EMERGING CONTAMINANTS SUMMIT

DETECTION // TREATMENT // REGULATION

In Situ Sequestration of Per- and Polyfluoroalkyl Substances (PFAS) from Contaminated Groundwater

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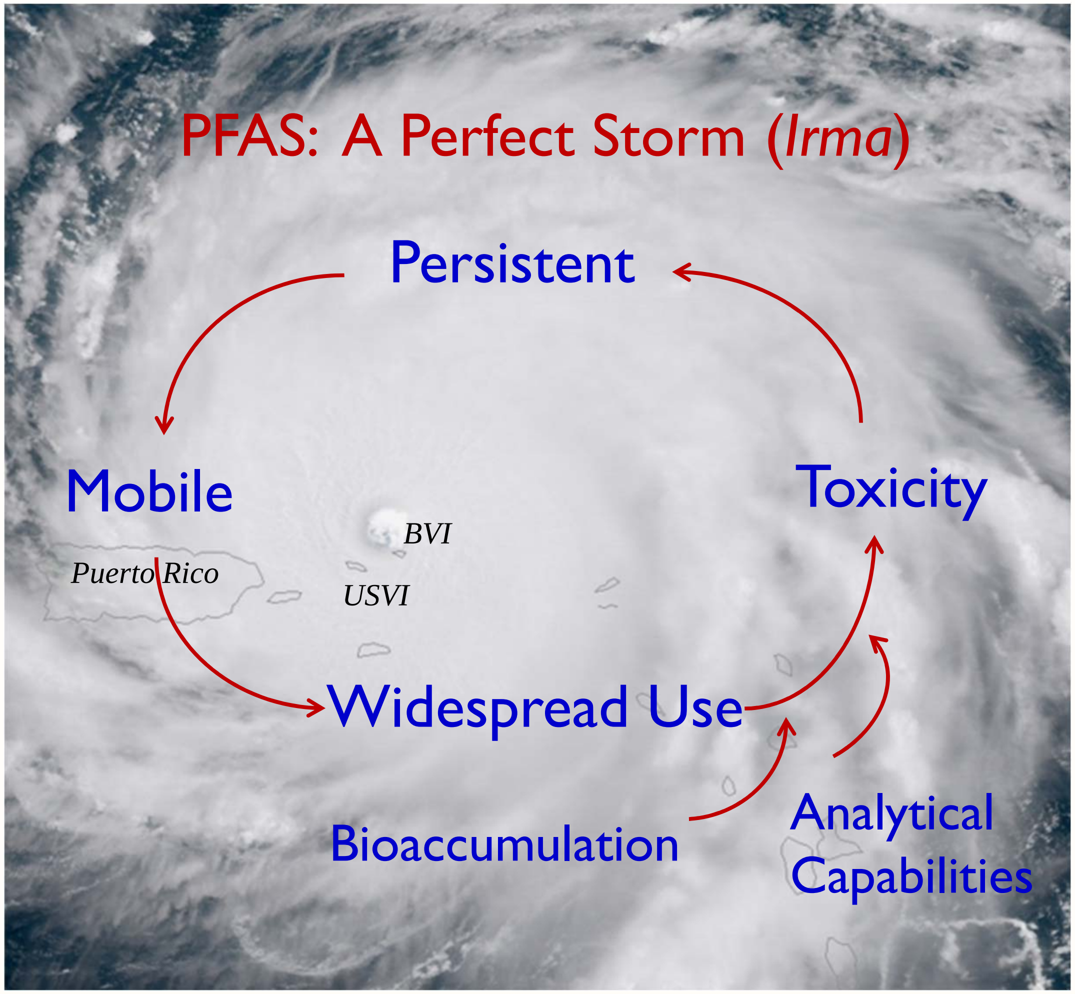
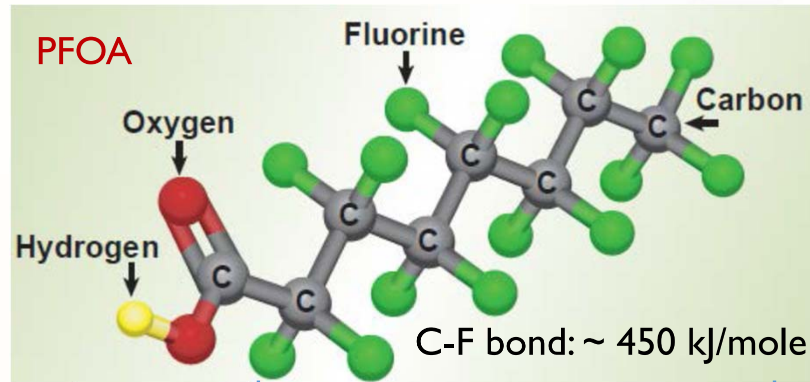


Conventional in situ technologies are not well suited for PFAS:



Hydrophilic "head" group   Hydrophobic/lipophilic "tail"

- Low Volatility ~~(Thermal)~~
- Recalcitrant ~~(Bioremediation, ISCO)~~
- Surfactant (Interfaces/Sorption?)

Potential PFAS Treatment Options

Technology	Summary of PFAS Treatment		
	PFOA	PFOS	Application
Chemical Oxidation	YES[1,2,3,4]	Partial[4]	Ex-Situ (Reactor) In-Situ (?)
Chemical Reduction	YES[5,6]	Partial[5,6]	Ex-Situ (Reactor) In-Situ (?)
Electrochemical	YES[7,8]	YES[7]	Ex-Situ (Reactor) In-Situ (?)
Sorption/Sequestration	YES[9,10]	YES[9,10]	~~Ex Situ (GAC/Resin)~~ In-Situ (Injection/Barrier Wall)
Biological Treatment	NO	NO	Unlikely, PFAS may inhibit chlorinated solvent degradation

[1]Liu et al. 2012, *Sep and Purf Tech:* Heat-activated persulfate
[2]Mitchell et al 2013, *ES&T Letters*: Catalyzed hydrogen peroxide
[3]Vecitis et al. 2009, *Front. Environ. Sci. Engin. China*: UV with TiO_2
[4]Park et al., 2016, *Chemosphere*: Heat-activated persulfate
[5]Ochoa-Herrera et al. 2008, *ES&T*: Ti(III)-citrate and Vit B_{12}
[6]Wang et al., 2017, *Chem. Eng. J*., Photocatalytic reactivity
[7]Schaefer et al., 2015, *J. Haz. Mater.*: $TiRuO_2$ anode
[8]Zhou et al., 2017, J. Electro. Chem.: PbO_2 electrode + PVDF
[9]Zhang et al., 2016, *Chemosphere*: GAC
[10]Yu et al., 2009, *Water Res.*: GAC and resin

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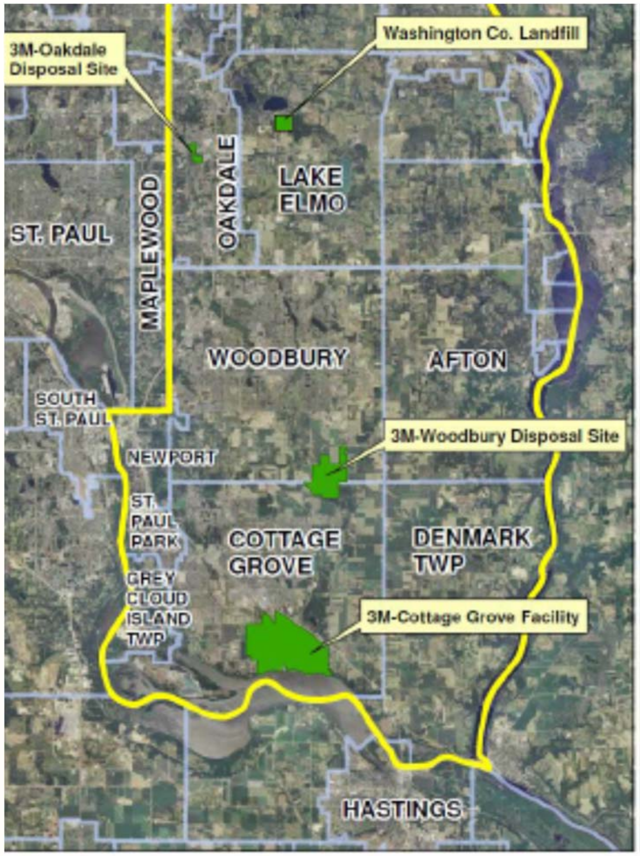
Conventional Pump & Treat PFAS Remediation

Washington County, MN



3M Settles Minnesota Lawsuit for $850M (Feb 20, 2018)

MN Department of Health/3M

Breakthrough times:

- PFBA = 30 days
- PFOA = 286 days
- PFOS = 550 days

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Commercially Available (Proprietary) PFAS Sorbents

RemBind™-Tersus

Activated carbon, aluminum hydroxide, organic matter and other additives, intended for near surface soil mixing

InTreat WATER BY InSite

InTreat SOIL BY InSite

PlumeStop® Liquid Activated Carbon™–Regenesis

Activated carbon (1-2μm) suspended in water dispersed with organic polymer

- ❖ Limited independent verification
- ❖ Limited data (e.g., mass balance)
- ❖ In situ delivery issues rarely addressed

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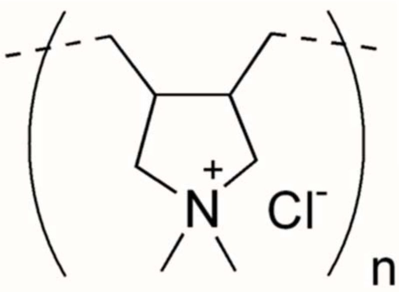
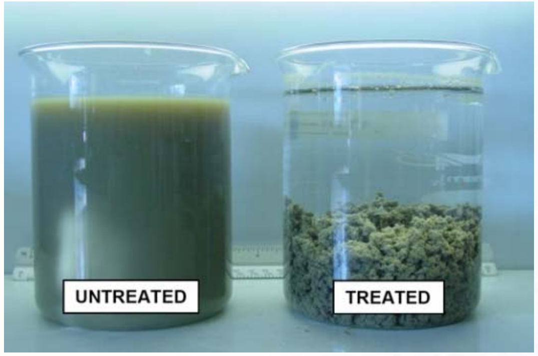
Coagulant polymers (cationic surfactants)

SERDP Project ER-2425 (Simcik, Arnold, Pennell, Hatton)

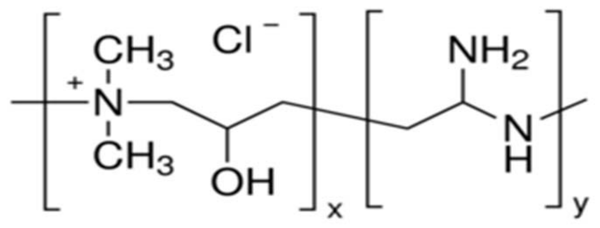
Poly-DADMAC (PDM)



- Accepta 4351
- ~ 28% OC
- Quaternary Amine
- diallyl dimethylamine
- MW ~ 350,000



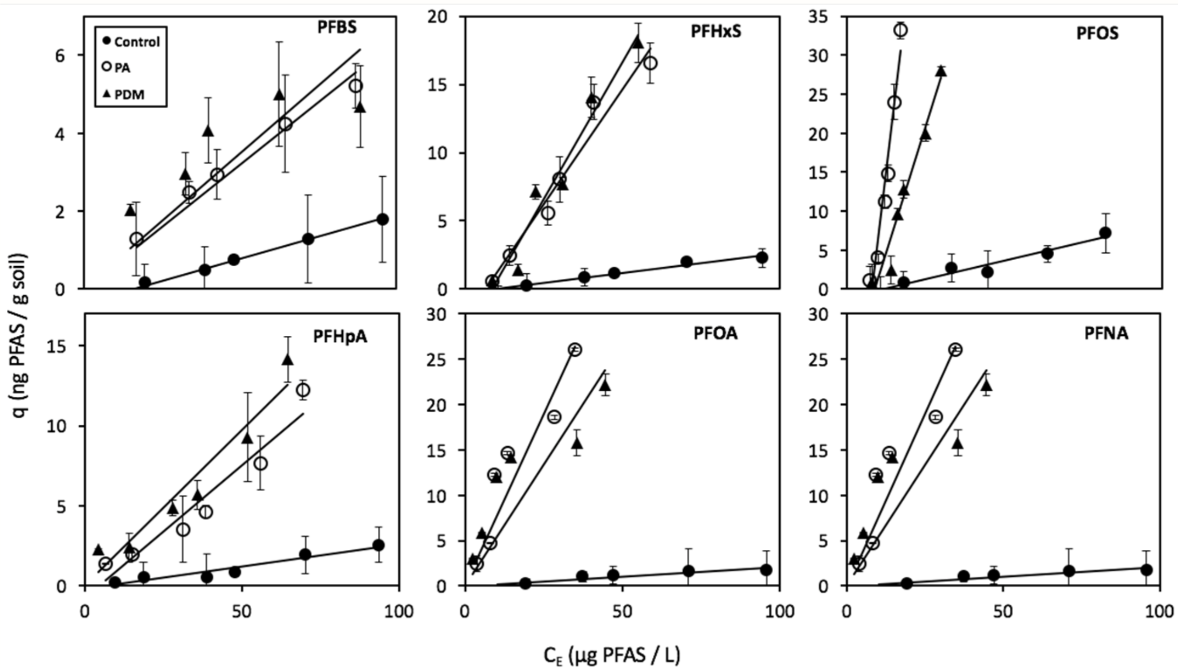
Polyamine (PA)



- Accepta 4350
- ~ 26% OC
- Quaternary Amine
- epichlorohydrine and dimethylamine
- MW ~ 240,000

Batch PFAS Sorption Tests: PDM and PA

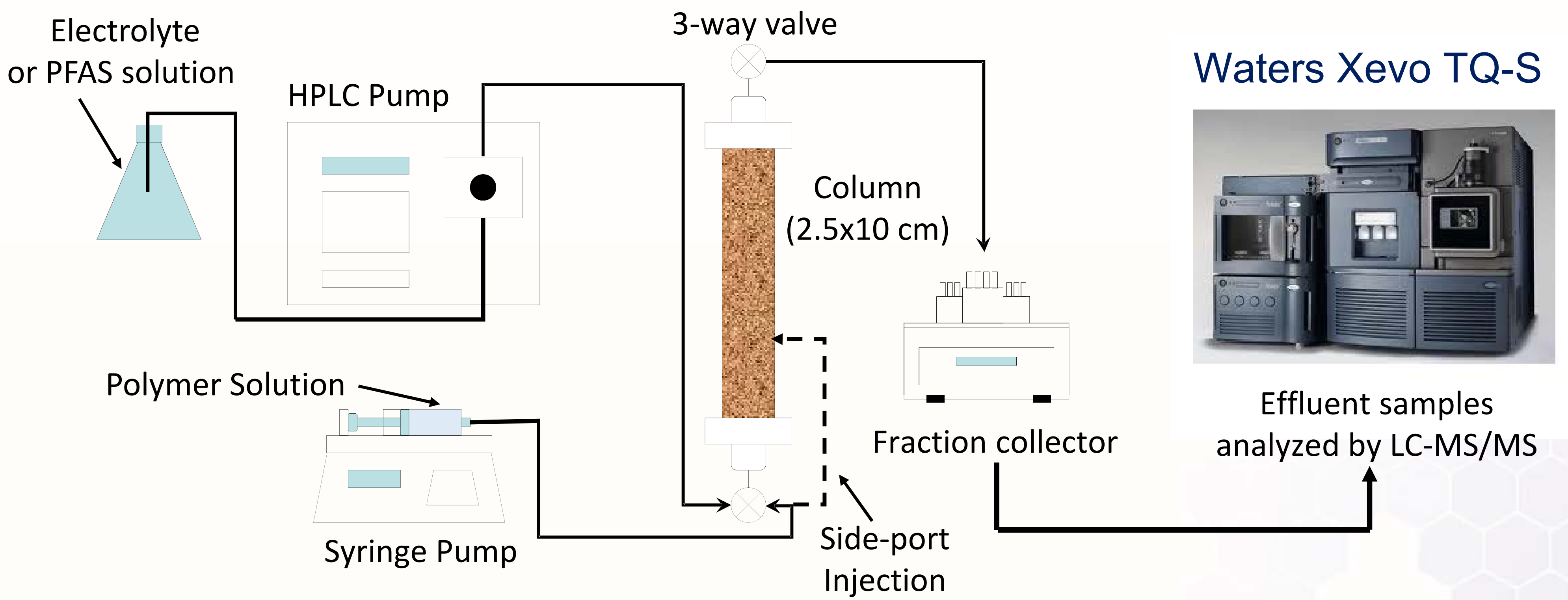
40-50 mesh Ottawa Sand



- ❖ Addition of PDM or PA increased PFAS sorption by Ottawa sand and Tinker AFB soil
- ❖ PFAS Sorption coefficients were 3.8 to 45-fold greater in the presence PDM or PA
- ❖ PDM yielded slightly greater sorption improvements than PA

Aly et al., 2018, J. Env. Eng., (in press)

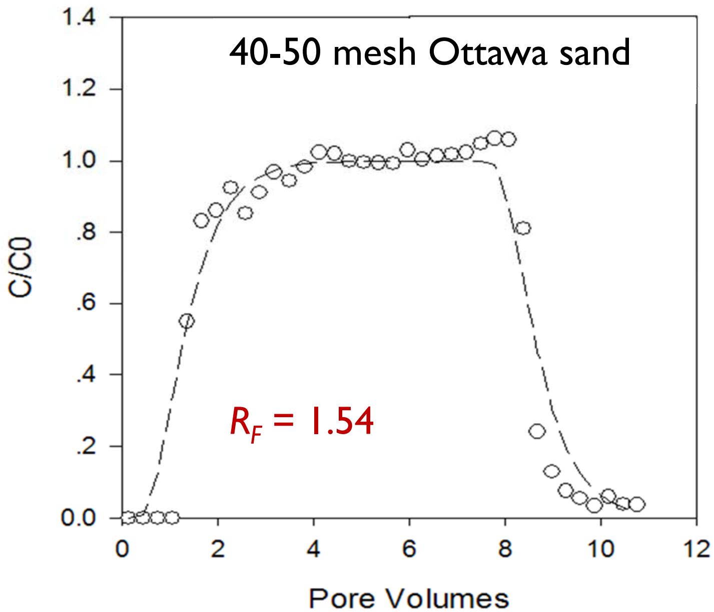
Schematic Diagram of 1-D Column System



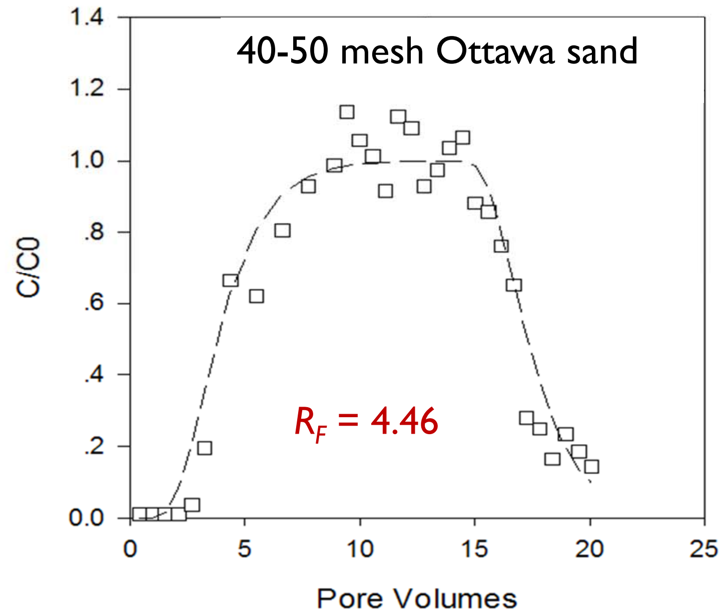
(1) Non-reactive tracer test (pulse injection), (2) Inject PDM+PAC suspension,
(3) Inject background electrolyte, (4) Inject PFAS solution (e.g., 100 ug/L PFOS)

PFAS Column Tests: Control (w/o PDM or PA)

PFOA (100 µg/L)



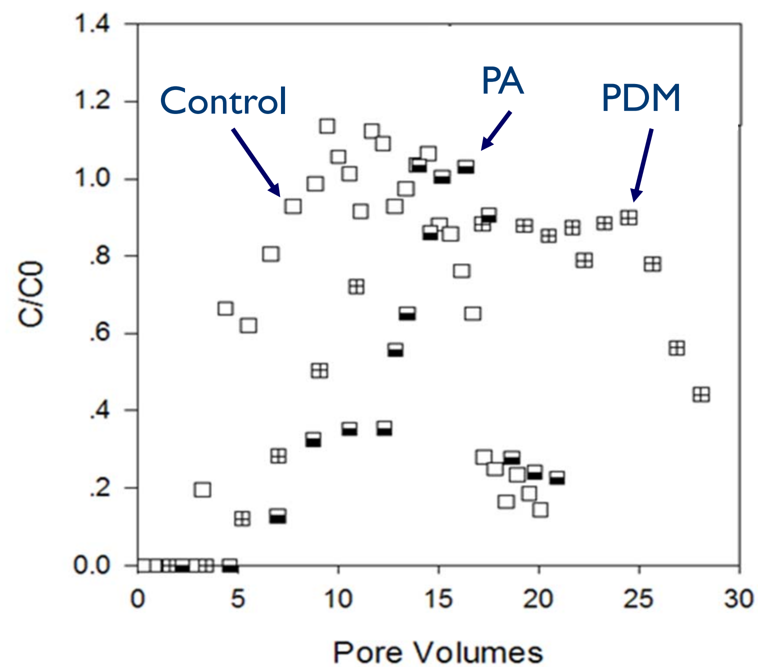
PFOS (100 µg/L)



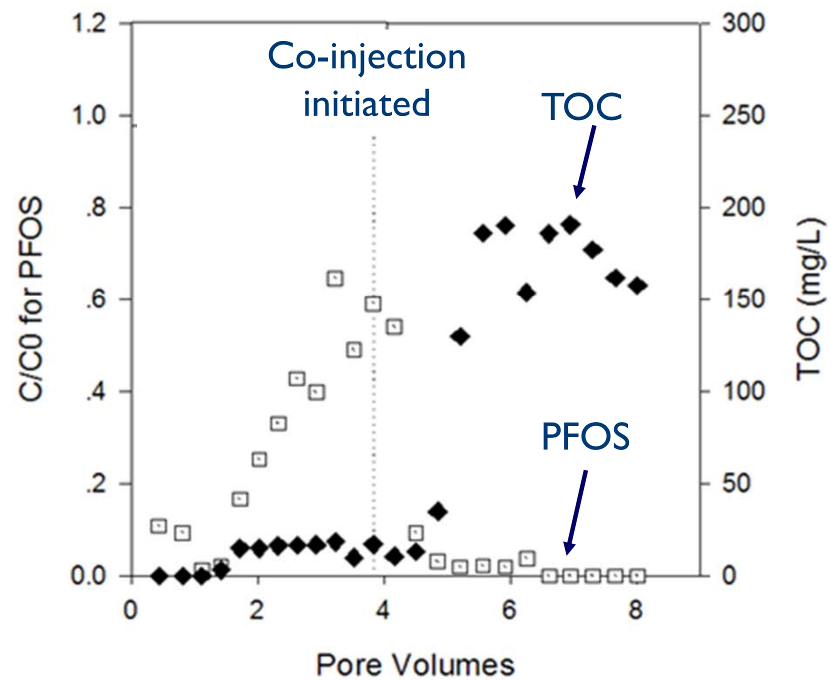
Aly et al., 2018, J. Env. Eng., (in press)

Pretreated and Side-Port Co-injection: PDM + PFOS

Pretreated 40-50 mesh Ottawa sand (100 ug/L PFOS)



Side-Port Co-injection 40-50 mesh Ottawa sand (100 ug/L PFOS)



Aly et al., 2018, J. Env. Eng., (in press)

Summary of PFAS Column Results: PDM or PA

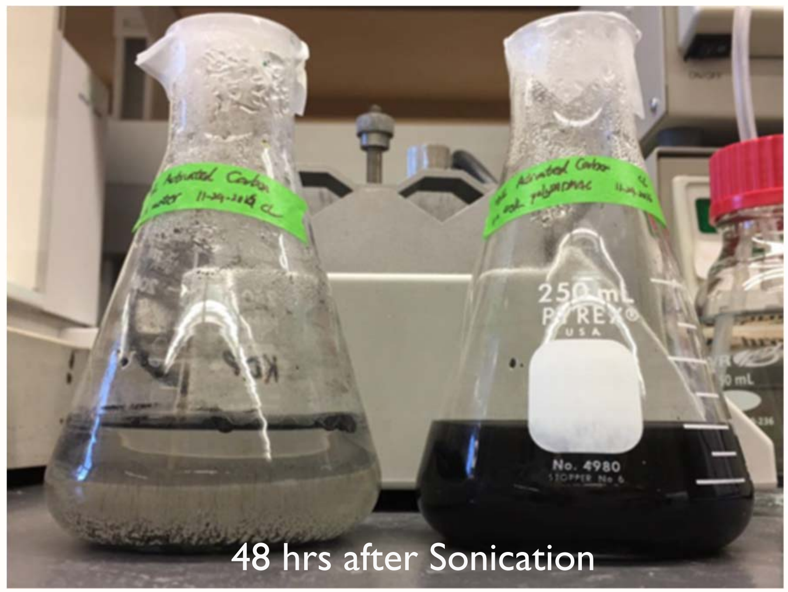
	PFAS Retention (ng/g sand)	PFAS Retention (%)	Enhancer retention (ng/g sand)	Retained PFAS/Retained Enhancer mass ratio
PFOA				
control	5.97	8.95%	n/a	n/a
PDM pre-treatment	8.38	9.50%	21.68	0.11
PA pre-treatment	20.10	21.16%	50.83	0.28
PDM side port injection	30.62	49.22%	60.3	0.41
PFOS				
control	4.20	6.23%	n/a	n/a
PDM pre-treatment	91.94	34.91%	21.68	4.04
PA pre-treatment	43.59	50.04%	77.00	0.51
PDM side port injection	196.06	83.22%	42.86	4.47

To improve performance….combine Powdered Activated Carbon (PAC) with polyDADMAC (PDM)

- ❖ PDM acts to stabilize PAC in suspension, facilitates delivery
- ❖ Both PDM and PAC can serve as sorbents (wide range of effectiveness)

1 g/L PAC 1 g/L PAC + 5 g/L PDM

1 g/L PAC 1 g/L PAC + 5 g/L PDM



DARCO® 100 mesh (150 µm) Powdered Activated Carbon (Sigma Aldrich)

Provisional Patent Application: Reg. No. 41,942, Docket No. 70011-067P01v (September, 2017)

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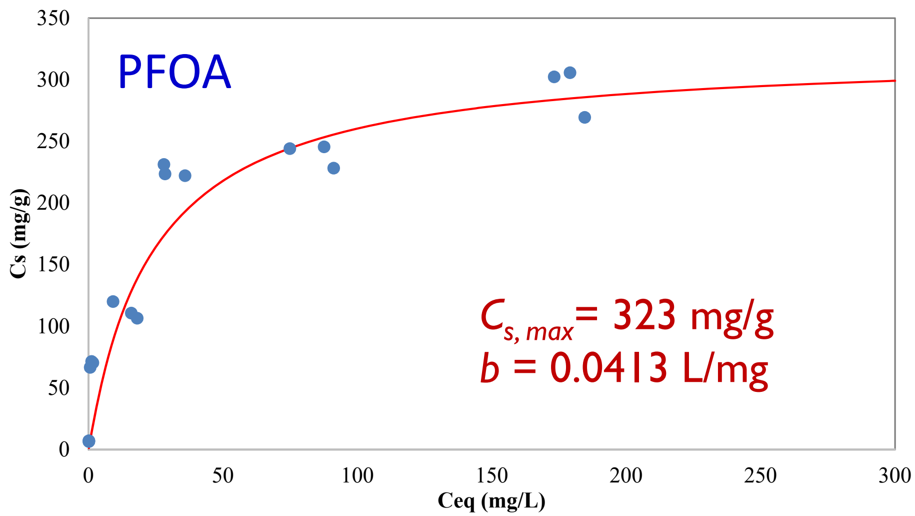
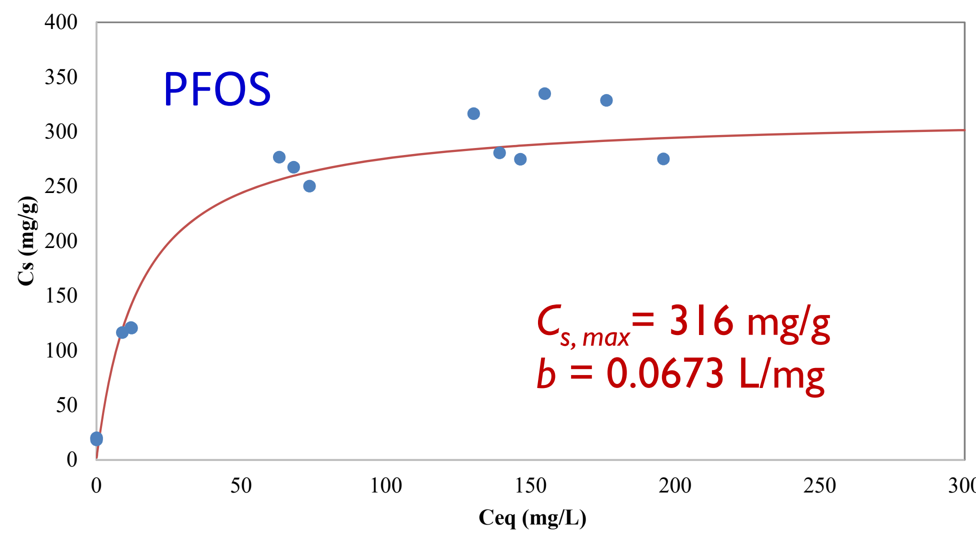
PFOA and PFOS Batch Adsorption Studies With Darco® PAC (100-mesh)



Langmuir Isotherm

$$C_s = \frac{C_{s,\ max} * b * Cw_{,\ eq}}{1 + b * C_{w,\ eq}}$$

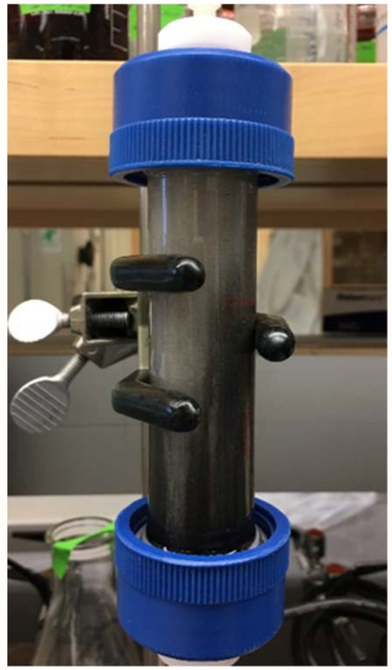


Injection of PDM+PAC Suspension

Flow Direction

t = 0 PV

after 3.5 PV PAC+PDM



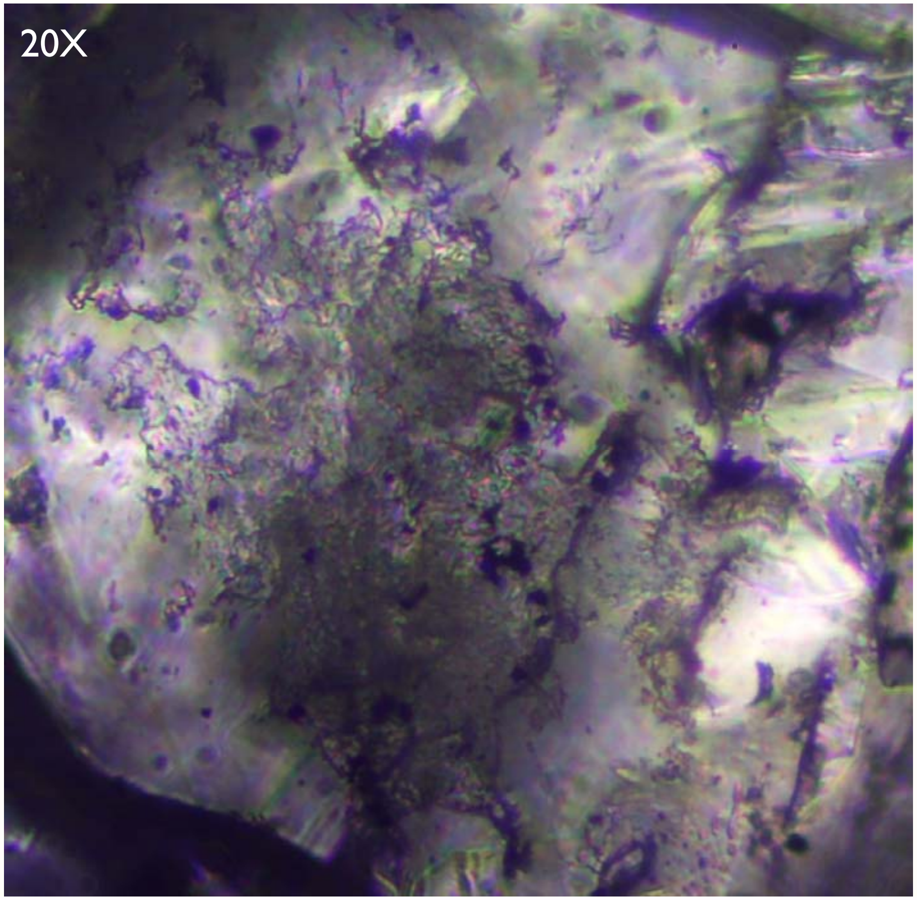
after 3.5 PV Background

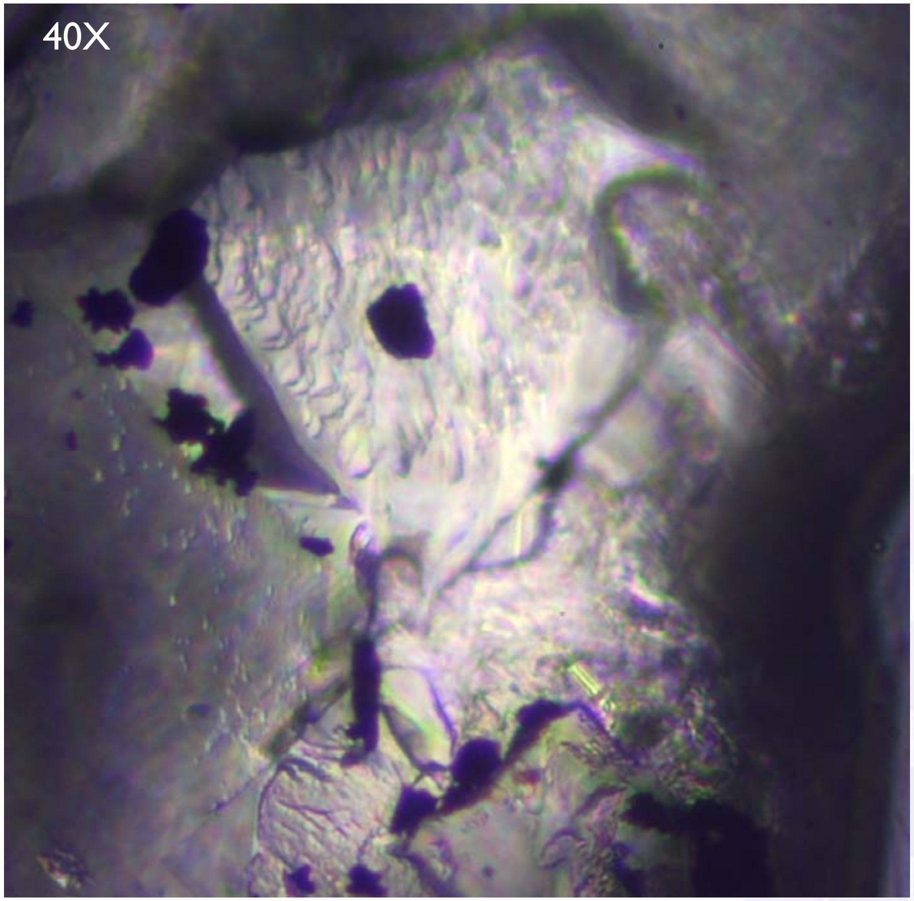
26.8 mg of PAC retained in column

40-50 mesh Ottawa Sand (d_{50} = 358 um), k_i = 7.37x10^{-11} m^2, n = 0.37, SSA = 0.0125 m^2/g, PV = 22 mL
PDM+PAC Suspension: 1,000 mg/L PAC + 5,000 mg/L PDM, viscosity = 1.18 cP
Flow rate: 0.12 mL/min; pore-water velocity ~1.0 m/day

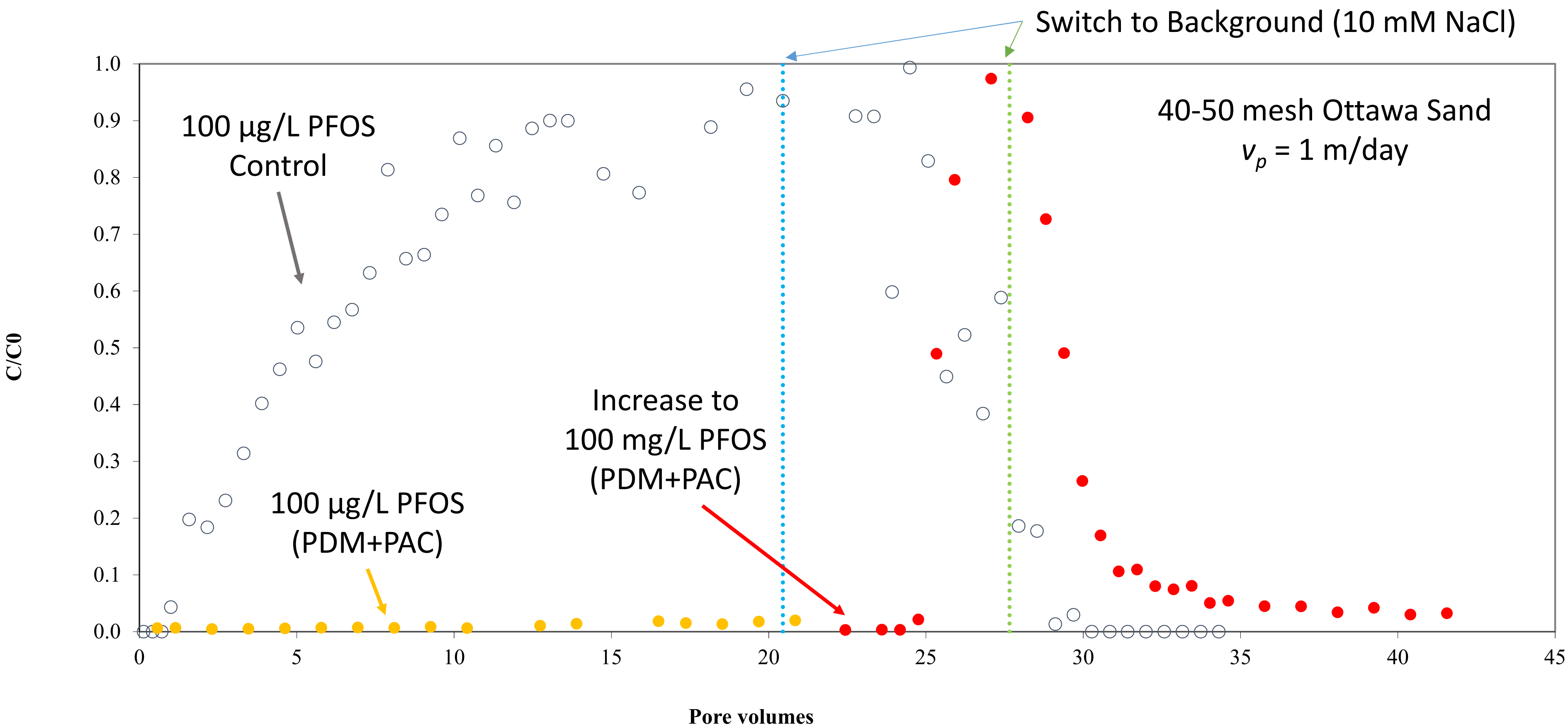
Images of PDM+PAC Treated Ottawa Sand

Leica DM IL LED

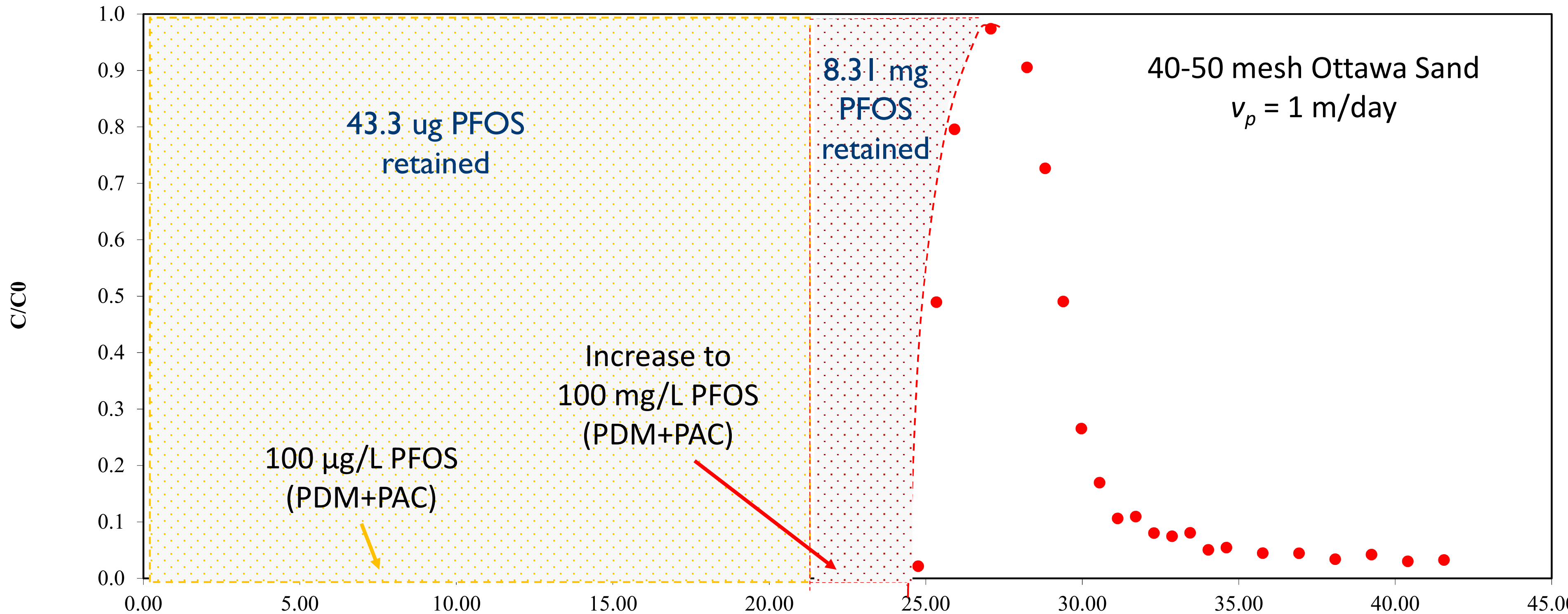




PFOS Column: Control; PDM+PAC treated Ottawa Sand



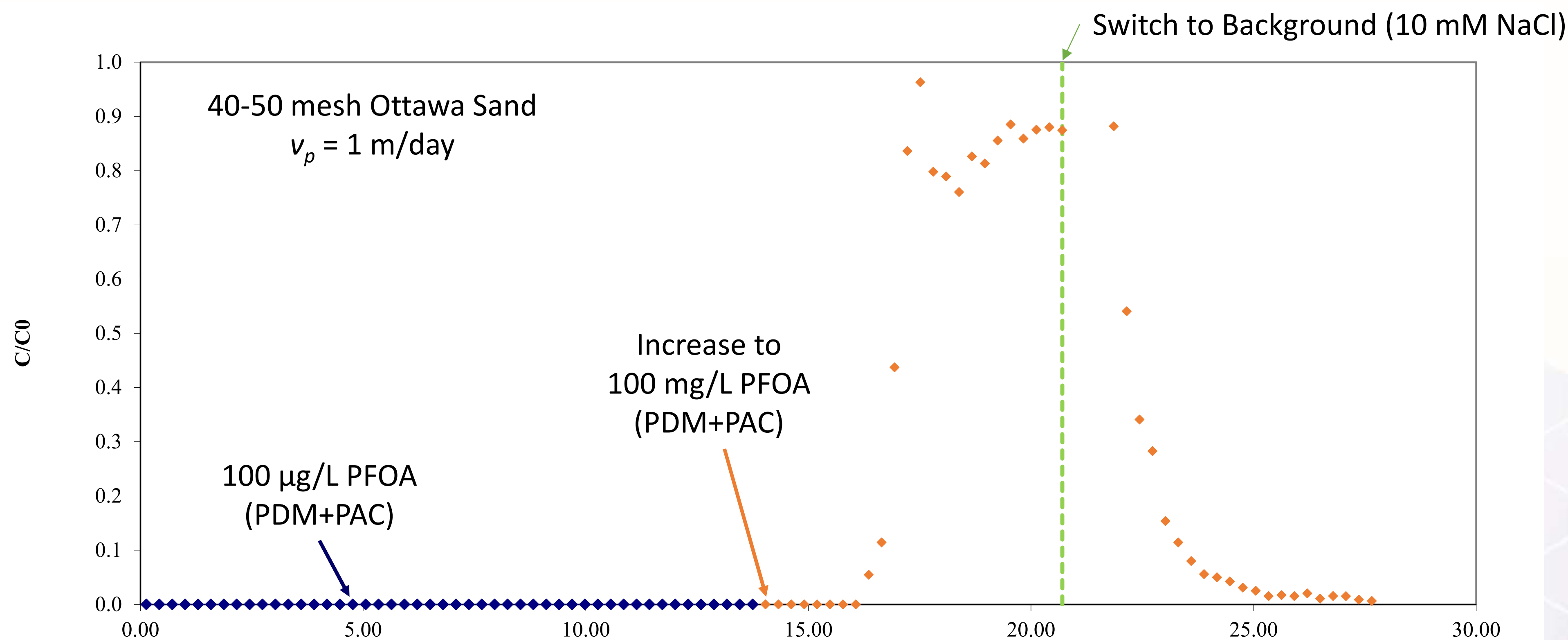
Retention of PFOS Mass by PDM+PAC Treated Sand



Based on the measured $C_{s,max}$ = 316 mg/g and mass of retained PAC (~27 mg), the capacity of the column should be ~ 8.65 mg PFOS, consistent with the observed column retention of ~8.35 mg PFOS

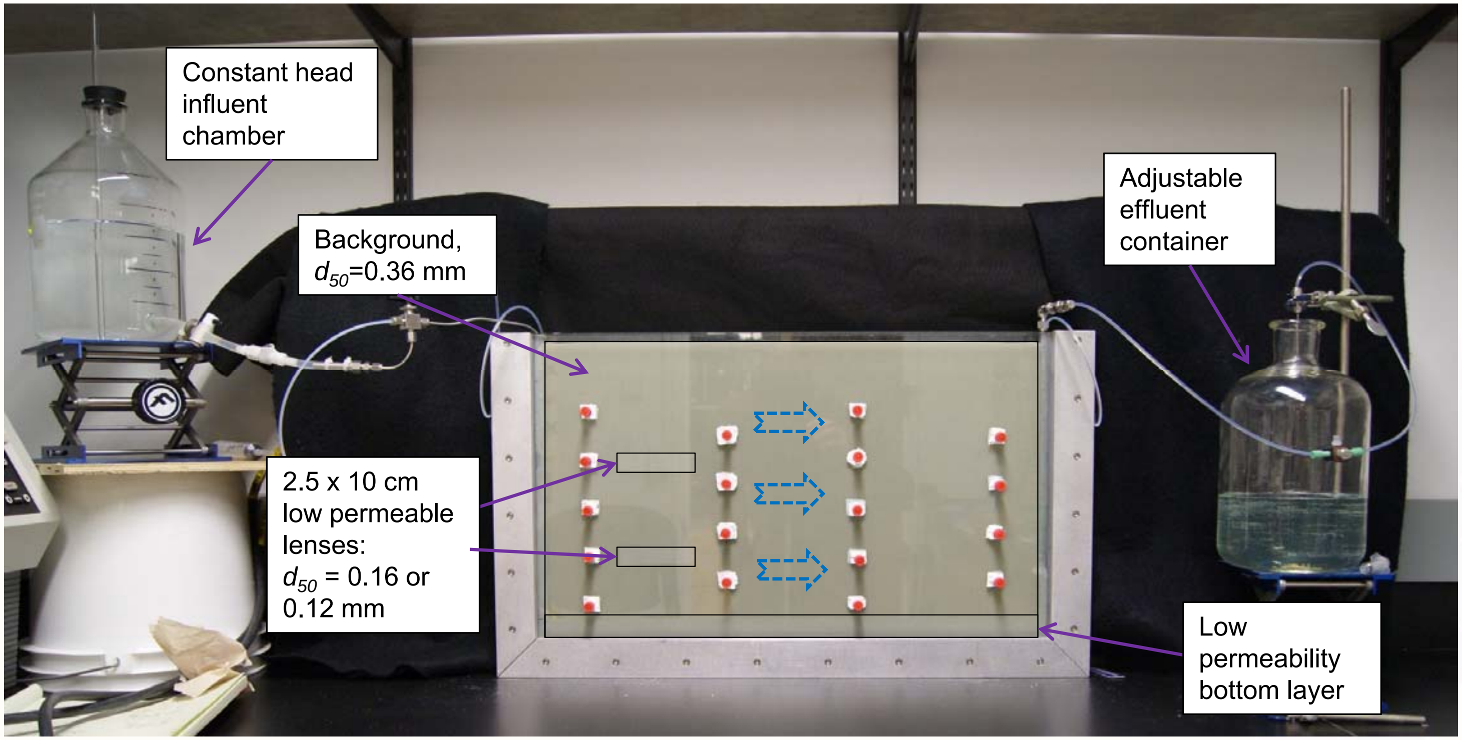
For 100 µg/L injection; ~2.1 ug PFOS retained/PV, capacity would be reached after ~4,100 PV

PFOA Column: PDM+PAC treated Ottawa Sand



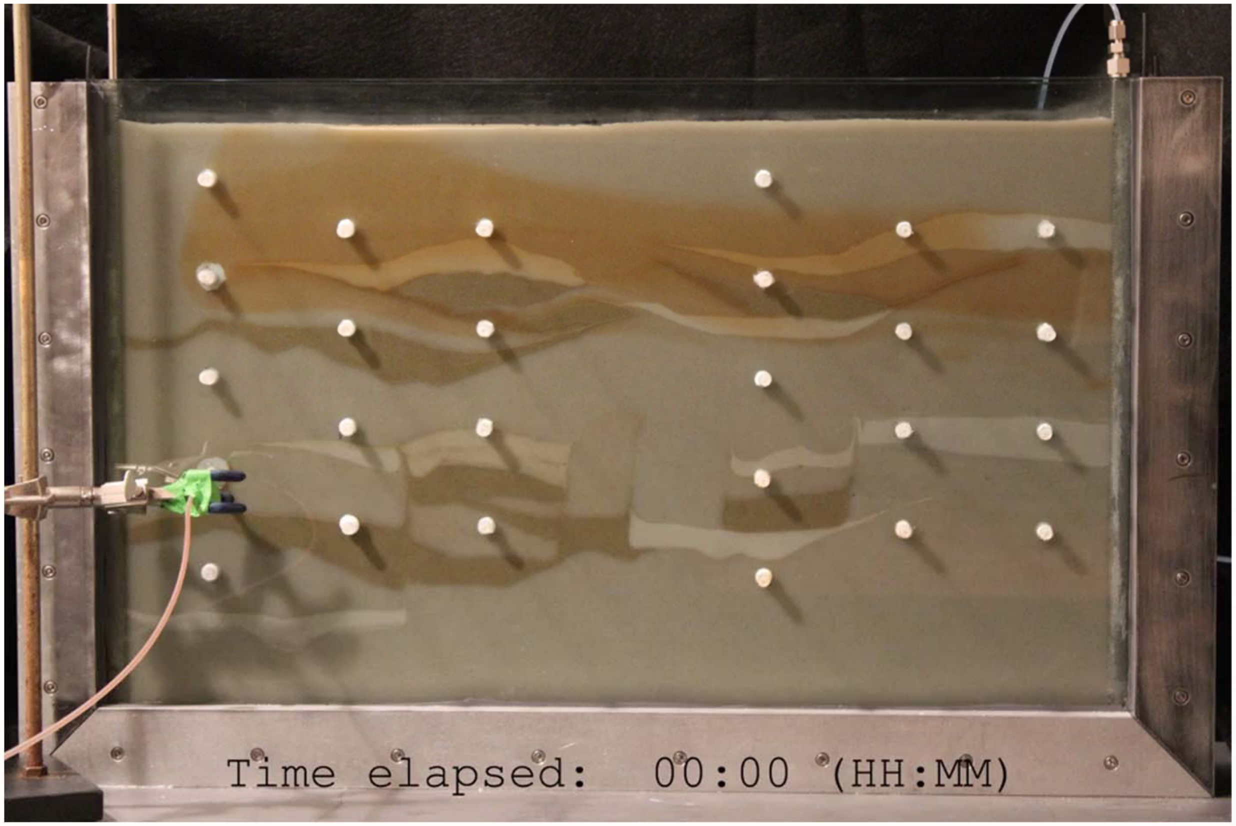
Based on the measured $C_{s,max}$ = 323 mg/g and mass of retained PAC (~27 mg), the capacity of the column should be ~ 8.72 mg PFOA, consistent with the observed column retention of ~8.48 mg PFOA

Heterogeneous 2.5-D Flow Cell



Dimensions: 40.0 cm (ht) x 63.2 cm (length) x 1.4 cm (thickness)

Injection of Iron Nanoparticles in Heterogeneous Domain

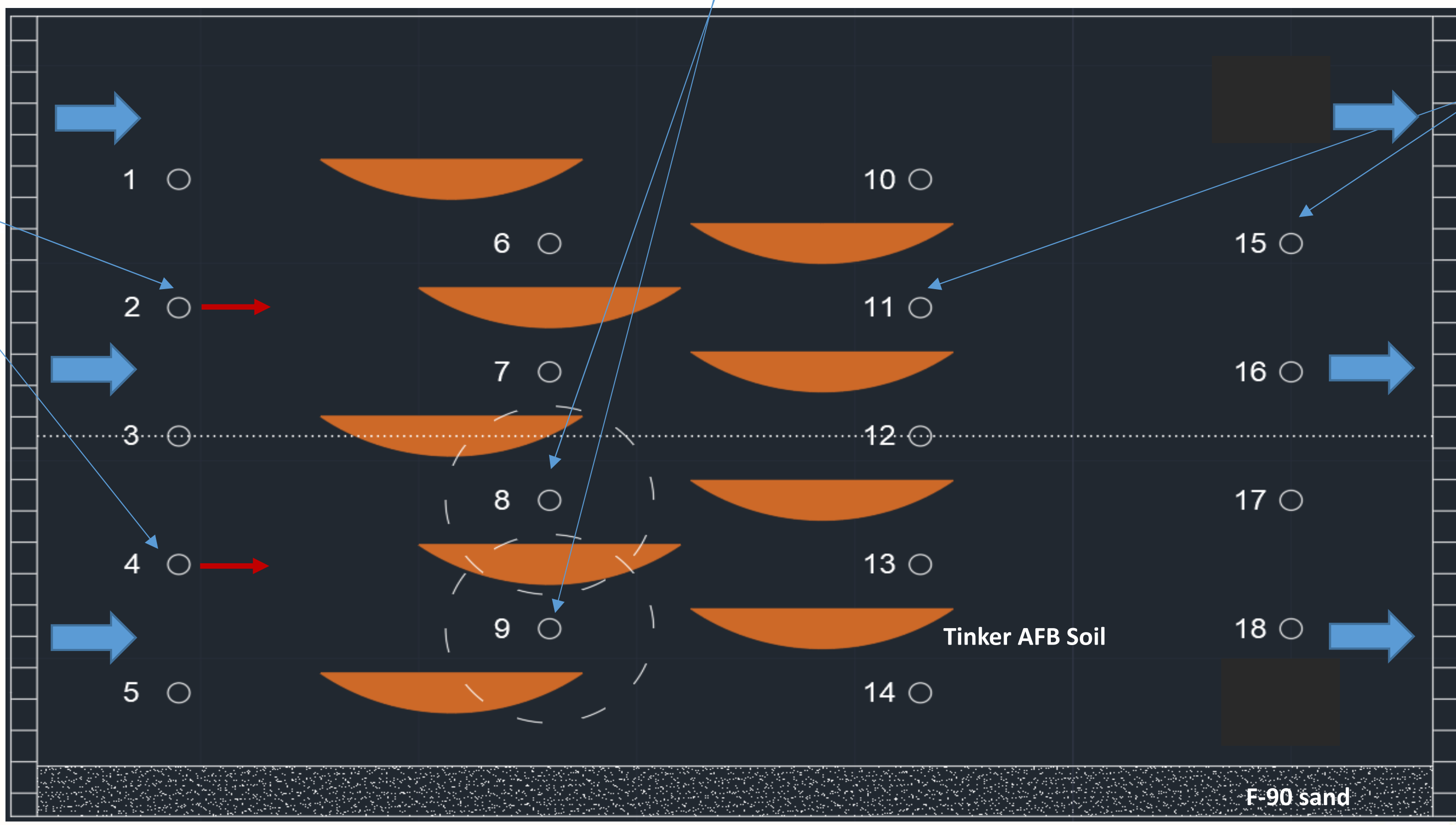


Background velocity = 2 m/d, nMag conc. = 2500 mg/L, gum arabic conc. = 1000 mg/L, injected vol. = 100 mL, background = API brine

Configuration of PFAS 2.5D Flow Cell

PDM+PAC Injection Ports

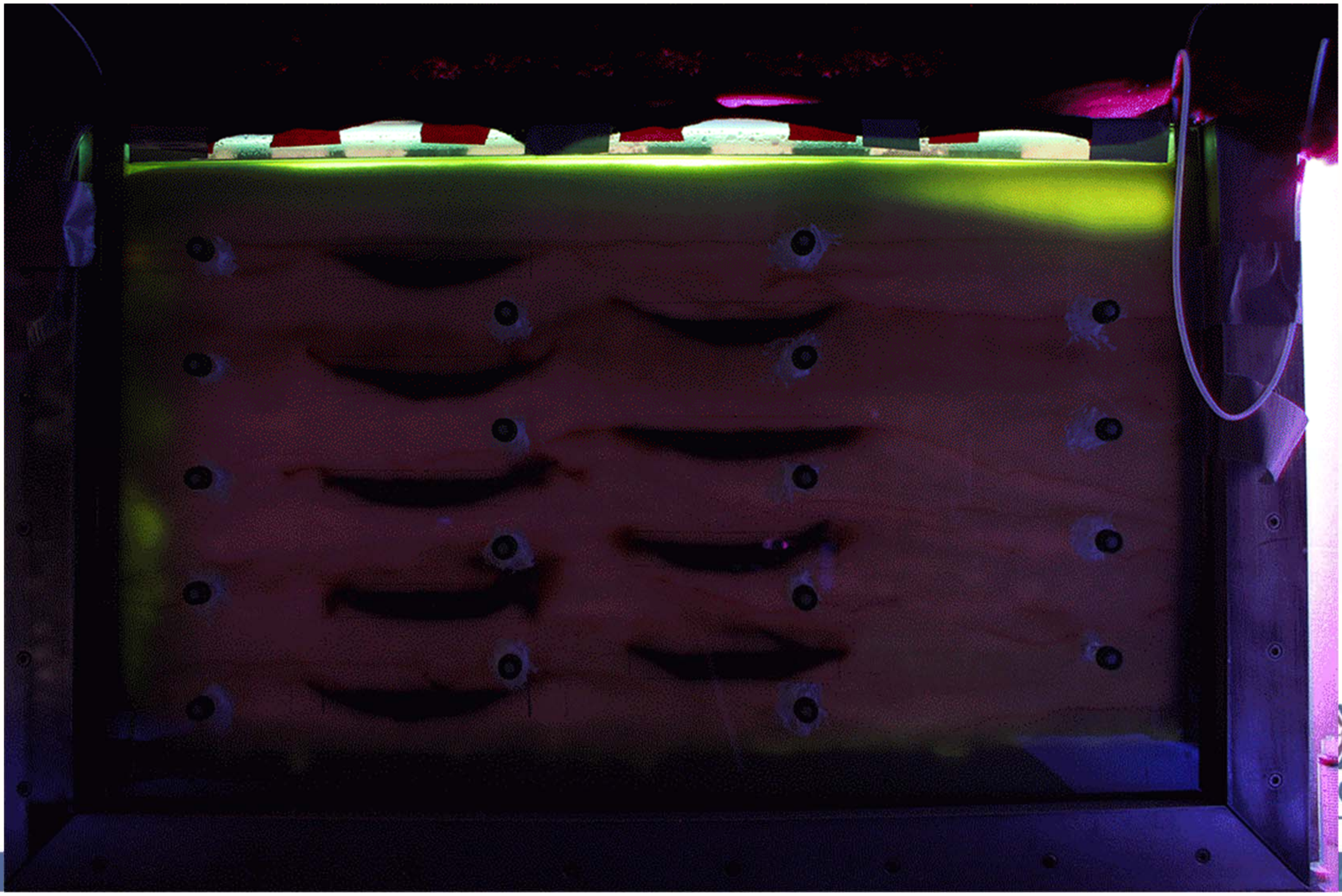
PFAS Injection Ports



Downgradient Sampling Ports

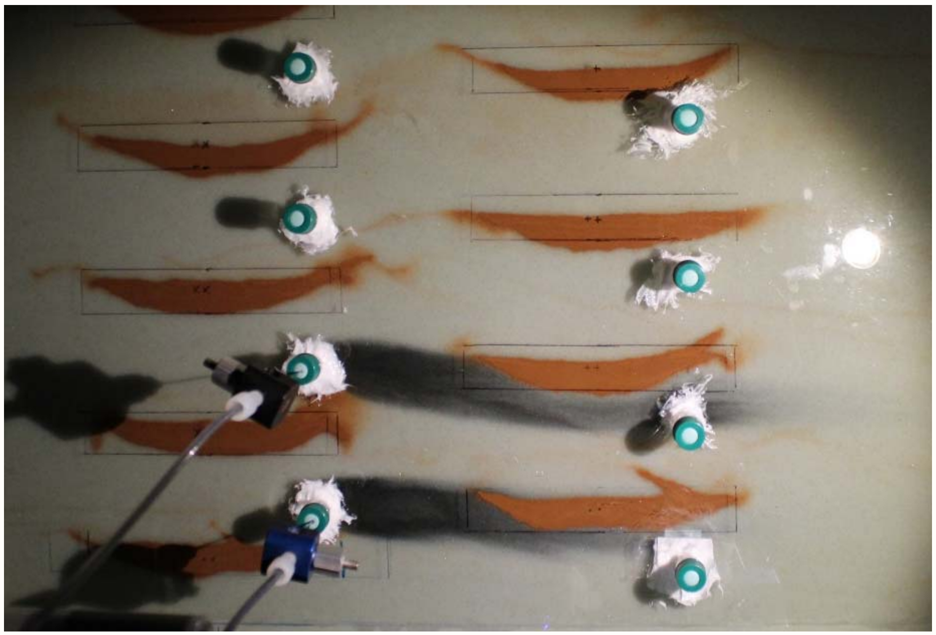
PV=1.45L

Tracer Test Before PDM+PAC Injection

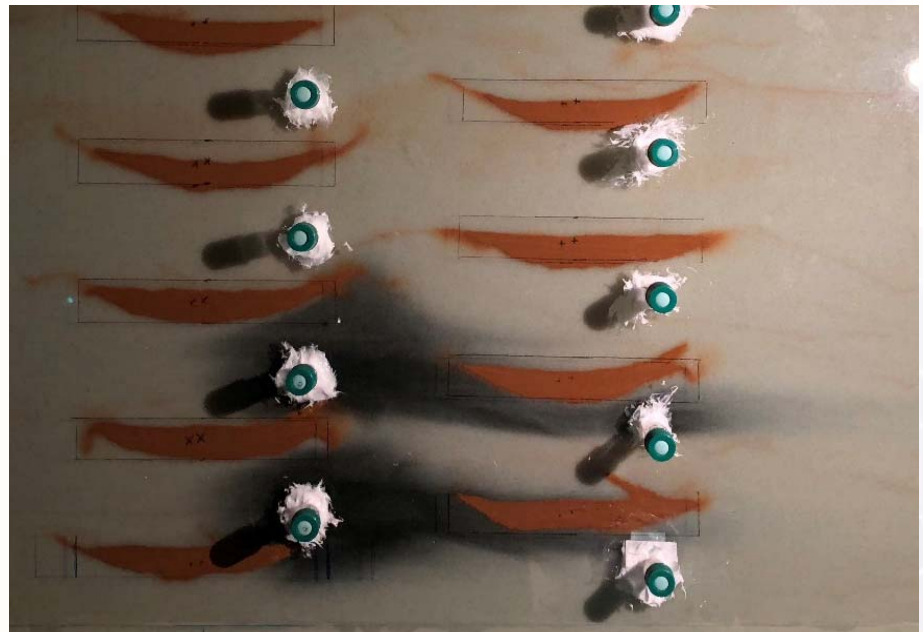


Side-port Injection of 1 g/L PAC + 5 g/L PDM

40 mL (0.08 mL/min) with background flow (2.4 mL/min)



80 mL (0.08 mL/min) with no background flow



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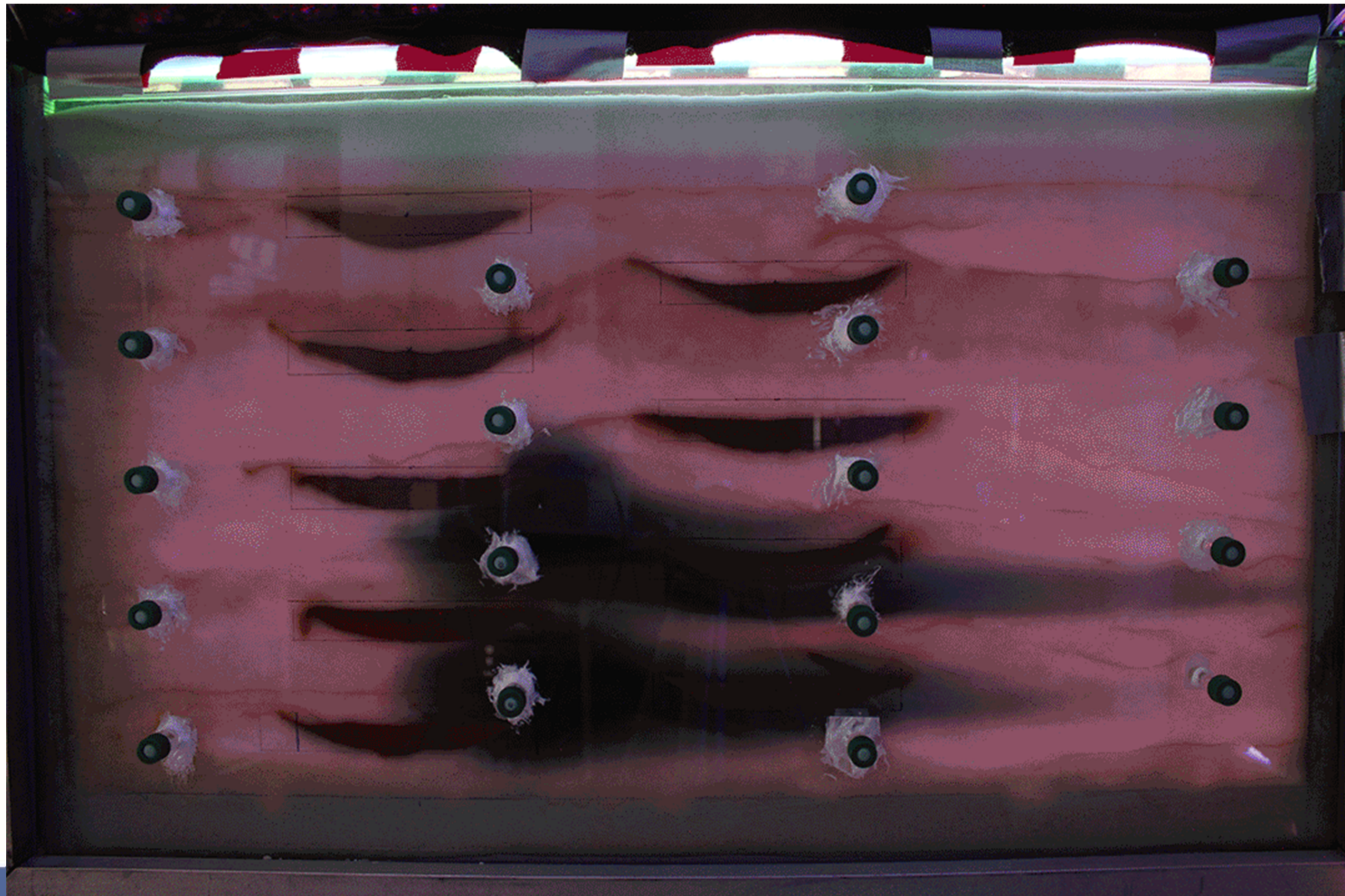
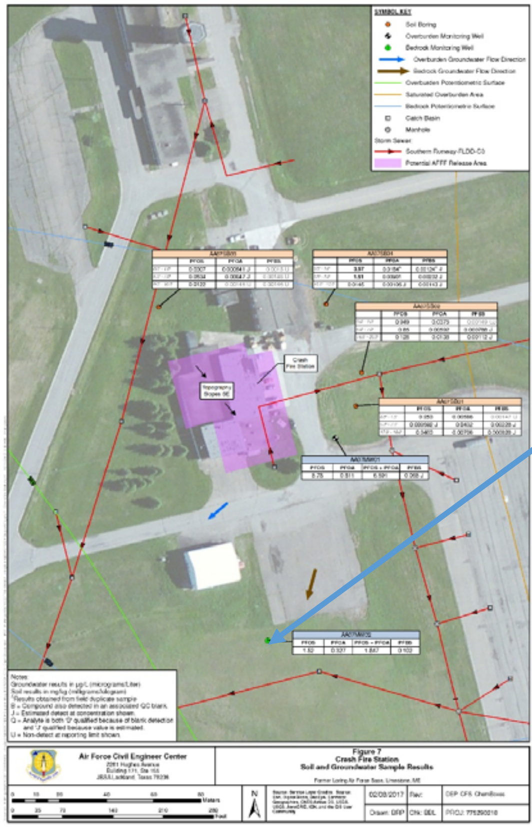
Tracer Test After PDM+PAC Injection



Collection of PFAS-Impacted Soil & Groundwater Samples

Former Loring AFB, Limestone, ME



	AA07MW02	
Compound	***Avg (ng/L)***	***Std. Dev (ng/L)***
PFBA	153.01	11.48
PFPeA	377.77	8.56
PFBS	108.36	2.29
PFHxA	632.10	147.02
4:2-FTS	27.54	9.57
PFHpA	147.78	8.08
PFHxS	1341.42	151.11
PFOA	396.86	17.47
6:2-FTS	1145.98	85.72
PFNA	78.42	29.71
PFOS	1604.65	145.16
PFDA	12.20	11.44
8:2-FTS	98.30	26.13

Conclusions

- Cationic polymers (PDM or PA) increased PFAS sorption by a factor of 3 to 45 based on batch and column experiments.
- The combination of powdered activated carbon (PAC) and PDM formed a stable suspension that can be delivered in situ to form a reactive zone.
- Column and aquifer cell studies demonstrated the sizable capacity of PDM+PAC-treated sand to retain PFOS and PFOA.

Future Work

- Conduct column and aquifer cell experiments with PFAS mixtures, both laboratory prepared and field groundwater samples (Loring AFB)
- Evaluate the potential release of retained PFAS over time and subject to changing pH and ionic strength.
- Evaluate competitive effects of NOM and other organic contaminants.

SERDP
DOD ▪ EPA ▪ DOE

Projects ER-2425 and ER-2714

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