

Actionable Science on Fate and Transport and Degradation and Remediation of Per- and Polyfluoroalkyl Substances
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Ethan Weikel, PG Deputy Director – USGS MD-DE-DC Water Science Center 5522 Research Park Drive Baltimore, MD 21228 Office: 443-498-5543 eweikel@usgs.gov	Brian P. Shedd, PG U.S. Army Corps of Engineers Geology and Investigations Section CENAB-ENG-G Baltimore District Office: 410-962-6648 Cell: 443-462-0337 Brian.P.Shedd@usace.army.mil
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U.S. Department of the Interior
U.S. Geological Survey

* All data in this presentation is provisional.

Characterization and Assessment of Remedial Effectiveness

- The USGS MD-DE-DC Water Science Center is collaborating with the US Army Corps of Engineers to research two critical needs related to PFAS.
- 1) Factors controlling fate and transport processes, and empirical determination of fate and transport parameters.
- 2) Potential methods for remediation using a robust microbial consortium and multiple biodegradation pathways.



Research Partners




Special thanks to:
Michelle Lorah, USGS MD-DE-DC Water Science Center
Brian Shedd, USACE Baltimore District




Factors controlling fate and transport processes, and empirical determination of fate and transport parameters

- This work, via award from SERDP, is being led and managed by the U.S. Army Corps of Engineers – Baltimore District.
- Fate and transport processes relevant to PFASs is identified as a critical priority research need.
- An evaluation approach that eliminates chemical unknowns and natural environmental variance helps meet this need.
- An approximately one-fifth scale physical aquifer model for testing and evaluation has been developed. Soils are from an uncontaminated area of a site for correlation with in-situ conditions.




Physical Aquifer Model for Testing and Evaluation

- In order to be able to properly characterize and evaluate remediation of PFAS plumes, critical fate and transport parameters and processes need to be understood.
- effect of gravity and potential for vertical partitioning of PFASs under lateral flow conditions
- sorption and transport attenuation of PFASs under “continuous” source conditions
- transverse vertical dispersivity and lateral dispersivity
- initial effect of matrix diffusion and subsequent breakthrough curves in saturated soil



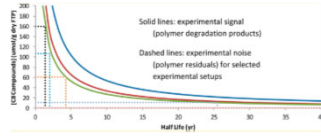
Why these parameters?

- In addition to basic parameters necessary for modeling, recent research has indicated, despite high solubility, “adsorption at the air-water interface [is] a primary source of retention for both PFOA and PFOS, ...~50% of total retention” (Brusseau, 2017)
- However this and other research uses parameters for PFOA and PFOS from literature on commercial products
- Aging and degradation in place, at some sites occurring over decades, could reasonably cause a significant change in the surface-active and sorptive properties.

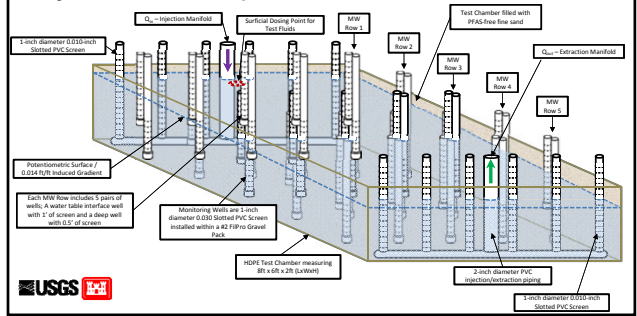


Age Matters (for PFASs)

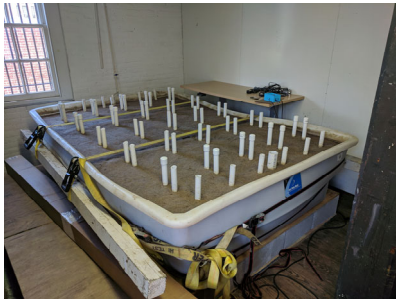
- Research into the degradation of PFASs (Washington et al., 2014) shows the impact of aging of fluorotelomer products.
- However the work by Washington et al., 2014 does not directly address in-situ aging and resulting impacts to sorption or retention at the air-water interface
- Using a physical model, the effects of aging of contaminants can be directly observed instead of relying on a mathematical model



Physical Model Set Up

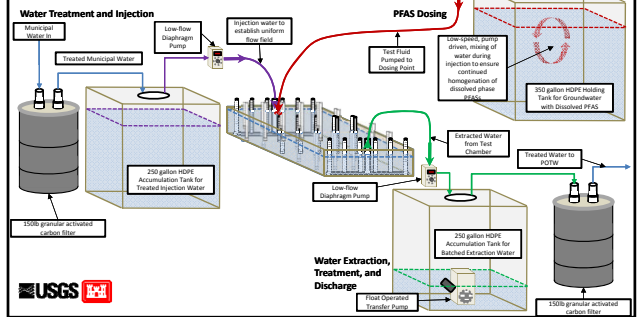


Physical Model Set Up



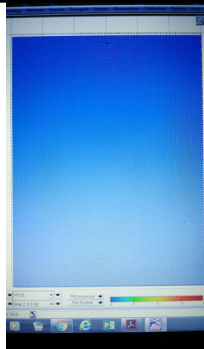
*Photo from U.S. Army Corps of Engineers Scaled Aquifer Facility for Testing and Evaluation (SAFTE) at Fort McHenry, Maryland

Injection, Dosing, and Extraction



Modeling prior to Testing

- Prior to beginning test flow in the physical aquifer was modeled with analytic element modeling using VisualAEM.
- Parameters
 - Hydraulic Conductivity: 30 ft/day
 - Hydraulic Gradient: 0.014 ft/ft
 - Aquifer Thickness: 1.5 ft
 - Porosity: 0.3
- Source/Transport Parameters
 - PFOS @ 2 mg/day for 1 day
 - M.W. 500.13 g/mol
 - Diffusion Coefficient of 0.0003069 ft²/day
 - Longitudinal to Transverse Dispersivity: 7.18:1
 - Duration: 23 Days
- Assumptions
 - Uniform flow field
 - No sorption, biodegradation, or matrix diffusion



Travel time longer than modeled.

Process and Data Collection during Testing

- Dissolved phase PFASs from contaminated site dosed at point source, while steady-state hydraulic gradient and lateral flow is maintained.
- Water sampling completed periodically based upon breakthrough time established by the tracer test.
- Continued sampling and analysis to assess attenuation and transport rates simulating apparent source removal.
- At peak concentrations a variety of sampling methods used to collect duplicate samples to evaluate effects of sampling methods on analytical result.



Specific Factors being Evaluated

- 1) Velocities of PFASs under controlled aquifer conditions versus conservative tracer.
- 2) Effect of gravity and vertical partitioning of PFASs .
- 3) Degree of sorption and transport attenuation of PFASs.
- 4) Transverse dispersivity of PFASs versus a conservative tracer.
- 5) Establish breakthrough curves in saturated soil for PFASs over time.
- 6) Establish effect of matrix diffusion on dissolved phase PFASs once source material is removed.

Results expected in January 2019.



Switching Gears - Potential methods for remediation of PFASs

- This work is funded by the USACE – Baltimore District and led and managed by USGS.
- The apparent recalcitrant nature of PFASs is a current roadblock to remediation.
- Methods of potential remediation including biotransformation has been identified as a critical research need.
- Technology transfer from the biotransformation of chlorinated and brominated compounds could help meet this research need.



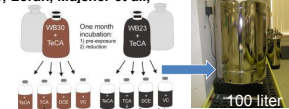
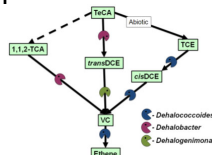
Research Direction

- With action levels and regulatory limits for PFASs in the low parts per trillion, remedial methods are urgently needed.
- In general what lessons can we learn from other contaminants that are difficult to remediate.
- Can some direct translations be made from methods for treating brominated and chlorinated compounds?
- Ability to quickly scale from the microcosm to pilot to full scale is important.



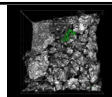
WBC-2 Microbial Consortium

- "WBC-2" is an enriched, mixed microbial consortium capable of degrading chlorinated VOCs, RDX, perchlorate, and other compounds to non-toxic end products (Jones et al., 2006; Lorah, Majcher et al., 2008; Lorah, Vogler et al., 2008)

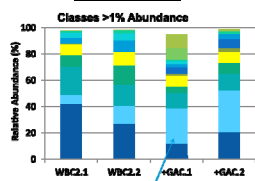
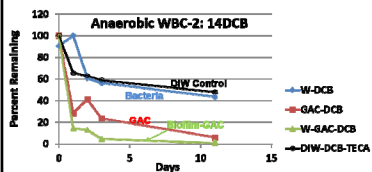


A nice place to live....

- The WBC-2 culture thrives on granular activated carbon.



WBC-2 on GAC (from Staci Capazzi, Univ. of Maryland)



Significant increase in Dehalococcolales on GAC.
f__Dehalococcolalesaez__Dehalococcolales
f__Dehalococcolalesaez__Dehalogenimonas



Microcosm treatments for PFASs

Several microcosm treatments in 164mL serum bottles with simulated groundwater, sGW.

Name	Description	Amendments			
		Lactate	WBC-2	PFAS	cVOC
LC	Site sediment and sGW				
SED1	Site sediment and sGW	✓		✓	✓
WSED	Site sediment and sGW	✓	✓		
WSED1	Site sediment and sGW	✓	✓	✓	✓
GAC	5% GAC in site sediment, sGW	✓		✓	✓
WGAC	5% GAC in site sediment, sGW	✓	✓	✓	✓
DI	Boiled, N ₂ -purged DI-H ₂ O			✓	✓



Microcosm Preparation

- 2:1 simulated groundwater: sediment
- cVOCs added:
 - 1,1,2,2-Tetrachloroethane (TeCA) = 1,000 µg/L
 - Trichloroethene (TCE) = 100 µg/L
- PFAS added:
 - PFOS = 100 µg/L
 - PFOA = 50 µg/L
 - 6:2 FtS = 100 µg/L
- WBC-2 added at 30 % by liquid volume or directly seeded onto GAC for 7 days
- Prepared and stored in anaerobic chamber, in box
- Manually shaken every work day

(Structure figures from ITRC Fact Sheet, 2018)

Methane Generation

Methanogenic conditions evident in the samples.

Microcosms - PFOA and 6:2FtS Results in Water

- PFOA and 6:2 FtS removal in GAC treatments, as expected.
- Awaiting sediment PFAS analytical data to discern sorption to GAC vs. biotransformation

Microcosms - PFOS Results in Water

- PFOS removal in two microcosms (SEDT and WSED) with sediment and with added cVOCs (with & without WBC-2)
- 25 to 45% PFOS removal (after accounting for loss in DI control)
- Microcosm with sediment and no added cVOCs (WSED) did not show consistent PFOS removal
- Microcosms with GAC, even more removal

Microcosms - cVOCs in Water and Sediment

- Faster cVOC degradation in WBC-2 bioaugmented sediment (WSED) and less daughter product accumulation
- cVOCs also degrade in natural site sediment (SEDT)
- Greatest PFOS removal in sediment microcosms with WBC-2 (WSED) where cVOC degradation was greatest.
- Apparent link between cVOC degraders and PFOS degraders.

Takeaways

- There is an apparent link between cVOC degraders and PFOS degraders (more research needed to identify specific metabolites).
- The combination of WBC-2 and GAC may be very effective at PFAS treatment.
- Bioremediation may have a viable role for PFASs.

More results expected in January 2019.

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Questions?

