

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



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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



What are PFAS?



Perfluorosulfonic Acids

PFBS, PFHS, **PFOS**

Perfluorocarboxylic Acids

 C_6 acid – C_{12} acid **PFOA C8 acid**



<u>Fluorotelomer Alcohols</u> – produced chemical and manufacturing residual

6:2, 8:2 and 10:2



• Perfluoroalkyl Sulfonates



Perfluoroalkyl Carboxylates



Fluorotelomer Sulfonates



Fluorotelomer Sulfonamides Amines

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Backe et al. 2013 ES&T

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Environmental Protection



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



Regulatory Levels

Selected Concentrations for Military Base Sampled

Chemical	Ground Water/ Surface Water		Soil/Sediment (mg/kg)	
	US EPA	State X	US EPA	State X
PFOA	70 ng/L ^a	400 ng/L ^d	1.26 ^c	1.6 to 0.0017 d
PFOS	70 ng/L ^a	400 ng/L ^d	1.26 ^c	1.6 to 0.003 ^d
PFBS	380 µg/L ^ь	-	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. <u>https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016</u>

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 Department of Environment and Conservation. 2016.

United States Environmental Protection Why Examine PFAS Treatment Options?

- The problem seems insurmountable why bother?
 - 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 U.S. Regulatory Levels
 - 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 and Activated Carbon are two used to treat for PFAS in drinking water
 - Other media such as solids (soils and sediments) not studied thoroughly





PFAS Stabilization Literature



Review

- 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

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- Sediments
- Surface water







Experimental Approach for Testing Sorbents for S/S



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



Analysis on LC-MS/MS

Sample dilution Surrogates & Internal standard spiked



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



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

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



Schedule

- April: Identify, acquire, and characterize sorbents
- May: Conduct sorbent kinetics study and select one sorbent for future study
- June/July: Laboratory Isotherm/Partitioning study using two soils from PFAS-contaminated sites (EPA Region 2 and EPA Region 8)
- July/August: Soil Treatability study using synthetic Precipitation Leaching Procedure (SPLP) Test results
- September/October: Final technical report summarizing results of the tested sorbents to stabilize U.S. EPA PFAS-contaminated field soils.