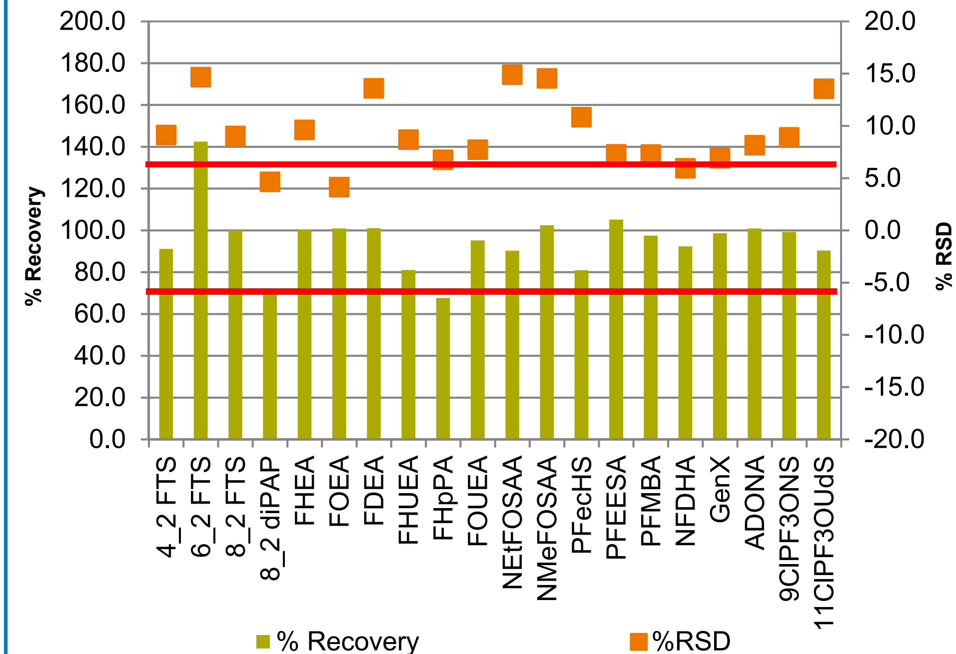
Carboxylates and Sulfonates



Overall Recoveries: **75 – 130%**

*PFBA, 6:2 FTS > 200% - common contaminants

Other Compounds

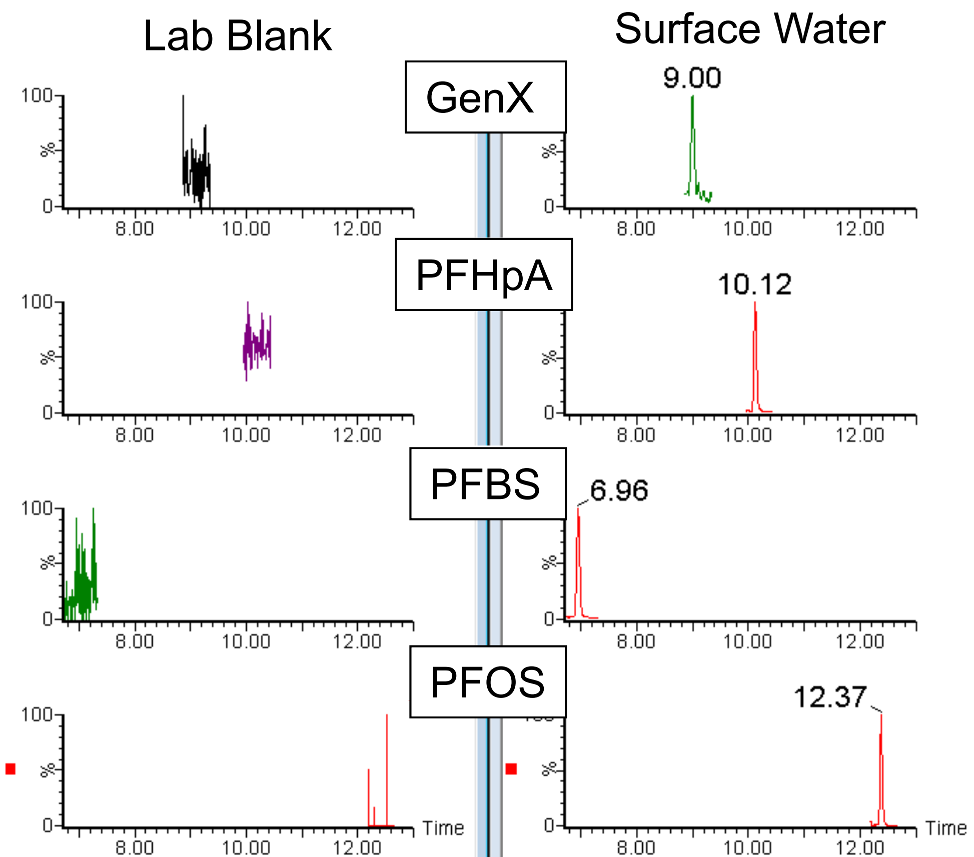


Method RSD calculated from n=5 extractions of ground water.

Overall RSD: **< 15 %**

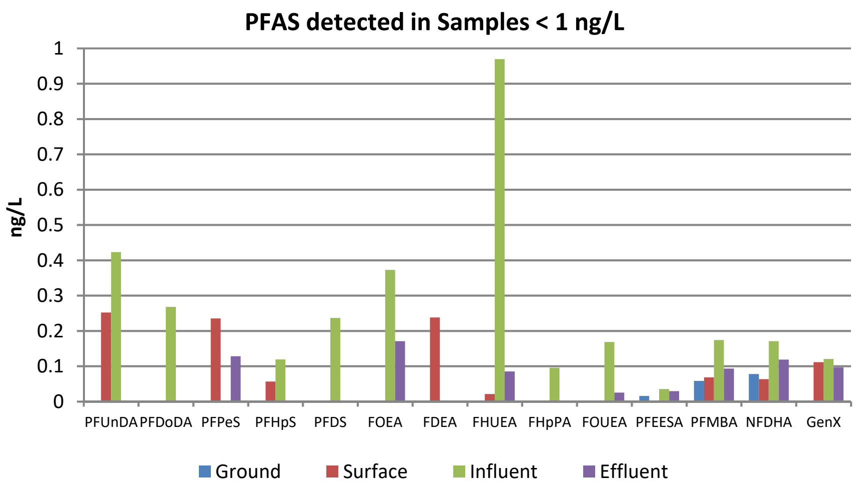
Environmental Water (Unknown) Samples

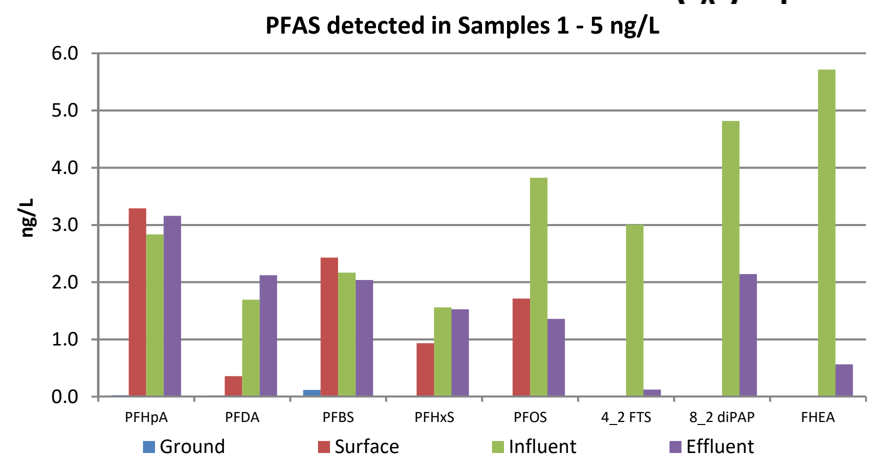
Surface Water example

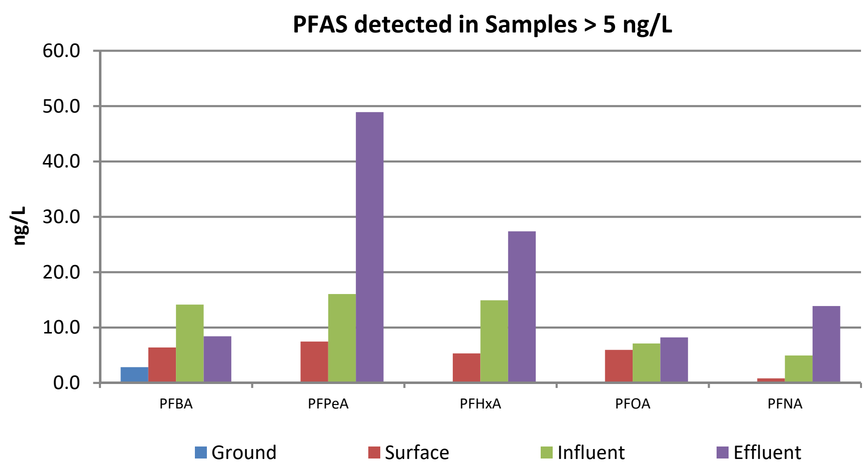


Compound	Conc vial (ng/L)	Conc sample (ng/L)
FHEA	< 8	< 0.32
FHUEA	< 2	< 0.008
GenX	43.6	0.2
N-EtFOSAA	< 2	< 0.008
PFBA	22000	88.0
NFHDA	10.93	0.04
N-MeFOSAA	< 2	< 0.008
PFBS	607.8	2.4
PFDA	88.1	0.4
PFHpA	818.8	3.3
PFHpS	10.77	0.04
PFHxA	1327.6	5.3
PFHxS	228.5	0.9
PFMBA	9.88	0.04
PFNA	204.4	0.8
PFOA	1485	5.9
PFOS	420.2	1.7
PFPeA	1861.5	7.4
PFPeS	59.1	0.2
PFUnDA	61.1	0.2
PFecHS	5.2	0.02

PFAS detected in all water samples







Conclusions

- PFAS are ubiquitous environmental contaminants that are detected around the globe
- Solid Phase Extraction (SPE) provides significant sample enrichment allowing detection at sub parts per trillion (ppt) levels
- The ISO 25101 method was successfully adapted for a basic range of legacy PFAS normally monitored as well as new emerging PFAS
- Weak Anion Exchange (WAX) chemistry is best for extraction of a large range of PFAS from water samples

Acknowledgements

- EPA
  - Larry Zintek
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  - Lauren Mullin
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