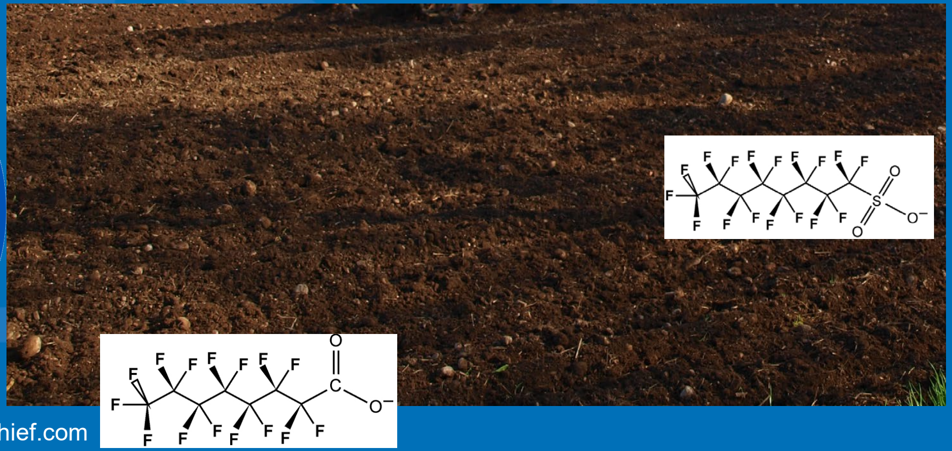
Identification of an Immobilization Technology for Per- and Polyfluoroalkyl Substances (PFAS) Contamination in Soil and Sediments



Pictures courtesy: Wikimedia Commons, Firechief.com

John McKernan, Sc.D., CIH; Ed Barth, Ph.D., PE, CIH; Carolyn Acheson, Ph.D.; Marc Mills, Ph.D.; Mark Johnson, PhD; Chunming Su, PhD; Diana Bless, MS; U.S. EPA, ORD

Diana Cutt; Robyn Henderek; Sharon Hartzell; U.S. EPA Region 2

Kavitha Dasu, Ph.D.; Ramona Iery, Ph.D.; Amy Dindal, PMP; Battelle Memorial Institute

United States Environmental Protection Agency

Disclaimer

- The findings and conclusions in this presentation have not been formally disseminated by the U.S. EPA and should not be construed to represent any agency determination or policy.

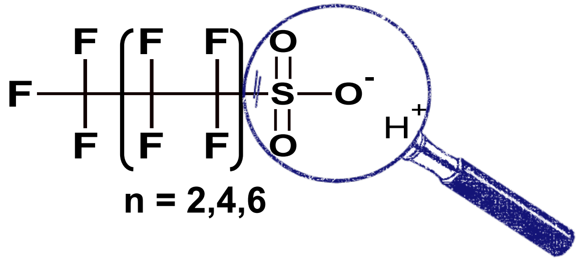
Outline

- What are PFAS?
- How are PFAS used?
- Where are they used?
- Production and transport
- Health effects and select U.S. regulatory activity
- Examination of treatment options
- What is solidification and stabilization
- Experimental background and methodology for studying sorbents for stabilization

United States Environmental Protection Agency

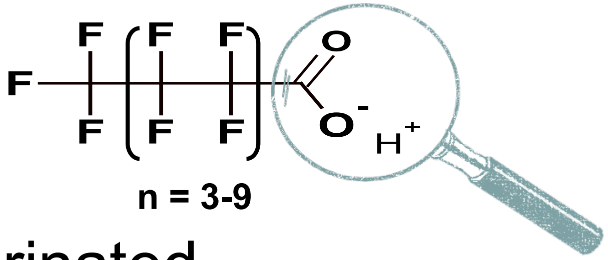
What are PFAS?

- Perfluorinated



Perfluorosulfonic Acids

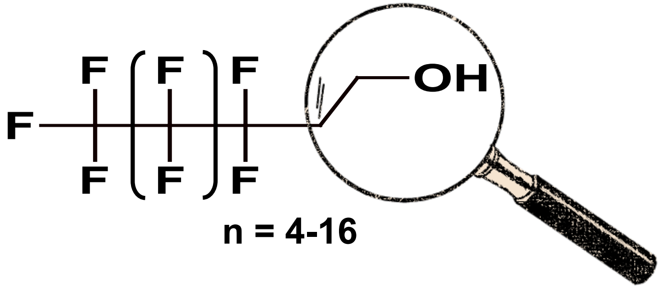
PFBS, PFHS, **PFOS**



Perfluorocarboxylic Acids

C_6 acid – C_{12} acid
PFOA C8 acid

- Polyfluorinated



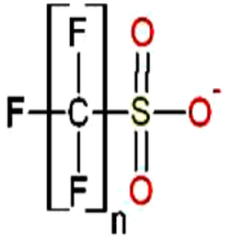
Fluorotelomer Alcohols – produced chemical and manufacturing residual

6:2, 8:2 and 10:2

United States Environmental Protection Agency

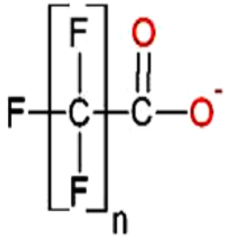
More Examples of PFAS

- **Perfluoroalkyl Sulfonates**



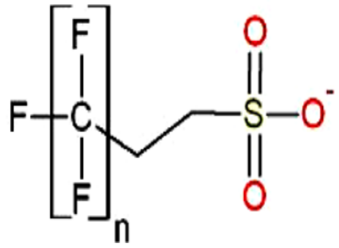
PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

- **Perfluoroalkyl Carboxylates**



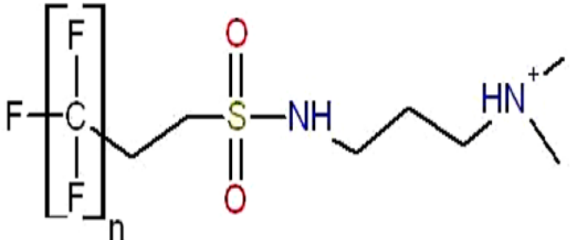
PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

- **Fluorotelomer Sulfonates**



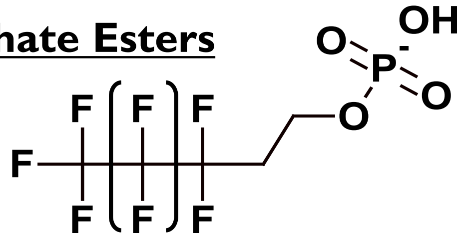
4:2 FtS	n = 4
6:2 FtS	n = 6
8:2 FtS	n = 8

- **Fluorotelomer Sulfonamides Amines**



6:2 FtSaAm	n = 6
8:2 FtSaAm	n = 8

- **Phosphate Esters**



n = 4,6,8

Backe et al. 2013 ES&T

How are PFAS used?

Physical and chemical properties:

- **Oil and water repellence**
- **Thermal stability and temperature resistance**
- **Friction reduction**

Products include:

- **Coatings for textiles, paper, surfaces, and cookware**
- **Thermal resistant plastics**
- **Hydraulic fluids**

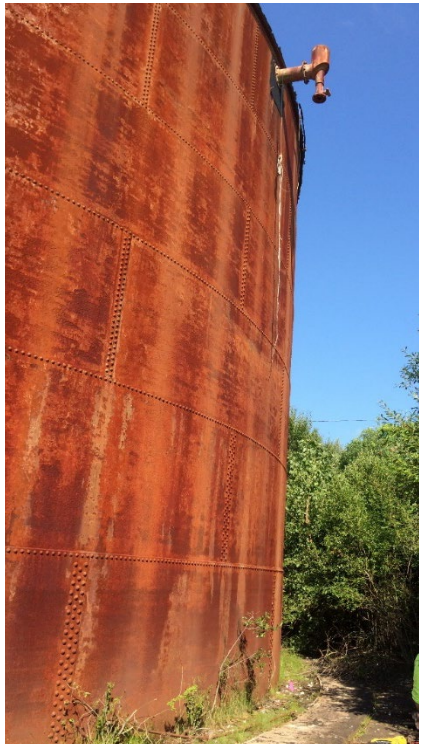
Where are PFAS used?

Manufacturing

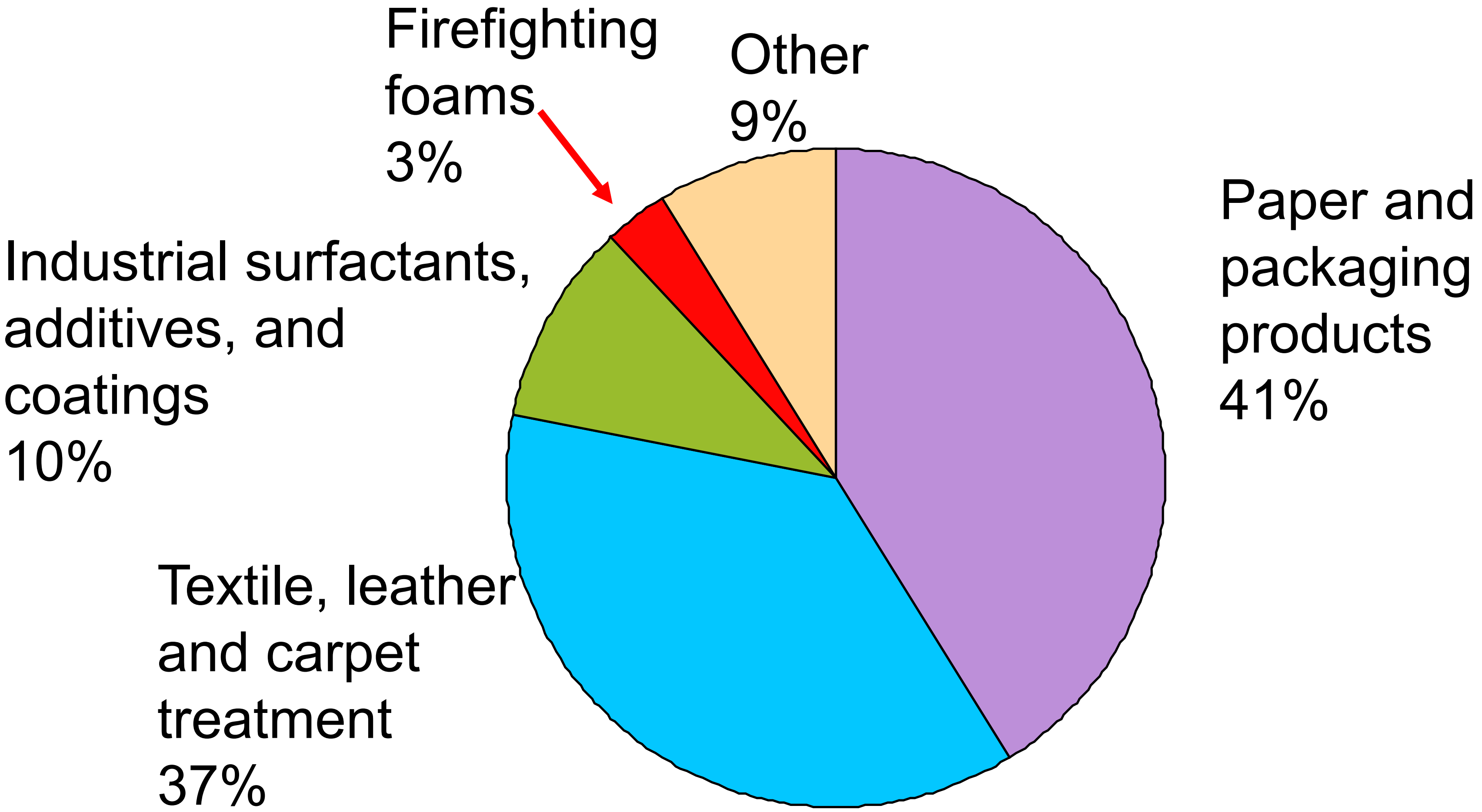
- **Primary manufacturing of PFAS products**
- **Secondary manufacturing and industrial use**
  - **Textiles and papers** – surface treatment to repel stains, oil, and water
  - **Plastics** – coatings, resins, and flame retardants
  - **Metal Plating and Etching** – corrosion prevention, mechanical wear prevention, fume suppressant, post-plating cleaner
  - **Photolithography, semi-conductor** – photoresists, etchants, wetting agents
  - **Aqueous Film Forming Foams** – fire suppression, fire training, flammable vapor suppression, and asphyxiation of diseased poultry CAFOs

Commercial and Consumer Use

- **Textiles and paper products**
- **Hydraulic fluids**
- **Surface preparation agents** - cleaning agents, polishes, paints, varnishes, dyes, and inks
- **Medical Products**

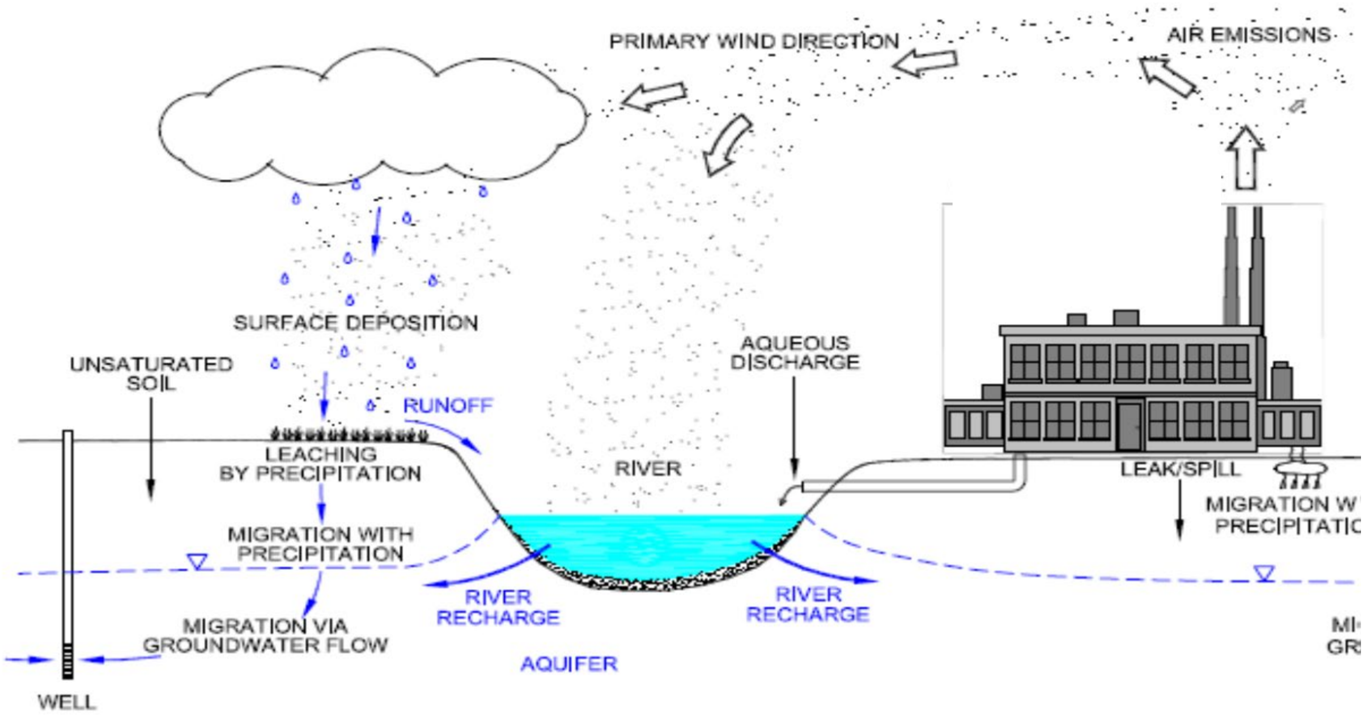


PFOS Production in 2000 by 3 M



Schultz et al, 2003 Env Engr Sci

Transport in the environment



- Air and water discharges can carry PFAS contamination
- PFAS may deposit on soil and sediment which then become a source
- Previous remediation activities may affect transport at a site
- Mobility dependent on
  - Chain length
  - Geochemistry of water and soil and sediment, especially pH
  - Hydrology of the site

PFAS Health Effects

- **PFOA and PFOS**
  - **Low birth weights for infants**
  - **Affects the immune and thyroid systems, cholesterol metabolism**
  - **Kidney and testicular cancer**

- **Other PFAS**
  - **Data gaps exist**
  - **Cross Agency Human Health/Toxicity work group - gather information from literature and conduct studies**
  - **Other parts of U.S. Govt. (ATSDR) evaluating PFAS toxicity**
  - **Other nations (e.g., Australia) also evaluating PFAS toxicity**

Levels of Concern

Selected Concentrations at Military Bases Sampled

Chemical	Ground Water/ Surface Water		Soil/Sediment (mg/kg)	
	US EPA	State X[d]	US EPA	State X[d]
PFOA	70 ng/L [a]	400 ng/L	1.26 [c]	1.6 to 0.0017
PFOS	70 ng/L [a]	400 ng/L	1.26 [c]	1.6 to 0.003
PFBS	380 µg/L [b]	-	1,600 [b]	-

a EPA 2016 “Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)”, EPA 2016 “Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)”

b EPA 2016 Regional Screening Level. https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016

c EPA risk-based screening levels calculated using the EPA Regional Screening Level calculator at https://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search . (US EPA, OLEM)

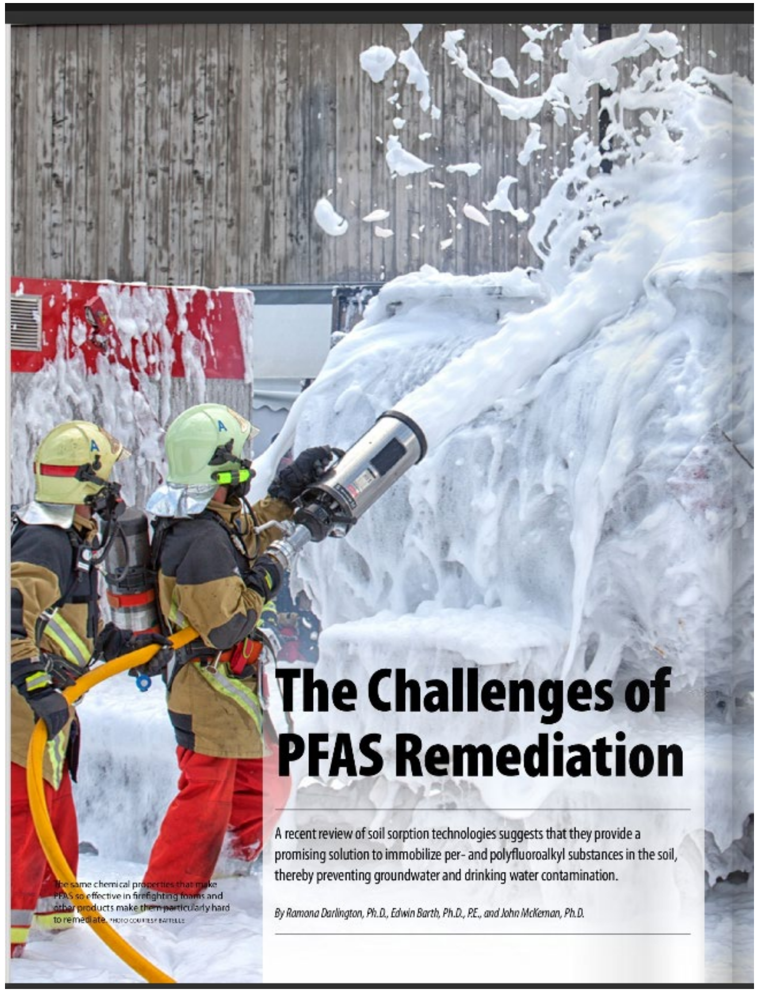
d State X. 2016.

United States Environmental Protection Agency

Why Examine PFAS Treatment Options?

- The problem seems insurmountable!
  - Industrial societies have used PFAS compounds since the 1940s-50s
  - They don't degrade substantially when released into the environment
  - Health implications – Prior slide on Levels of Concern
  - PFAS compounds are found in an ever increasing number of sites and media
- Treatment options
  - A number of treatment options have been suggested, but few are proven for use in the number of media found to be impacted
    - RO, activated carbon, and anion exchange resins are being used successfully to treat for PFAS in drinking water
  - Other media such as solids (soils and sediments) not studied thoroughly

PFAS Stabilization Literature Review

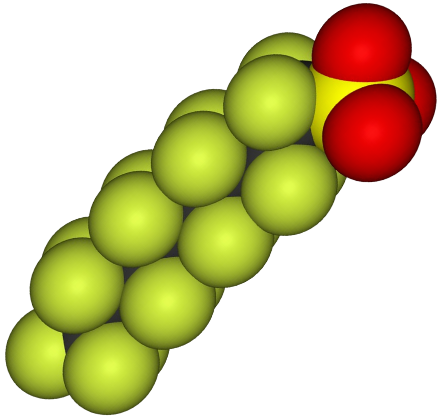


The Challenges of PFAS Remediation

A recent review of soil sorption technologies suggests that they provide a promising solution to immobilize per- and polyfluoroalkyl substances in the soil, thereby preventing groundwater and drinking water contamination.

By Ramona Darlington, Ph.D., Edwin Barth, Ph.D., P.E., and John McKernan, Ph.D.

The same chemical properties that make PFAS so effective in firefighting foams and other products make them particularly hard to remediate. PHOTO COURTESY BATTELLE



- Review of soil sorption technologies was conducted and published in The Military Engineer, Jan-Feb 2018 issue
- Literature review further indicated promise for the concept of binders to solidify PFAS in soil and sediment

http://themilitaryengineer.com/tme_online/TME_2018/2018JANFEB_online.pdf

Solidification/Stabilization Technology Application

- Solidification and stabilization (S/S) utilized at a number of Superfund contaminated sites since the program's inception
- Process where contaminated soil or sediment are 'contained' within a low-porosity matrix to reduce or eliminate leaching
- Immobilizes and encapsulates contaminants (does not destroy)
- Certain refuse materials from industrial processes can be 'beneficially reused' when concrete is used in the S/S process (e.g., fly ash)
- Low-porosity of treated, stabilized matrix keeps contaminants in the matrix and out of
    - Soils
    - Sediments
    - Surface water
    - Ground water

Experimental Approach for Testing Sorbents for S/S

Task 1
Task 1a Identify sorbents
Task 1b Sorbent Characterization

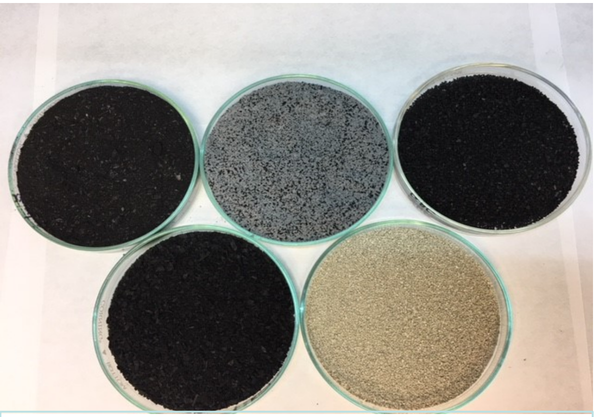
5 Sorbents plus control for initial screening

Task 2 (using PFAS mix)
Task 2a Sorbent Screening Kinetic study (5 sorbents plus Ottawa sand as control)
Task 2b Batch Sorption (1 sorbent)(out of 5 sorbents tested in Task 2a)

1 Sorbent selected for soil treatability study

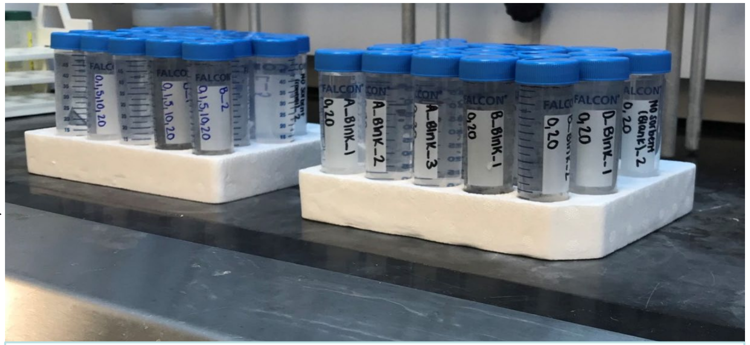
Task 3 (using PFAS mix)
Task 3a Physico-chemical properties of 2 PFAS-contaminated field soils
Task 3b Soil-Sorbent Treatability Studies using SPLP protocol in 2 PFAS-contaminated field soils plus Ottawa sand control

Sorbent Screening Kinetics Study



5 sorbents selected

5.0 mg: 50 mL sorbent to solution
0.01 M NaCl background electrolyte



Triplicates for all treatments including blanks and controls

Spike PFAS target analytes
Initial conc. 500 µg L^{-1}

Shaked at 125 rpm, 23±1ºC and sampled over 0-20 d

Sample dilution
Surrogates & Internal standard spiked

Analysis on LC-MS/MS

United States Environmental Protection Agency

Analytical Method and List of Six Native Analytes

- AB Sciex QTRAP 5500 Triple Quadrupole MS
- LC equipped with PEEK™ tubing and solvent delay column
- Negative electrospray ionization mode with MRM
- Column: Kinetex 2.6 µm C18 100 A 50 x 4.6 mm
- Run time: 10 minutes
- Quantitation Method: Isotope Dilution
- Dark blue – tested in kinetics studies

Native Analyte	Mass-labelled Surrogates	Internal Standards
PFBA	13C4-PFBA	13C3-PFBA
PFHxA	13C5-PFHxA	13C2-PFOA
PFOA	13C8-PFOA	13C2-PFOA
PFNA	13C9-PFNA	13C2-PFOA
PFBS	13C3-PFBS	13C4-PFOS
PFOS	13C8-PFOS	13C4-PFOS

Sorbent Screening Kinetics Testing

PFASs Tested

- **PFHxA**
- **PFOA**
- **PFNA**
- **PFBS**
- **PFOS**

5 Selected Sorbents

Activated Carbon

Biochar

Fe amended biochar

Trade name mineral binder 1 (B1)

Trade name mineral binder 2 (B2)

* Ottawa sand control

Sorbent Screening Kinetics Testing

Tested equilibrium concentrations (Isotherm/Partitioning) for all 5 sorbents

- Prepared solution of all 5 PFASs
- Added equal amount of solution to each of the 5 sorbents
- Determined concentrations of 5 PFASs left in solution after set time periods (2 hrs to > 400 hrs)
- B2 equilibrated after 24 hrs
- Others equilibrated at 120 hrs (5 days)

Sorbent Screening Kinetics Testing

Sorbents performed differently among the 5 PFASs tested:

- Surface area (BET and micropore) or Pore volume do not fully elucidate results
- pH, surface charge, hydrophobicity or other physicochemical effects may help in understanding results
- Better understanding of performance characteristics needed

Sorbents	pH
Act. Carbon	6.2
Biochar	7.0
Fe-Biochar	4.6
B1	5.2
B2	5.2
Ottawa Sand	4.7

Next Steps

- Continue reviewing Laboratory Isotherm/Partitioning study results
- Select sorbent for use in solidifying/stabilizing (S/S) two contaminated site soils from PFAS-contaminated sites (EPA Region 2 and EPA Region 8)
- Conduct EPA Synthetic Precipitation Leaching Procedure (SPLP) on these two S/S soils
- Analyze all data and prepare final technical report summarizing results of the tested sorbents to stabilize PFAS-contaminated field soils.