Field and Laboratory Data on Per- and Polyfluoroalkyl Substances (PFASs) in Groundwater to Inform the Selection of Sampling and Storage Conditions

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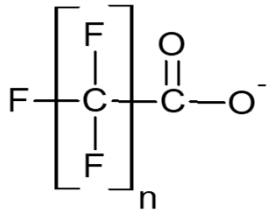
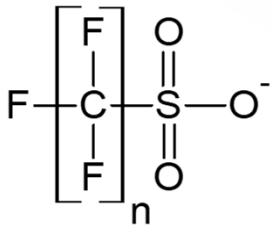
NEMC 2018

Background

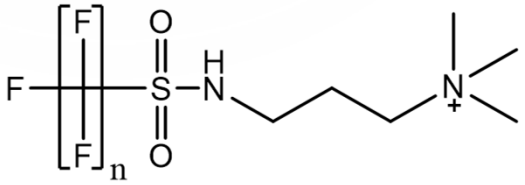
- Per- and Polyfluoroalkyl Substances (PFASs) chemistry
  - Carbon-fluorine chain attached to a polar head group
- Anthropogenic origins
- Applied in numerous sectors including consumer products, manufacturing processes, and in aqueous film forming foams (AFFFs) for suppression of hydrocarbon fuel fires
- **Potentially 1000's of potential PFASs** as a result of proprietary mixtures & impure chemistries



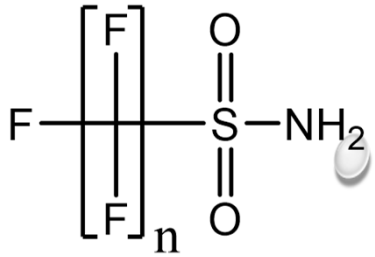
Ex. PFOA



Ex. PFOS



Ex. N-TAmP-FHxSA



Ex. FOSA

Consumer Products

Landfills

Manufacturing/ Production

WWTPs

Wastewater

Groundwater
Surface water
Drinking water

AFFF Application/Use

FTAs

Spill/Crash Applications

Manufacturing and Landfill photos from Stock Free Images

AFFF Impacted Groundwaters at Fire-Training Areas

- Aqueous Film-Forming Foams (AFFFs) are proprietary mixtures, commissioned by the US Military
- Fire-Training Areas
  - Used for fire-fighter training at military bases
  - Bi-monthly or monthly when active

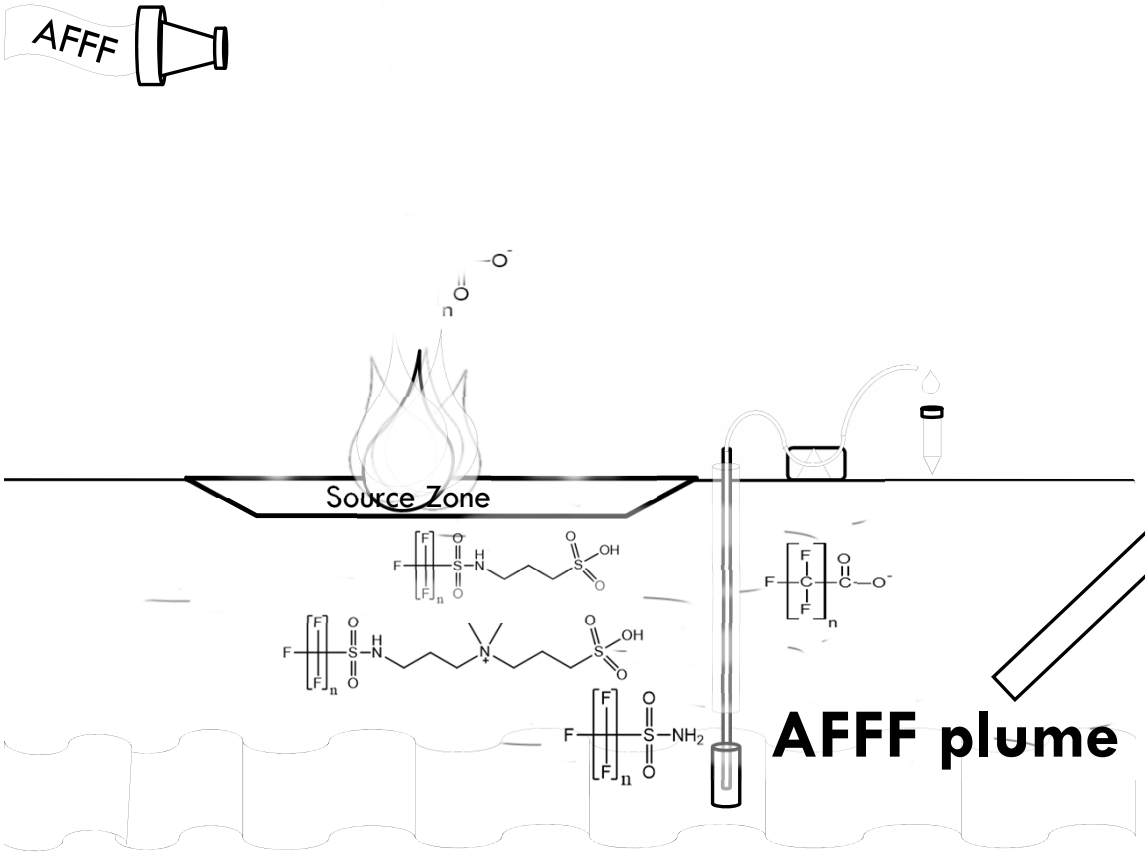
Photo Credit: Bill Gee

An example groundwater site:

Model from AECOM

- Site of AFFF spill and FTA where fire-training activities occurred for >30 years
- Only depicts PFOS/PFOA contamination

Application of AFFF at a military site



Contamination!

- Local water bodies
  - e.g. wetlands, ponds
- Aquifer
  - Confined
  - Unconfined
- Drinking water sources
- Soil/Sediment

Impacted Drinking Water

- US EPA UCMR3 program- 3 PFSAs & 3 PFCAs
  - ✓10-35% increase risk to exposure if military site located in watershed[1]
  - ✓6 million in US exceed EPA's lifetime HA 0.07 mg/L
- Drinking water important source of human exposure to short-chain PFASs[1-3]

[1]Gyllenhammar et al. 2015 Environ Res 140:673-683;[2]Eschauzier et al. 2013 Sci Tot Environ 458:477-485;[3]Weiss et al. 2012 Intl Hyg Environ Health 215:212-215;[4]Hu et al. 2016 ES&T Letters

Modified from EC Presentation 2018

Regulation in the U.S.

- Health Advisory Limits set by the US EPA as 70ng/L for PFOS and PFOA or a combination of PFOS and PFOA (May 2016)
  - Drinking water only
- Not enforceable
- Set based on non-cancer endpoints
  - Reduced birthweight (PFOS), developmental effects in bones, accelerated puberty (PFOA)

Analytical Methodologies for Drinking Water

Analyte	Acronym	Chemical Abstract Services Registry Number (CASRN)
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	–
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	–
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8

https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=198984&simpleSearch=1&searchAll=EPA%2F600%2FR-08%2F092+

- Method 537 (14 PFASs)
- Third unregulated contaminant monitoring rule (UCMR 3)
  - 6 of 21 contaminants

Method 537

- Drinking water method
- Modifications required for other matrices
- Method 537 requires use of solid phase extraction cartridge composed of styrene divinylbenzene (SDVB) for extraction
  - ✓reverse-phase (not ion exchange)
  - ✓performs poorly for short-chain PFASs (reason why C4 and C5 not in Method 537)

✓Limited number of analytes (14)

Method 537 Rev 1.1 Analytes

- 9 PFCAs (6-14)
- 3 PFSAs (4,6,8)
- 2 sulfonamido acetic acids

UCMR3:

- 3 PFSAs (4,6, & 8)
- 3 PFCAs (C7, C8, C9)

[1]United Nations Environment Program (UNEP) Chemicals Branch, April 2015, Geneva; https://www.epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf

Modified from EC Presentation 2018

Groundwater Sampling, Storage, and Stability

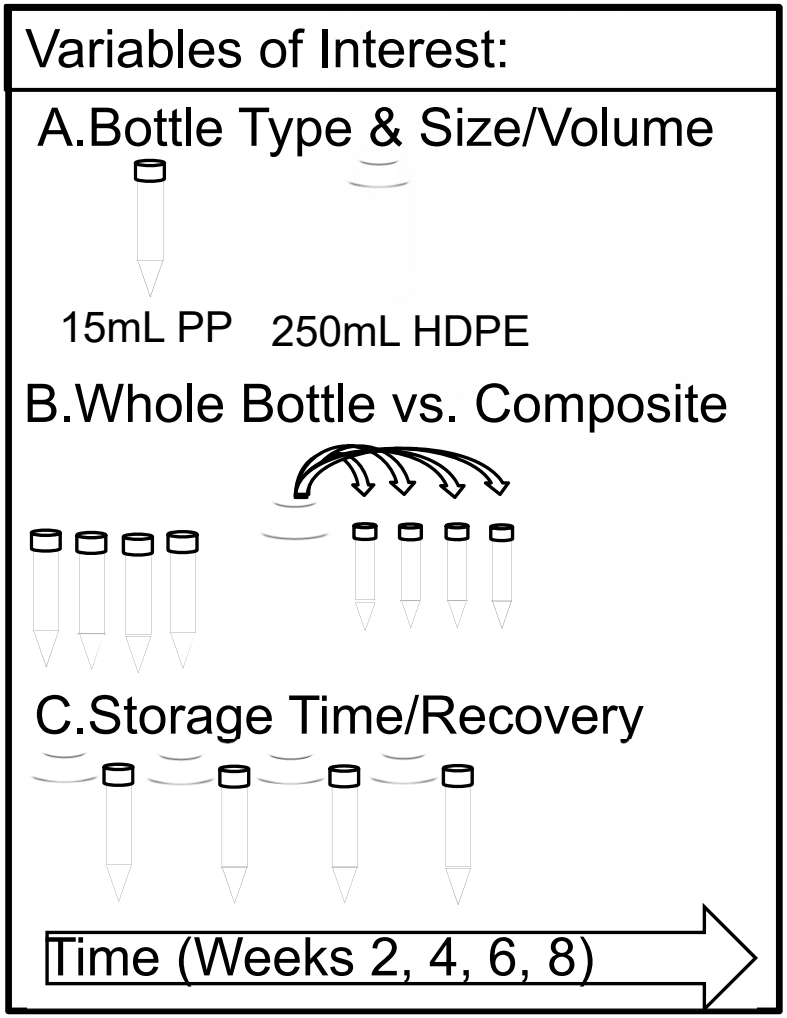
Rationale

There are few data to support many of the prescribed materials and steps in guidance provided by military on field collection for PFASs.

Few studies address sources of contamination that occur in the field due to handling and materials.

Few studies document stability under various storage conditions.

Objectives



1.Quantify variability in PFAS concentrations as a function of bottle type and sample volume

- PP and HDPE
- 15mL and 250mL

2. Quantify PFAS concentrations for whole bottle vs. sub-sampling

3.Quantify PFAS concentrations for up to 8 week at 4°C

Micro Liquid-Liquid Extraction into Organic Solvent

1) Add 10 µL 6M HCl to 3mL Groundwater Sample

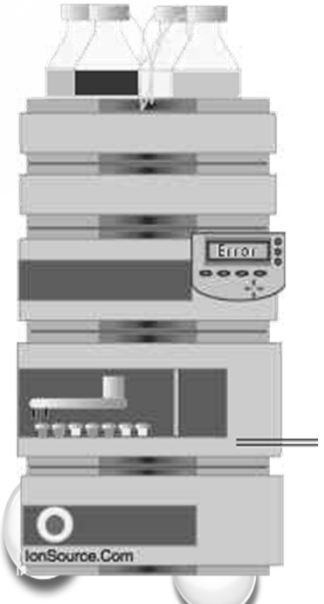
2) Saturate Groundwater with NaCl (~ 1 g)

3) Spike Internal Standards

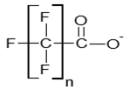
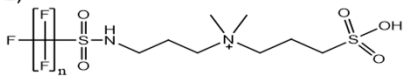
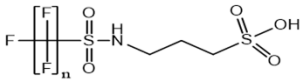
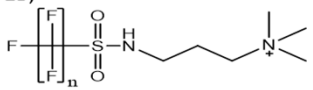
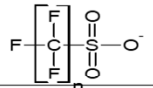
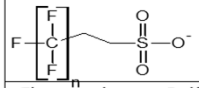
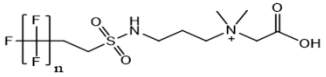
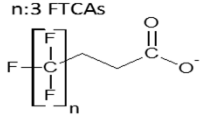
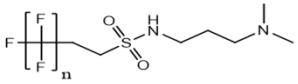
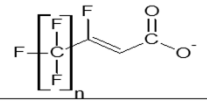
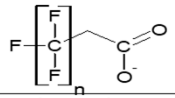
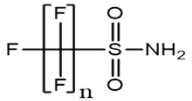
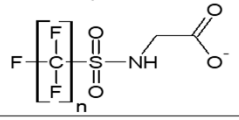
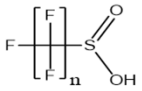
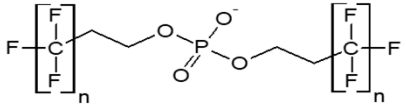
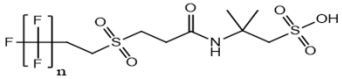
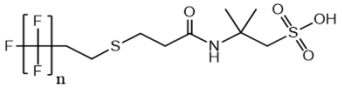
4) Extract 3x
10% TFE/90% EtOAc (1 mL)

4) Bring to 1.5 mL with MeOH

5) Inject 900 µL by LVI



Analytes of Interest

Compound Class	n	Compound Class	n
Perfluoroalkyl carboxylates (PFCAs) 	4-14	N-Sulfopropyldimethylammonio Propyl Perfluoroalkanesulfonamide (N-SPAmP-FASA, Class 2) 	4-6
N-Sulfopropyl perfluoroalkane Sulfonamide (N-SP-FBSA, Class 1) 	4-6	N-Trimethylammoniopropyl Perfluoroalkanesulfonamide (N-TAmP-FASA, Class 13) 	4-6
Perfluoroalkyl sulfonate (PFSAs) 	4-10	N-Methyl/Ethyl Fluoroalkyl sulfonamido acetic acids (EtFASAA) 	8,8
Fluorotelomer sulfonate (FtSs) 	4,6,8	Fluorotelomer carboxylates	
Fluorotelomer Sulfonamido Betaines (n:2 FtSAB) 	6	n:3 FTCAs 	5
Fluorotelomer Sulfonamide Amine (n:2 FtSaAm) 	6	n:2 FTUCAs  n:2 FTCA 	6,4
Perfluoroalkane Sulfonamide (FASA) 	3-6,8	Fluoroalkyl sulfonamido acetic acids (FASAA) 	8
Perfluoroalkanesulfinate (PFASi) 	4-6,8	Di-Substituted polyfluorinated phosphate esters diPAP 	6/6
n:2 tridecafluoroalkyl Sulfonyl(SO2) Propanoamido-MethylpropylSulfonate (n:2 O2 FtTAoS) 	6,8		
Fluorotelomer Thioether Amido Sulfonates (FtTAos) 	6		

52 individual PFASs analyzed by LC-MS/MS!

Materials Study

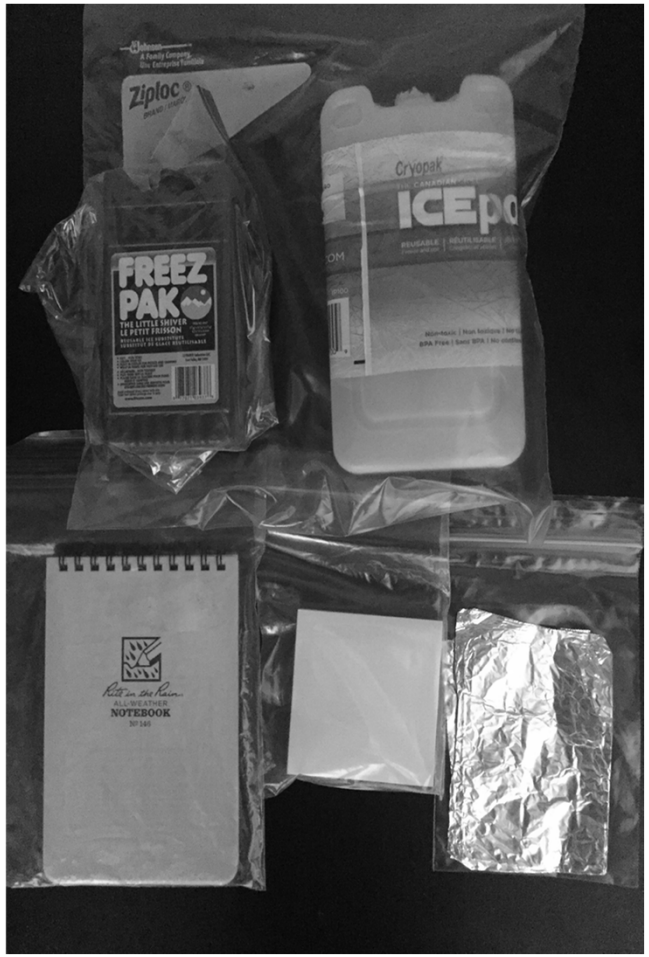
Rationale for materials

Many guidance documents make recommendations for avoidance or inclusion of various materials with little supporting data.

Extraction vs. Leaching

Methanol extraction represents “potential” for PFAS leaching.

Material Selection



- Selected some materials that have historically been avoided E.g.Blue ice, sticky notes
- Materials that are regularly used in the field (consultation with consultants/field engineers)
- Samples of convenience
  - Not a market basket study

Solid Materials

Type	Number/Type
Binder	1
Aluminum Foil	3
Teflon Tape	3
Ice Pack Outside	5
Post It	2
Label (sticker)	5
Rite in the Rain	1
Tape	4
Fabric Softner Sheet	3
Paper Towels	4
Nitrile Gloves	7
Core bag	1
Vinyl End Cap	1
PE bladder	1

Type	Number/Type
Kimwipe	5
Band Aid	2
Plastic Shovel	1
Plastic Bags	3
Writing Implement	3
Notebook Paper	3
Solid Putty Caulk	1
Solid Clear Resin	1
White Glue	1
Parafilm	1
MIP Membranes	1
PVC liner/screen	4
Core Catcher	2

Semi-Solid Materials

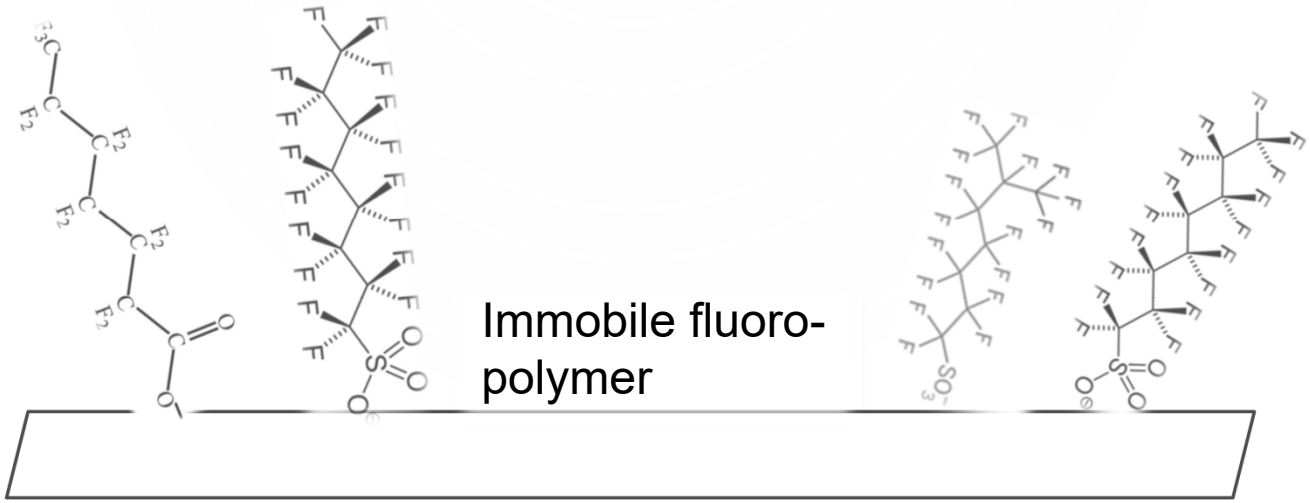
Type	Number/Type
Grease	2
Liquinox	1
Alconox	1
Writing inks	3
Glue	1
Ice Pack insides	5
Bug Spray	4
Poison ivy/oak treatment	3
sunscreen	5

Methods

- Methanol extraction as performed in Robel et al., 2017 with LC-MS/MS analysis used for groundwater extractions

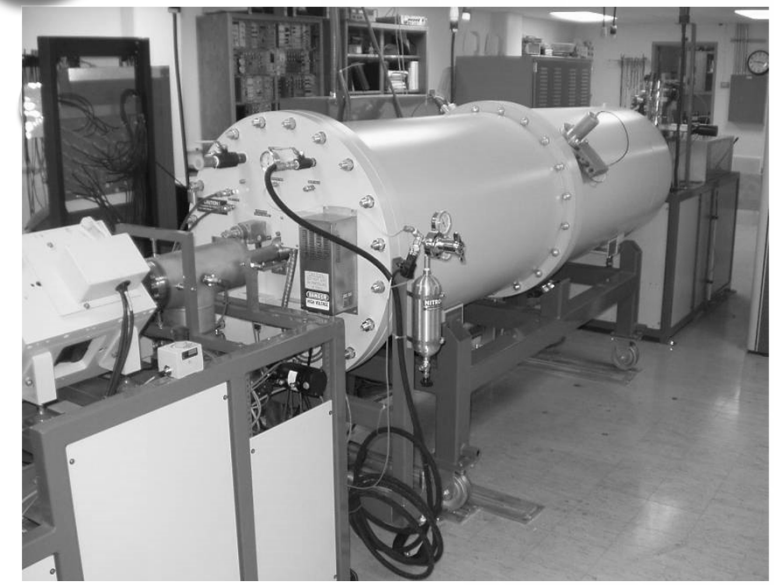
- PIGE for total fluorine

Material extraction- Robel et. al, 2017



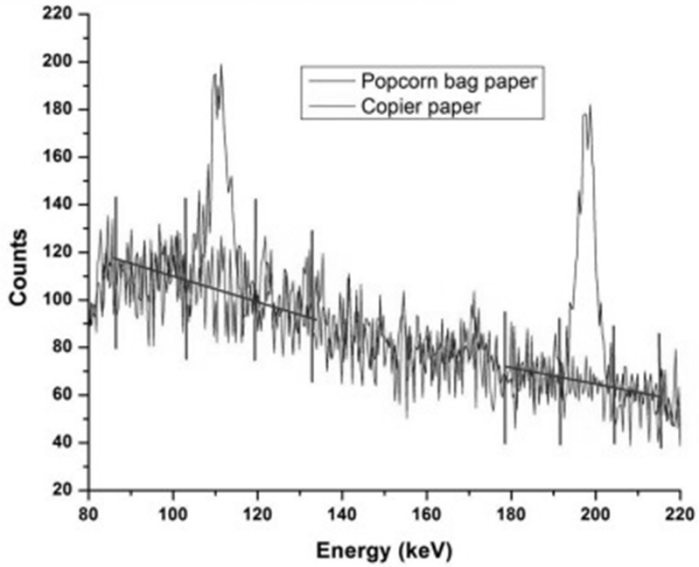
Extract generation: 0.3 ± 0.01g of material, 3.3mL methanol heated to 65°C added and shaken for 10min (x3), combined supernatant brought to 10mL in MeOH. 20x dilution in methanol, 900µL large volume injection

PIGE & Materials



- Excitation of light nuclei (F) results in nuclear excitation, emission of characteristic gamma rays
- Quantifies total fluorine (not individual PFASs)

- 2x2cm sample size, LOQ material dependent
  - 13 nmol F/cm(2) for papers and 24-45 nmol F/cm(2) for textiles
- 3 min analysis



Ritter, E. E.; Dickinson, M. E.; Harron, J. P.; Lunderberg, D. M.; DeYoung, P. A.; Robel, A. E.; Field, J. A.; Peaslee, G. F., PIGE as a screening tool for Per- and polyfluorinated substances in papers and textiles. *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms* **2017**, *407*, 47-54.

Conclusions

- **Extraction type (whole bottle vs. sub-sampling) play a more significant role** than material type (PP or HDPE).
- **Whole bottle extraction (15 mL PPE) is more effective than subsampling (250 mL HDPE)** for longer-chain PFASs including PFOS and PFNS whole bottle extraction reduces the variability in concentrations of longer-chain PFASs.
- **Hold times of 2 and 8 weeks at 4^0C provide equivalent data for Method 537 PFASs that were present in this groundwater sample (PFCAs, PFSAs).**

Acknowledgements

- This work was made possible through support of: Navy (ESTCP ER-201633) and AECOM (AFCEE BAA-12-001) as well as Oregon State University.