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Actionable Science on Fate and Transport and Degradation and Remediation of Per- and Polyfluoroalkyl Substances

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* 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

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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)

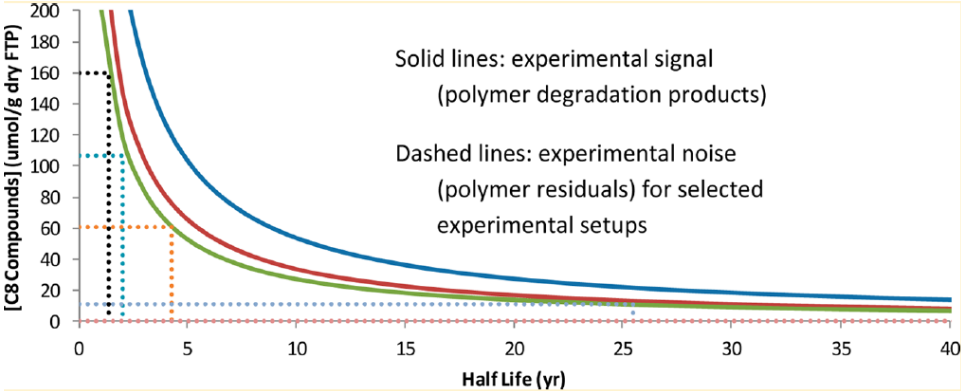
- However this and other research uses parameters for PFOA and PFOS from literature on commercial products

- 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)

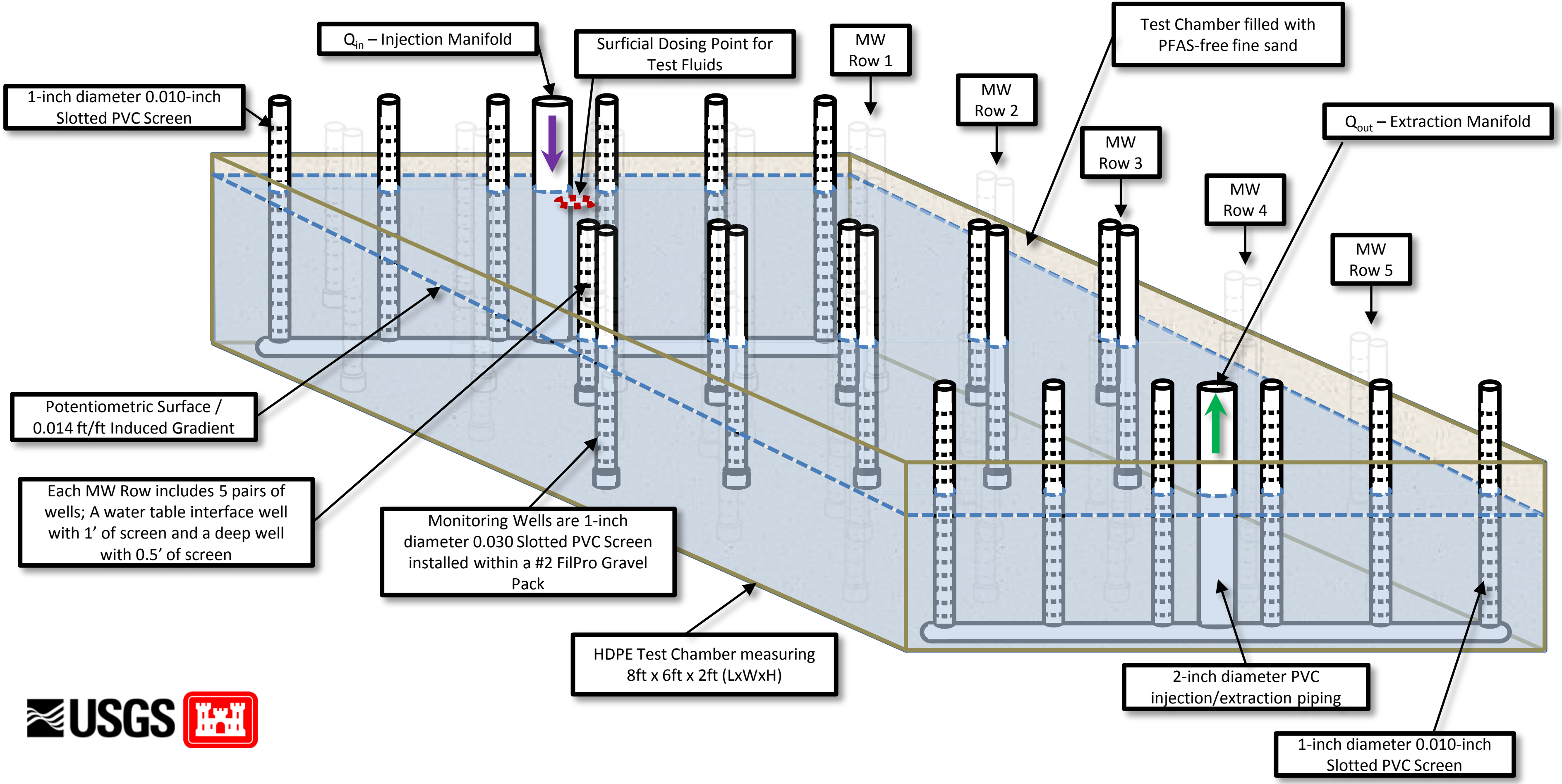
- Research into the degradation of PFASs (Washington et al., 2014) shows the impact of aging of fluorotelomer products.

- 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

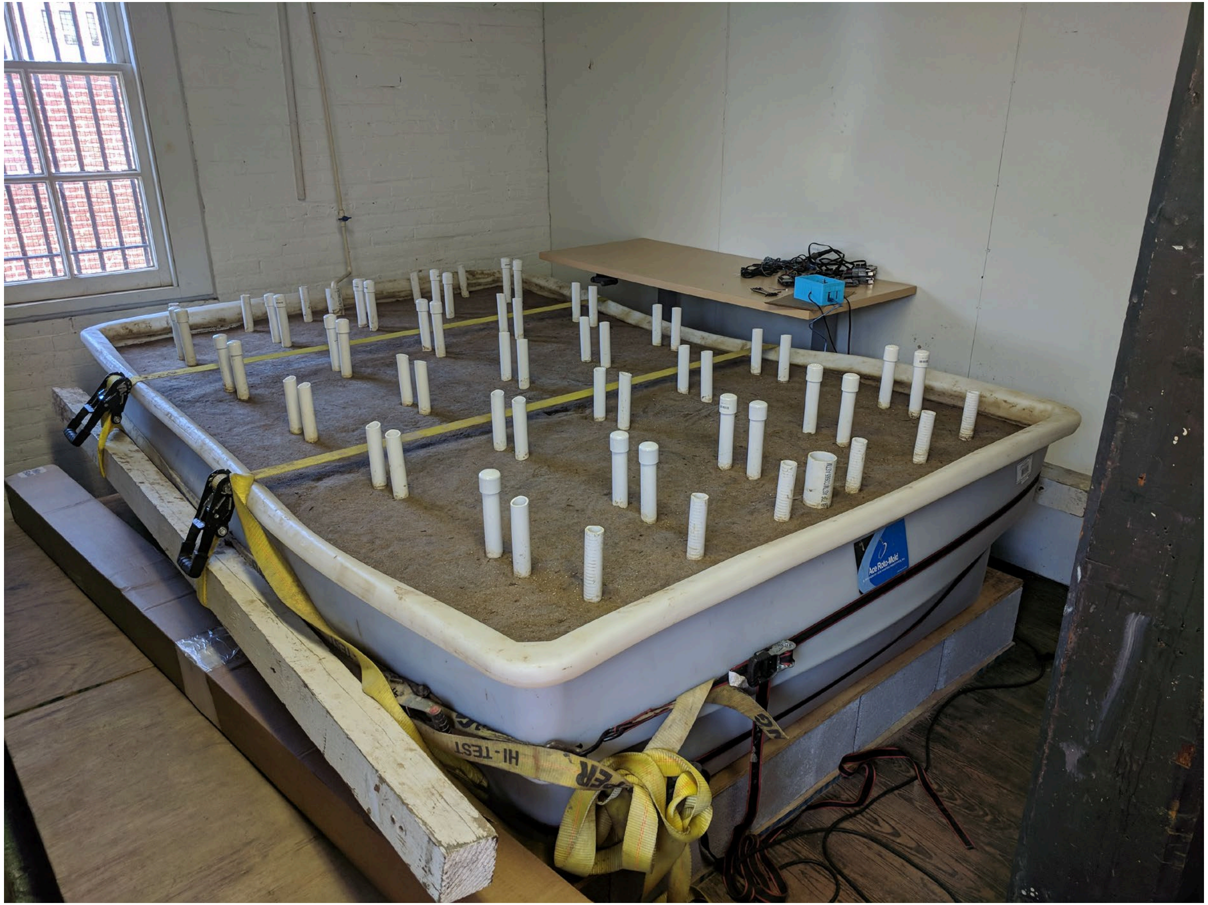


- Using a physical model, the effects of aging of contaminants can be directly observed instead of relying on a mathematical model

Physical Model Set Up

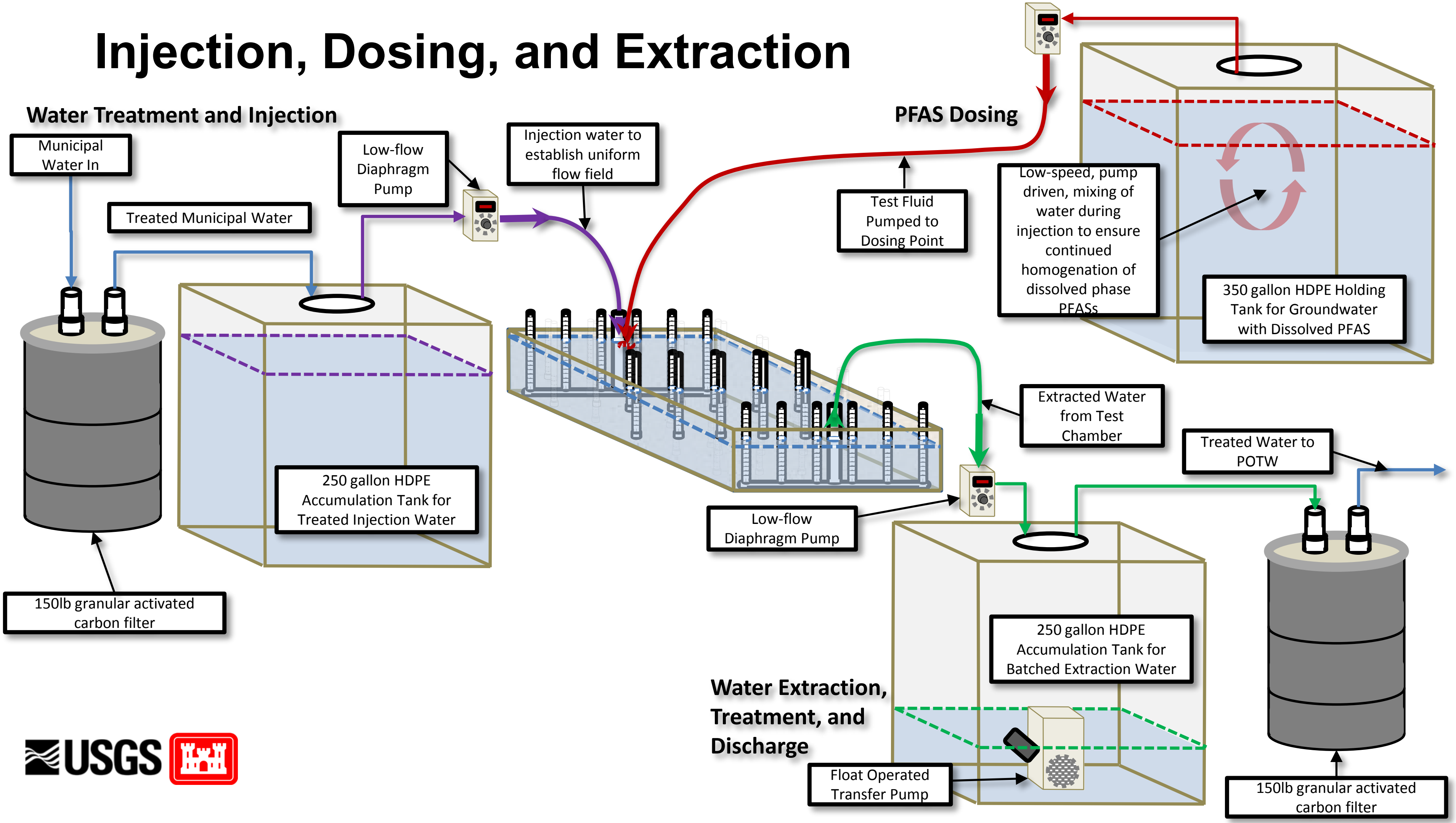


Physical Model Set Up



* 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 ft^2/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.

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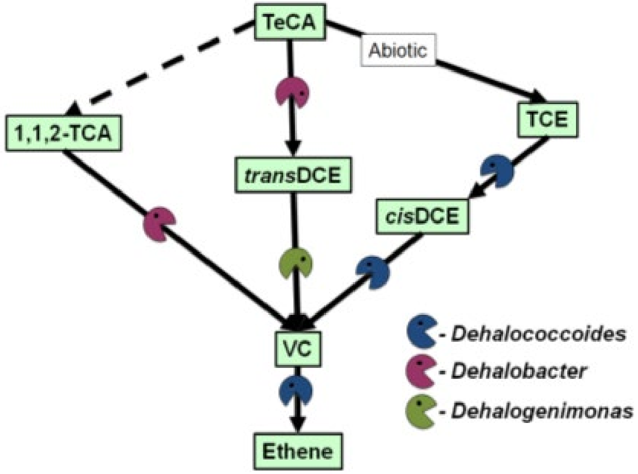
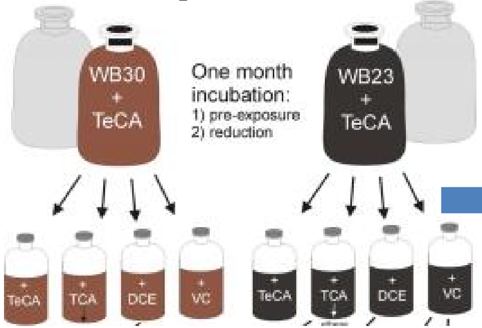
Research Direction

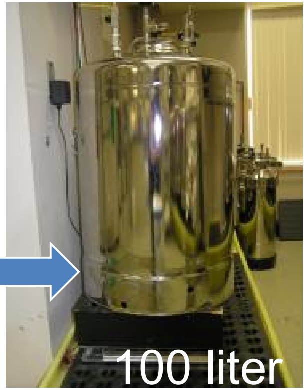
- With action levels and regulatory limits for PFASs in the low parts per trillion, remedial methods are urgently needed.
- In general what lessons can we learn from other contaminants that are difficult to remediate.
- Can some direct translations be made from methods for treating brominated and chlorinated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

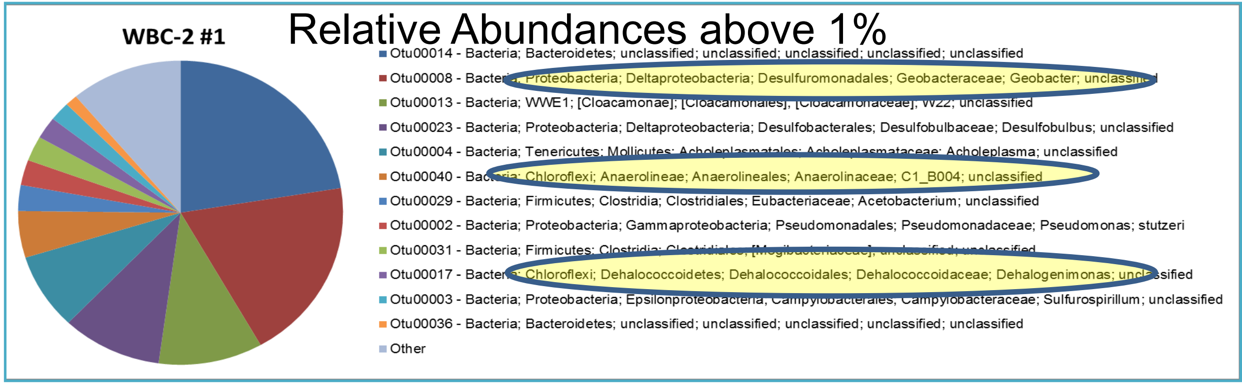
WBC-2 Microbial Consortium

- **"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)**



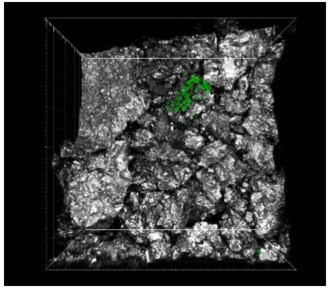




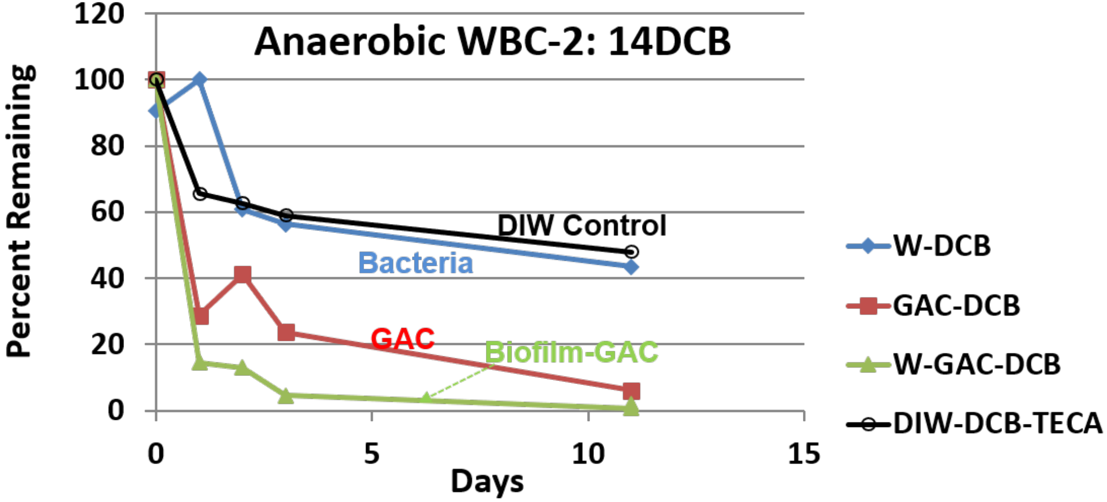


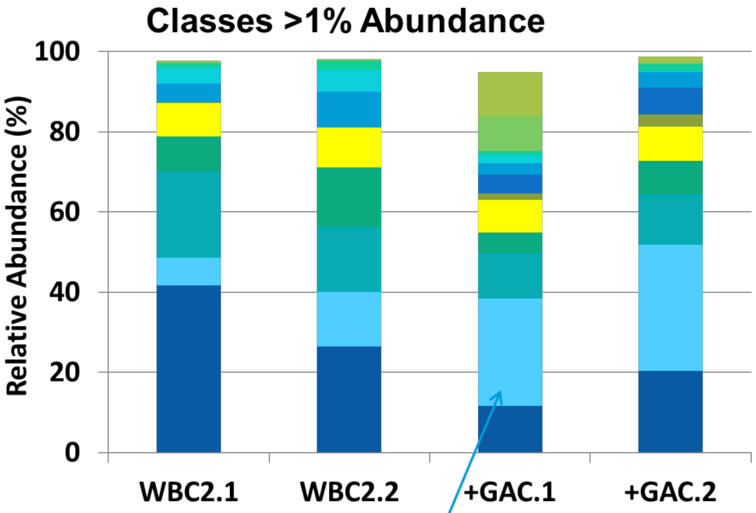
A nice place to live….

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



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





Significant increase in Dehalococcoidales on GAC.

f__Dehalococcoidaceae;g__Dehalococcoides
f__Dehalococcoidaceae;g__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				
SEDT	Site sediment and sGW	✓		✓	✓
WSED	Site sediment and sGW	✓	✓	✓	
WSEDT	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_2O			✓	✓

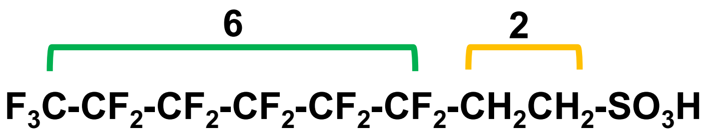
Microcosm Preparation

- 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

Perfluorooctane sulfonate (PFOS)

Perfluorooctane carboxylate (PFOA)

6:2 Fluorotelomer sulfonate (6:2 FtS)



(Structure figures from ITRC Fact Sheet, 2018)

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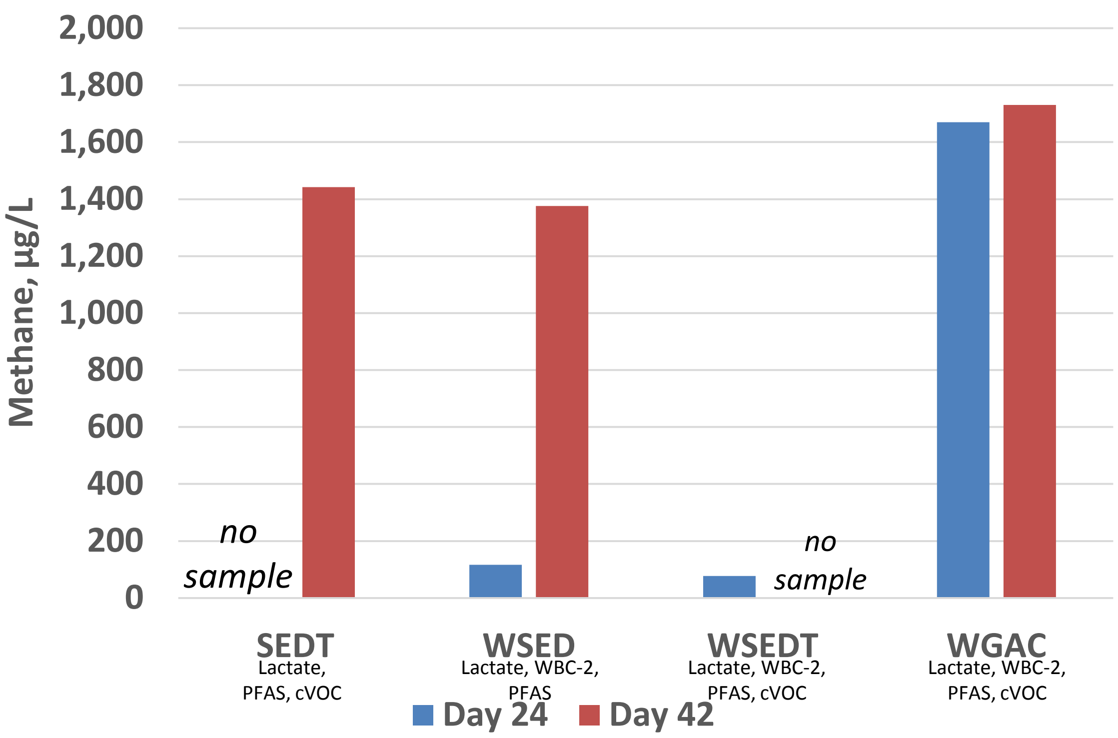
Methane Generation

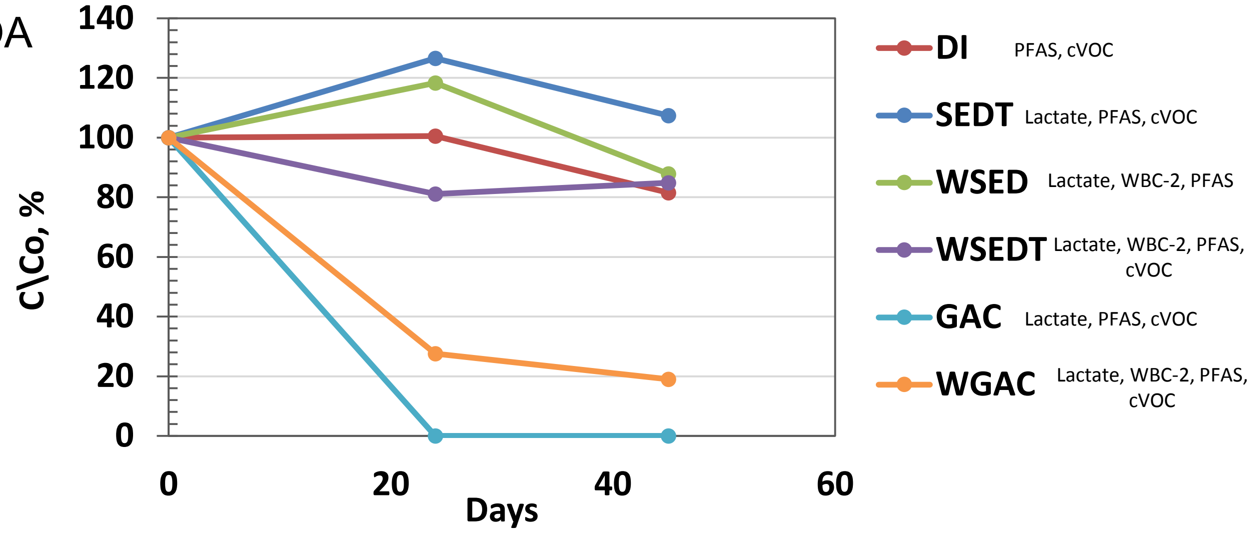
- Methanogenic conditions evident in the samples.



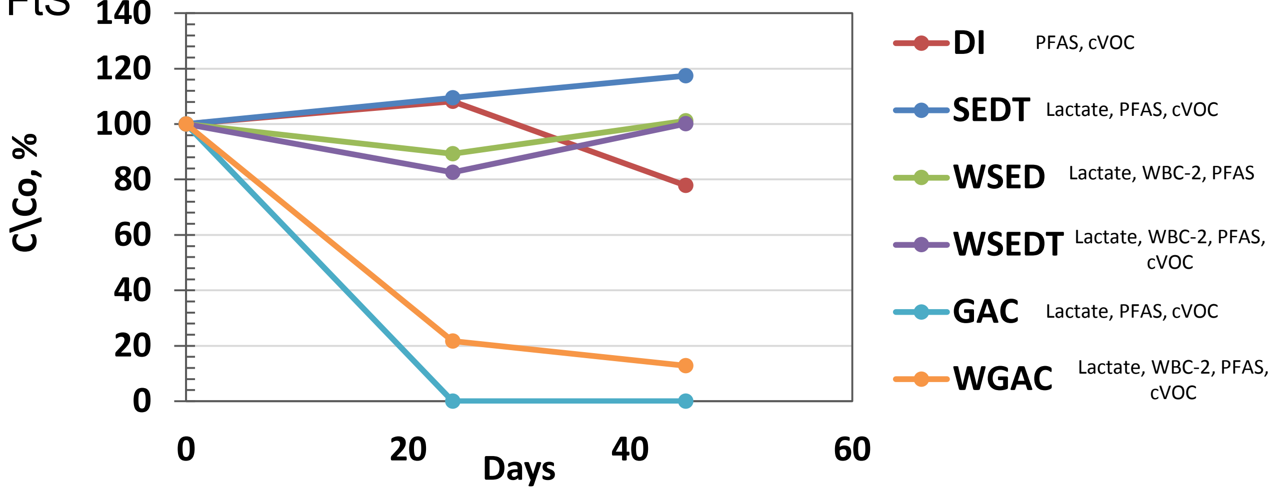
Microcosms - PFOA and 6:2FtS Results in Water

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

PFOA



6:2 FtS



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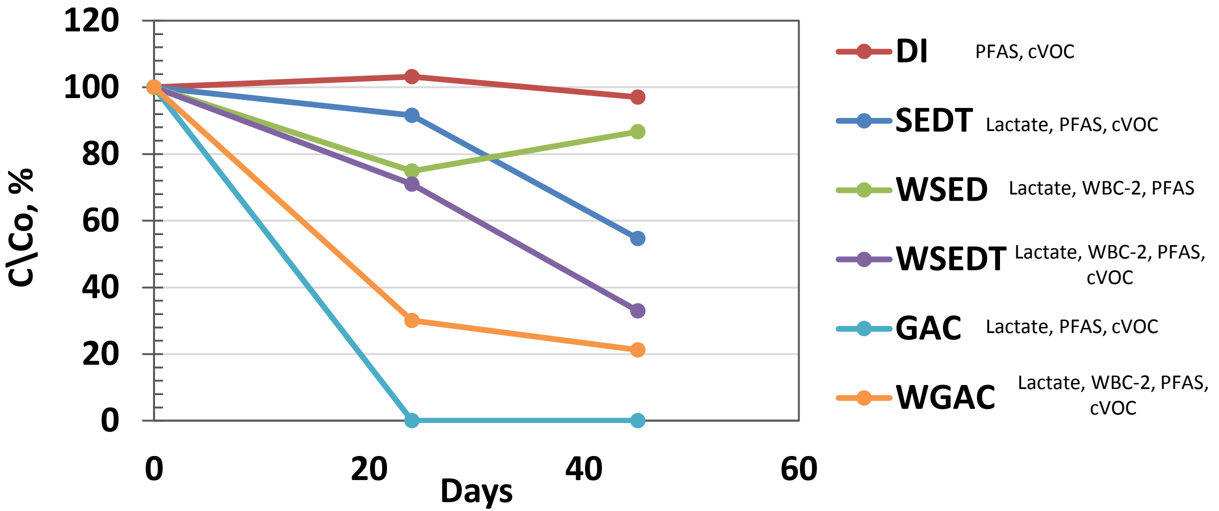
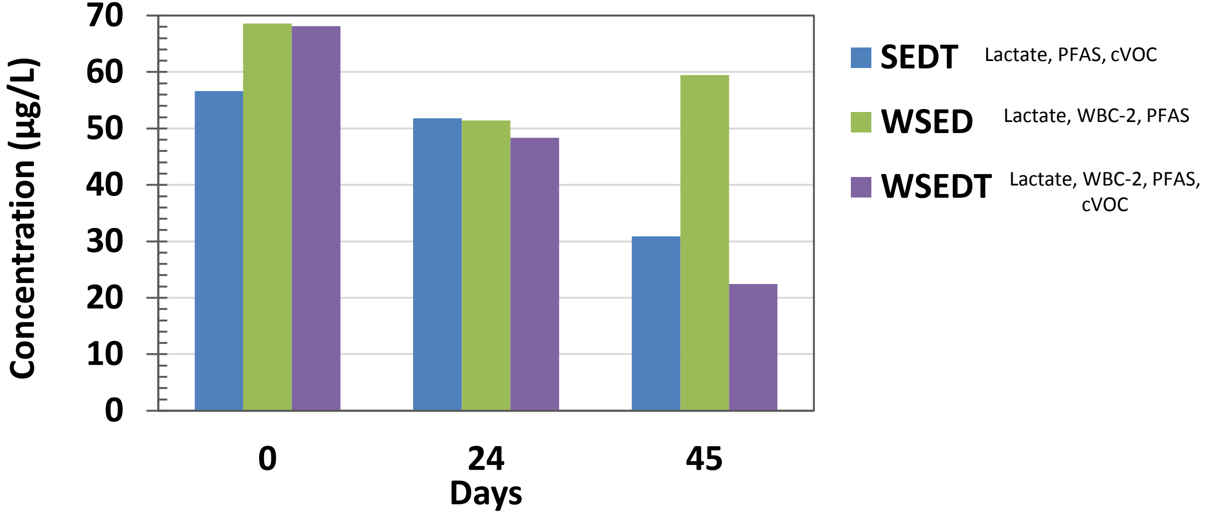
Microcosms - PFOS Results in Water

PFOS

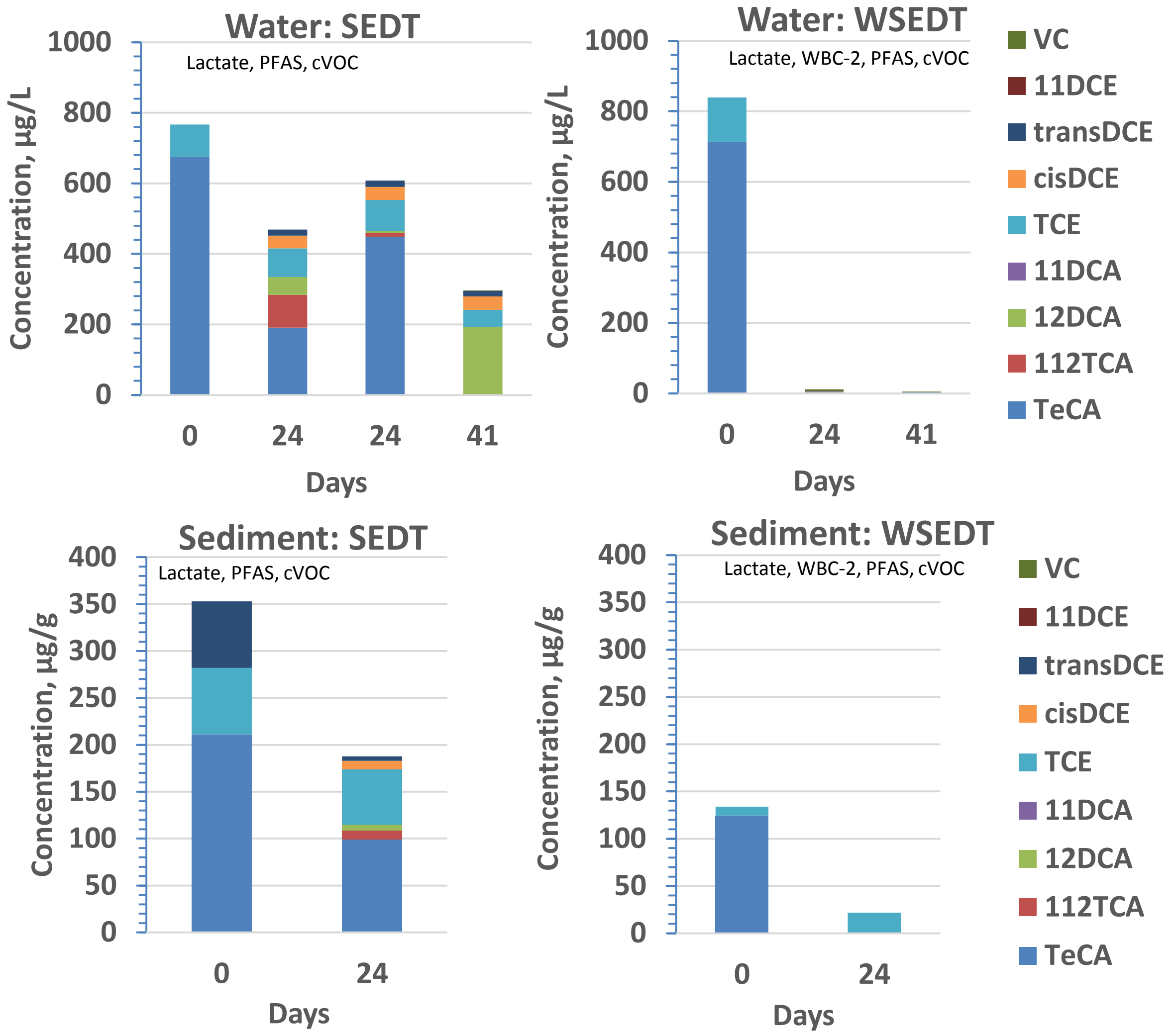
- PFOS removal in two microcosms (SEDT and WSEDT) with sediment and with added cVOCs (with & without WBC-2)
- 25 to 45% PFOS removal (after accounting for loss in DI control)
- Microscosm with sediment and no added cVOCs (WSED) did not show consistent PFOS removal
- Microcosms with GAC, even more removal





Microcosms - cVOCs in Water and Sediment

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



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Takeaways

1) There is an apparent link between cVOC degraders and PFOS degraders (more research needed to identify specific metabolites).

2) The combination of WBC-2 and GAC may be very effective at PFAS treatment.

3) Bioremediation may have a viable role for PFASs.

More results expected in January 2019.

Questions?