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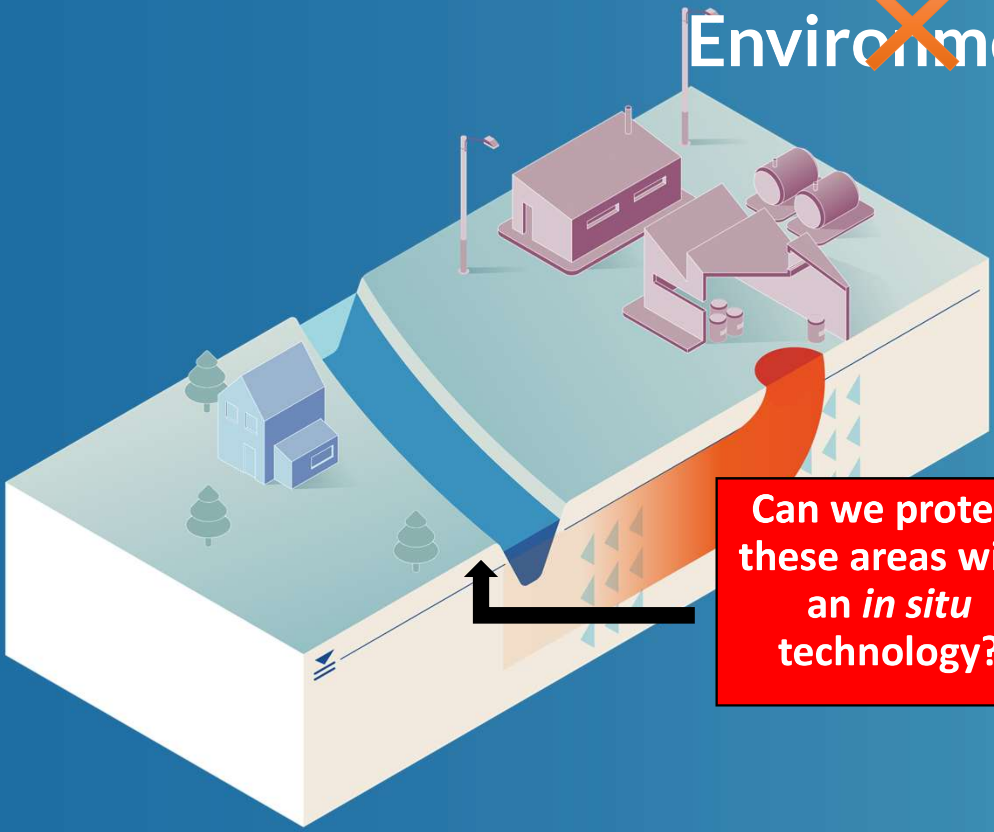
ENSOr 2020

First In Situ treatment of a PFAS plume in EU, using direct-push injection of Colloidal Activated Carbon

Kris Maerten
Regenesis Ltd

Sensitive Receptors at Risk

~~Environmental~~ Risk = Hazard x ~~Exposure~~

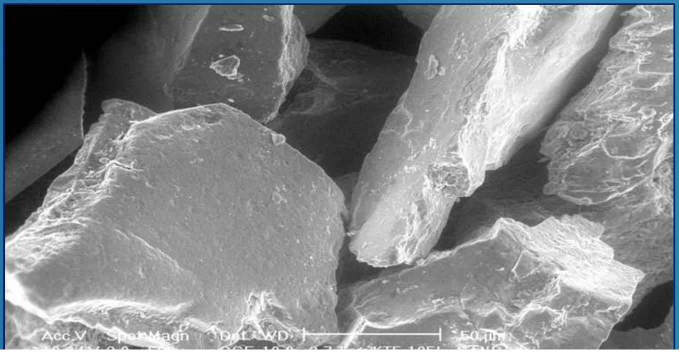


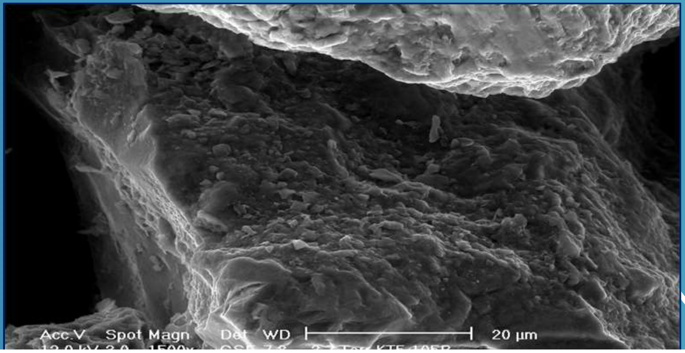
Can we protect these areas with an *in situ* technology?

- *Remediation strategy:*
  - Preventing contaminant migration
  - Removes exposure → removes the immediate risk

PlumeStop Colloidal Activated Carbon (CAC)

- Size: 1 – 2 µm (size of a red blood cell)
- Suspended in water
- Addition of cocktail of biodegradable polymers
- Wide area distribution
  - No high pressure fracturing needed
- Coats aquifer surfaces
  - Creates subsurface activated carbon filter
- Very fast sorption of PFAS
  - Smaller particles provide more exterior surface
  - Shorter distance to all the sorption sites compared to GAC
  - **Xiao, Ulrich, Chen & Higgins. Environ. Sci. Technol. 2017, 51, 6342-6351.**

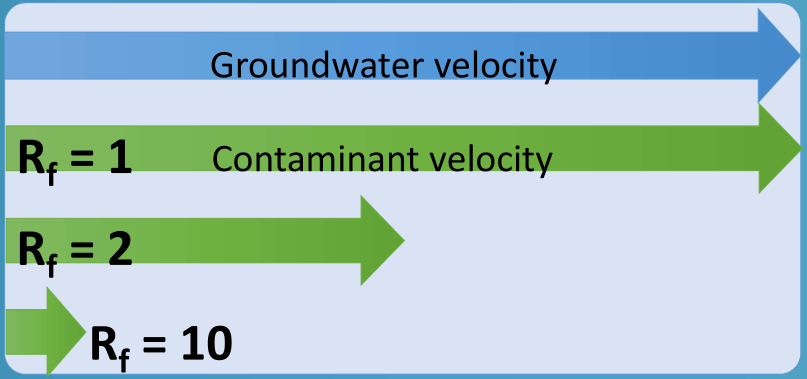




PlumeStop: Mode of Action with PFAS:

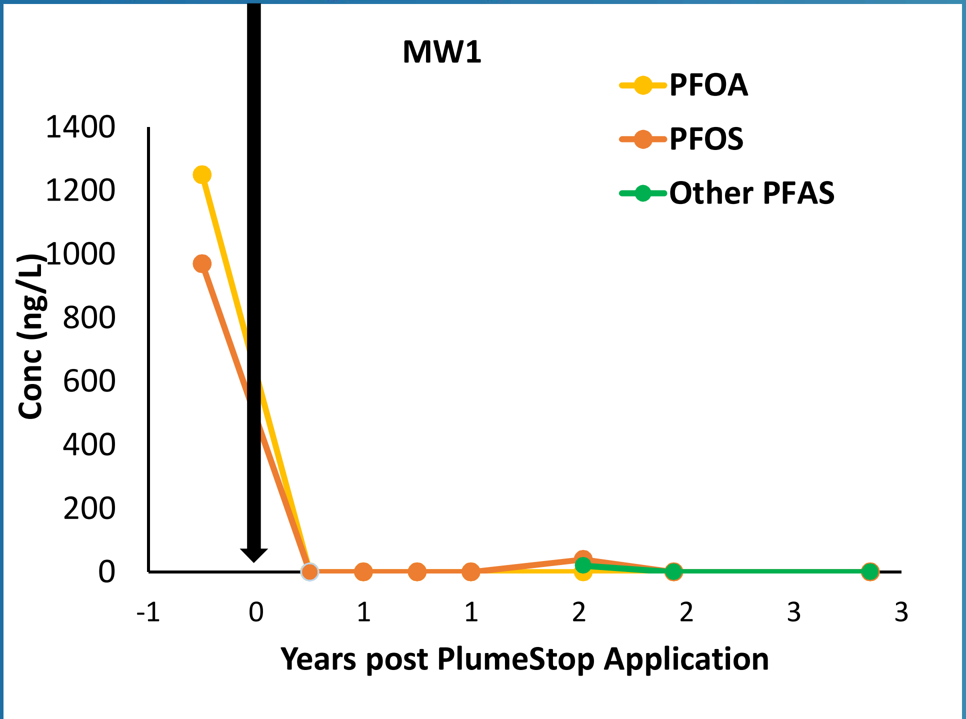
- Dynamic adsorption
  - Not a permanent immobilization
- Effect: Increases the retardation of a PFAS plume
  - Natural retardation factors for PFAS: 3-20
  - Retardation factors achievable with PlumeStop: 10,000

→Treatment of decades



Guelfo and Higgins, 2013. Environ. Sci. Technol.

Example Results: ONTARIO, CANADA



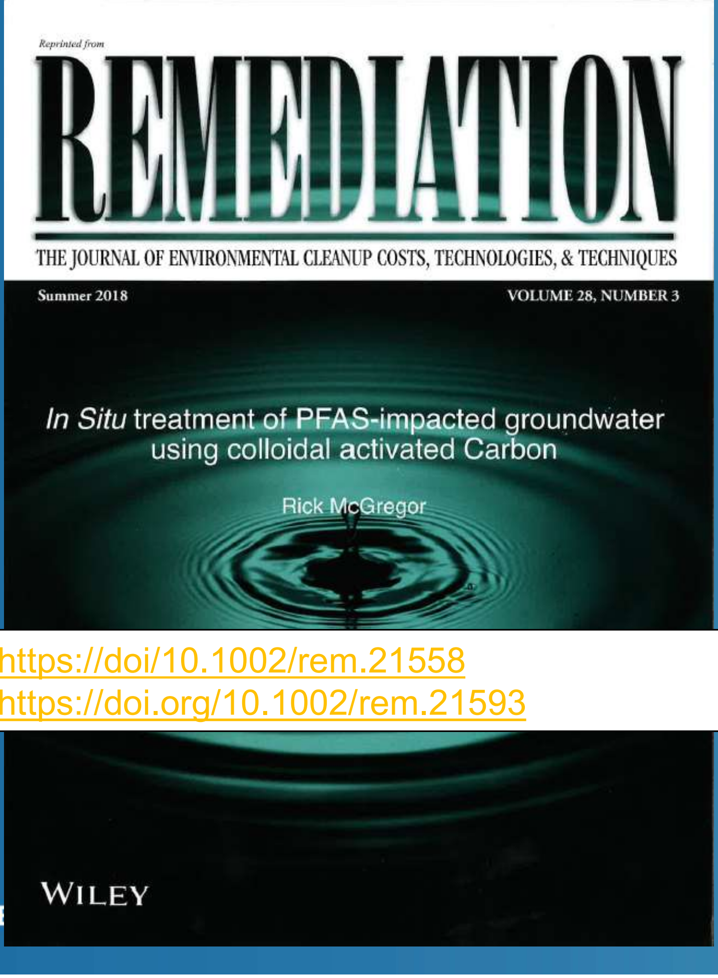
Monitoring events:

- PFOS + PFOA
  - Baseline
  - 3, 6, 9, 12, 18, 24, 32 months
- Extended PFAS list (12 more analytes)
  - 18, 24, 32 months
  - No baseline data available

Results for MW1 are shown

- Non-detect (typical RL = 20 ng/L)
- Only one hit of PFOS at 18 months, just above RL
- Data are representative of all 6 wells

Case Published:



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REMEDIATION

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Rick McGregor

WILEY

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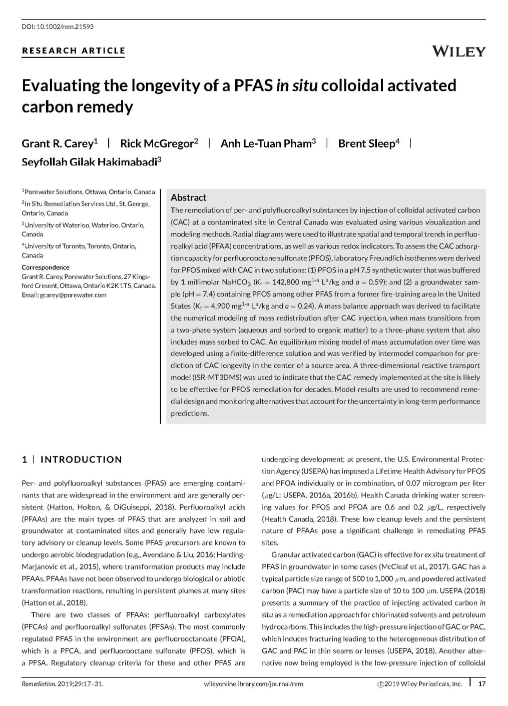
Abstract

1 | INTRODUCTION



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RESEARCH ARTICLE

WILEY

Evaluating the longevity of a PFAS *in situ* colloidal activated carbon remedy

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Abstract

The remediation of per- and polyfluoroalkyl substances by injection of colloidal activated carbon (CAC) at a contaminated site in Central Canada was evaluated using various visualization and modeling methods. Radial diagrams were used to illustrate spatial and temporal trends in perfluoroalkyl acid (PFAA) concentrations, as well as various redox indicators. To assess the CAC adsorption capacity for perfluorooctane sulfonate (PFOS), laboratory Freundlich isotherms were derived for PFOS mixed with CAC in two solutions: (1) PFOS in a pH 7.5 synthetic water that was buffered by 1 millimolar $NaHCO_3$ (K_f = 142,800 mg^{1-a} L^a/kg and a = 0.59); and (2) a groundwater sample (pH = 7.4) containing PFOS among other PFAS from a former fire-training area in the United States (K_f = 4,900 mg^{1-a} L^a/kg and a = 0.24). A mass balance approach was derived to facilitate the numerical modeling of mass redistribution after CAC injection, when mass transitions from a two-phase system (aqueous and sorbed to organic matter) to a three-phase system that also includes mass sorbed to CAC. An equilibrium mixing model of mass accumulation over time was developed using a finite-difference solution and was verified by intermodel comparison for prediction of CAC longevity in the center of a source area. A three-dimensional reactive transport model (ISR-MT3DMS) was used to indicate that the CAC remedy implemented at the site is likely to be effective for PFOS remediation for decades. Model results are used to recommend remedial design and monitoring alternatives that account for the uncertainty in long-term performance predictions.

1 | INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants that are widespread in the environment and are generally persistent (Hatton, Holton, & DiGuiseppi, 2018). Perfluoroalkyl acids (PFAAs) are the main types of PFAS that are analyzed in soil and groundwater at contaminated sites and generally have low regulatory advisory or cleanup levels. Some PFAS precursors are known to undergo aerobic biodegradation (e.g., Avendano & Liu, 2016; Harding-Marjanovic et al., 2015), where transformation products may include PFAAs. PFAAs have not been observed to undergo biological or abiotic transformation reactions, resulting in persistent plumes at many sites (Hatton et al., 2018).

There are two classes of PFAAs: perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs). The most commonly regulated PFAS in the environment are perfluorooctanoate (PFOA), which is a PFCA, and perfluorooctane sulfonate (PFOS), which is a PFSA. Regulatory cleanup criteria for these and other PFAS are undergoing development; at present, the U.S. Environmental Protection Agency (USEPA) has imposed a Lifetime Health Advisory for PFOS and PFOA individually or in combination, of 0.07 microgram per liter (μg/L; USEPA, 2016a, 2016b). Health Canada drinking water screening values for PFOS and PFOA are 0.6 and 0.2 μg/L, respectively (Health Canada, 2018). These low cleanup levels and the persistent nature of PFAAs pose a significant challenge in remediating PFAS sites.

Granular activated carbon (GAC) is effective for *ex situ* treatment of PFAS in groundwater in some cases (McCleaf et al., 2017). GAC has a typical particle size range of 500 to 1,000 μm, and powdered activated carbon (PAC) may have a particle size of 10 to 100 μm. USEPA (2018) presents a summary of the practice of injecting activated carbon *in situ* as a remediation approach for chlorinated solvents and petroleum hydrocarbons. This includes the high-pressure injection of GAC or PAC, which induces fracturing leading to the heterogeneous distribution of GAC and PAC in thin seams or lenses (USEPA, 2018). Another alternative now being employed is the low-pressure injection of colloidal

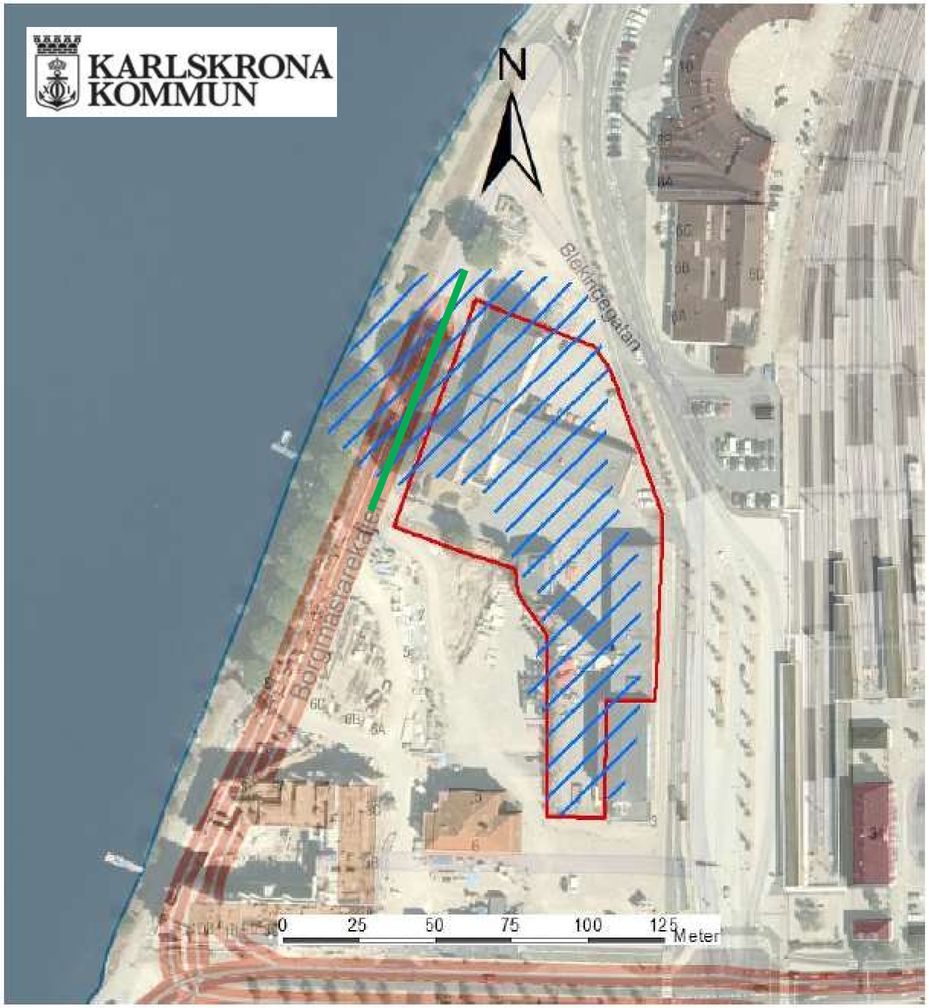
Remediation. 2019;29:17–31. wileyonlinelibrary.com/journal/rem

Applications Completed

- These sites are co-mingled plumes with TPH or CVOCs
- Total PFAS concentrations range: 100 ng/L to 170,000 ng/L

Case Study: Development in South Sweden

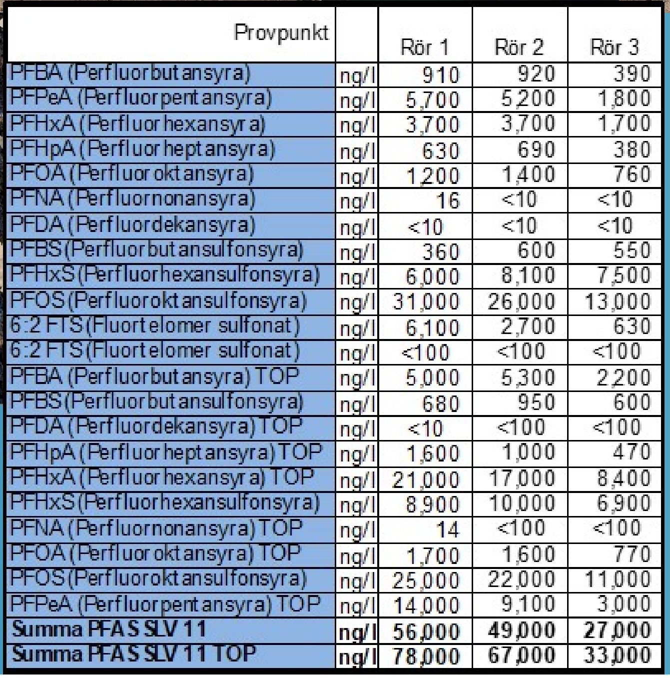
- Former industrial site
- Fire training area
  - Use of AFFF: PFAS
- To be redeveloped to residential
- Reclaimed land by Baltic sea
  - Highly heterogeneous
  - High organic content
  - High permeability conduits
  - Tidal effect
- GW Contamination
  - PFOS only identified initially (17µg/L)



Figur 11. Bedömt utbredningsområde för PFAS-förorenad jord.

Design Verification Testing (DVT)

- Geology/Hydrogeology
  - Define flux zones
    - Particle size distribution
    - Seepage velocity
  - Map surface of bedrock
- Contaminant loading and competitive sorption
  - Test for:
    - Total Oxidizable Precursor
    - Other contaminants
    - Natural organics
- Clean water injection
  - Test volume accepted
  - Pressure vs flow rate
    = good radius of influence



Provpunkt		Rör 1	Rör 2	Rör 3
PFBA (Perfluorbutansyra)	ng/l	910	920	390
PFPeA (Perfluorpentansyra)	ng/l	5,700	5,200	1,800
PFHxA (Perfluorhexansyra)	ng/l	3,700	3,700	1,700
PFHpA (Perfluorheptansyra)	ng/l	630	690	380
PFOA (Perfluoroktansyra)	ng/l	1,200	1,400	760
PFNA (Perfluornonansyra)	ng/l	16	<10	<10
PFDA (Perfluordekansyra)	ng/l	<10	<10	<10
PFBS (Perfluorbutansulfonsyra)	ng/l	360	600	550
PFHxS (Perfluorhexansulfonsyra)	ng/l	6,000	8,100	7,500
PFOS (Perfluoroktansulfonsyra)	ng/l	31,000	26,000	13,000
6:2 FTS (Fluortelomer sulfonat)	ng/l	6,100	2,700	630
6:2 FTS (Fluortelomer sulfonat)	ng/l	<100	<100	<100
PFBA (Perfluorbutansyra) TOP	ng/l	5,000	5,300	2,200
PFBS (Perfluorbutansulfonsyra)	ng/l	680	950	600
PFDA (Perfluordekansyra) TOP	ng/l	<10	<100	<100
PFHpA (Perfluorheptansyra) TOP	ng/l	1,600	1,000	470
PFHxA (Perfluorhexansyra) TOP	ng/l	21,000	17,000	8,400
PFHxS (Perfluorhexansulfonsyra)	ng/l	8,900	10,000	6,900
PFNA (Perfluornonansyra) TOP	ng/l	14	<100	<100
PFOA (Perfluoroktansyra) TOP	ng/l	1,700	1,600	770
PFOS (Perfluoroktansulfonsyra)	ng/l	25,000	22,000	11,000
PFPeA (Perfluorpentansyra) TOP	ng/l	14,000	9,100	3,000
Summa PFAS SLV 11	**ng/l**	**56,000**	**49,000**	**27,000**
Summa PFAS SLV 11 TOP	**ng/l**	**78,000**	**67,000**	**33,000**

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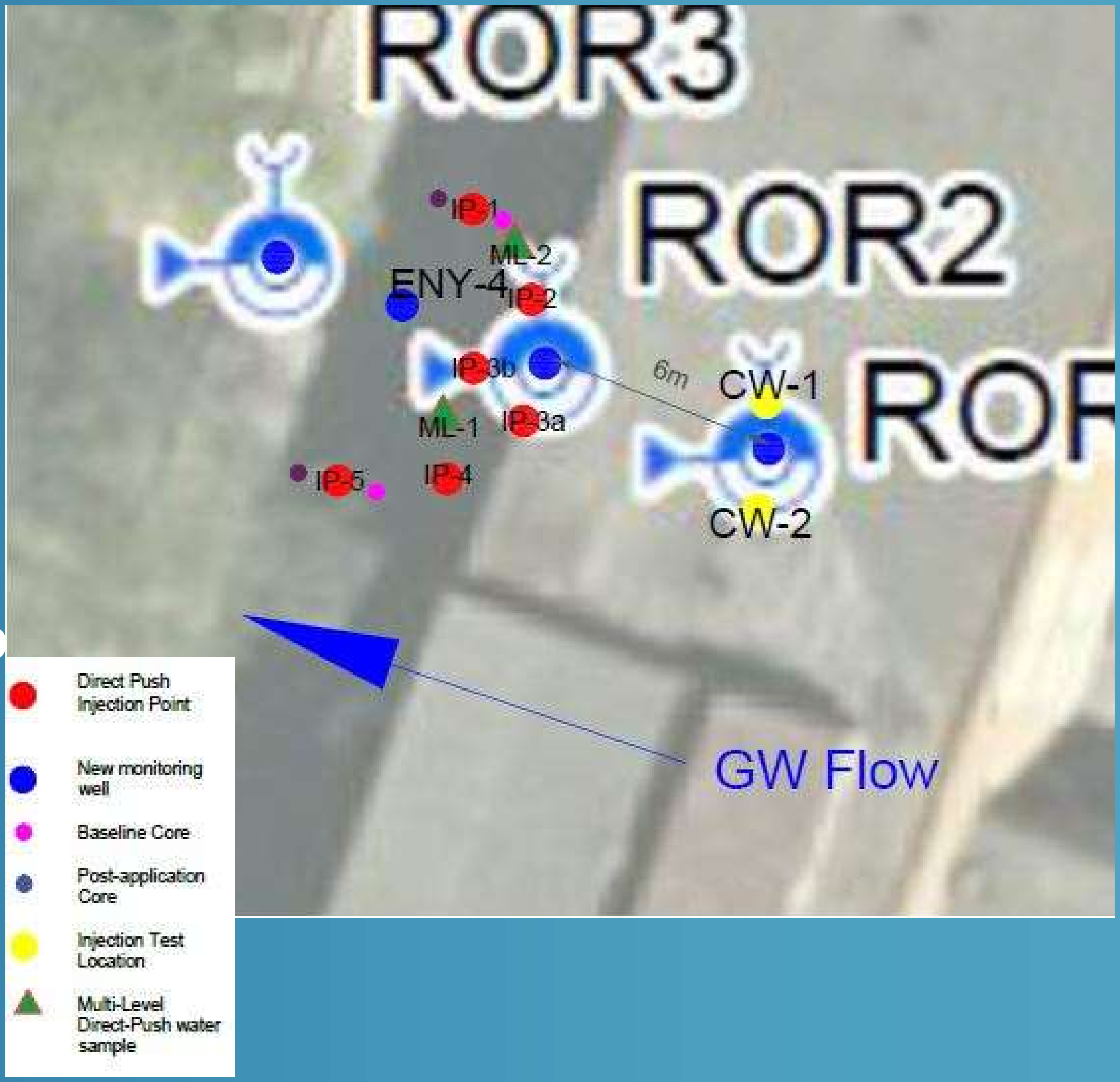
Pilot configuration

- Curved 10m injection line
  - GW direction questionable
- Close to property boundary
- Injection spacing 2.5 m
- Depth: 1.5 to 4 m BGL
  - Top gw to rockhead
- Bottom-up with retractable tip
- GW and soil distribution test



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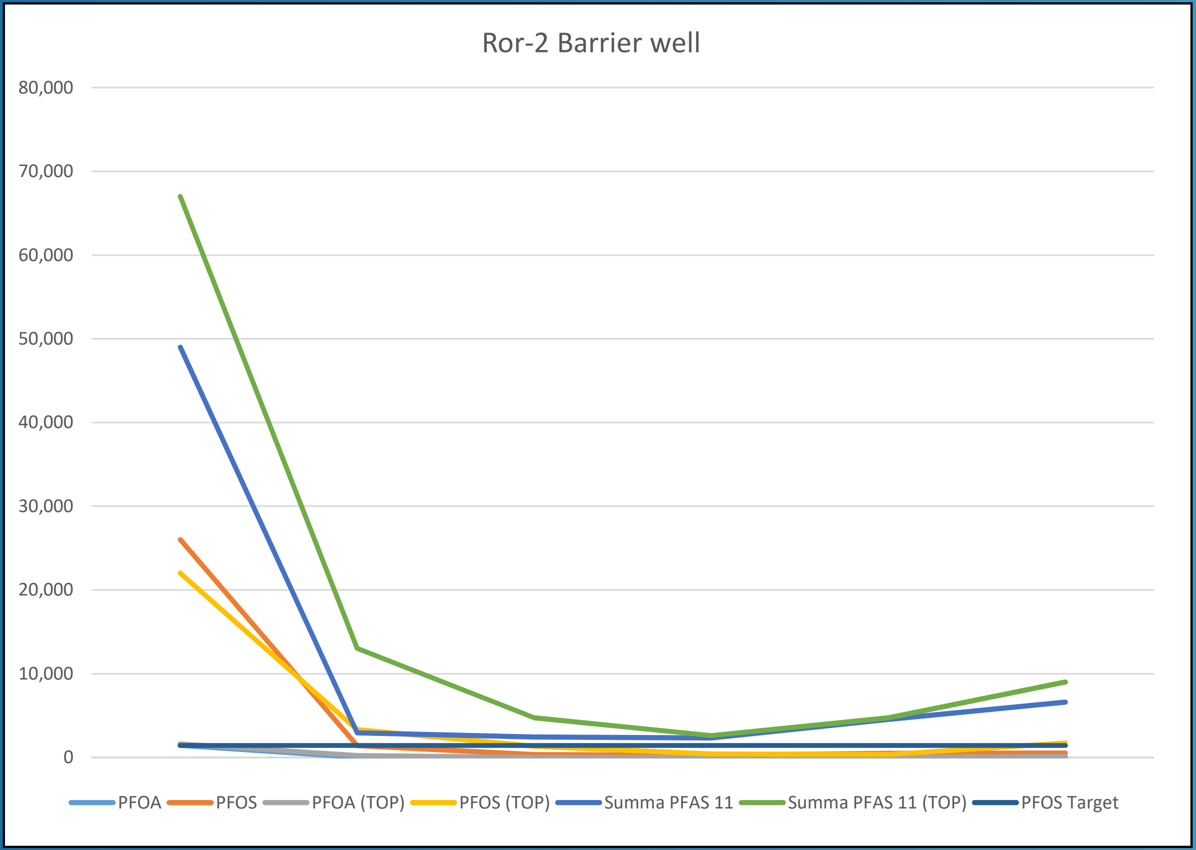
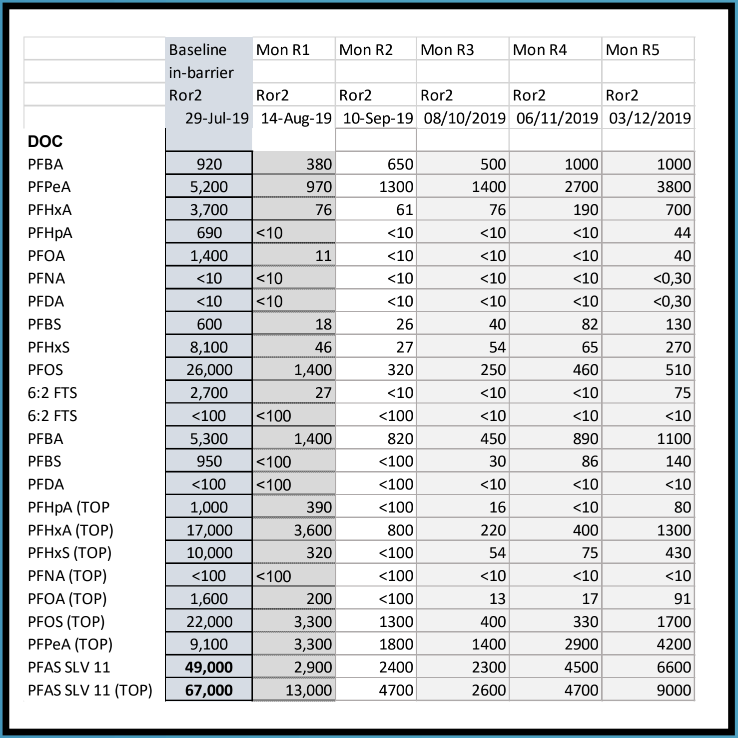
Pilot results … so far

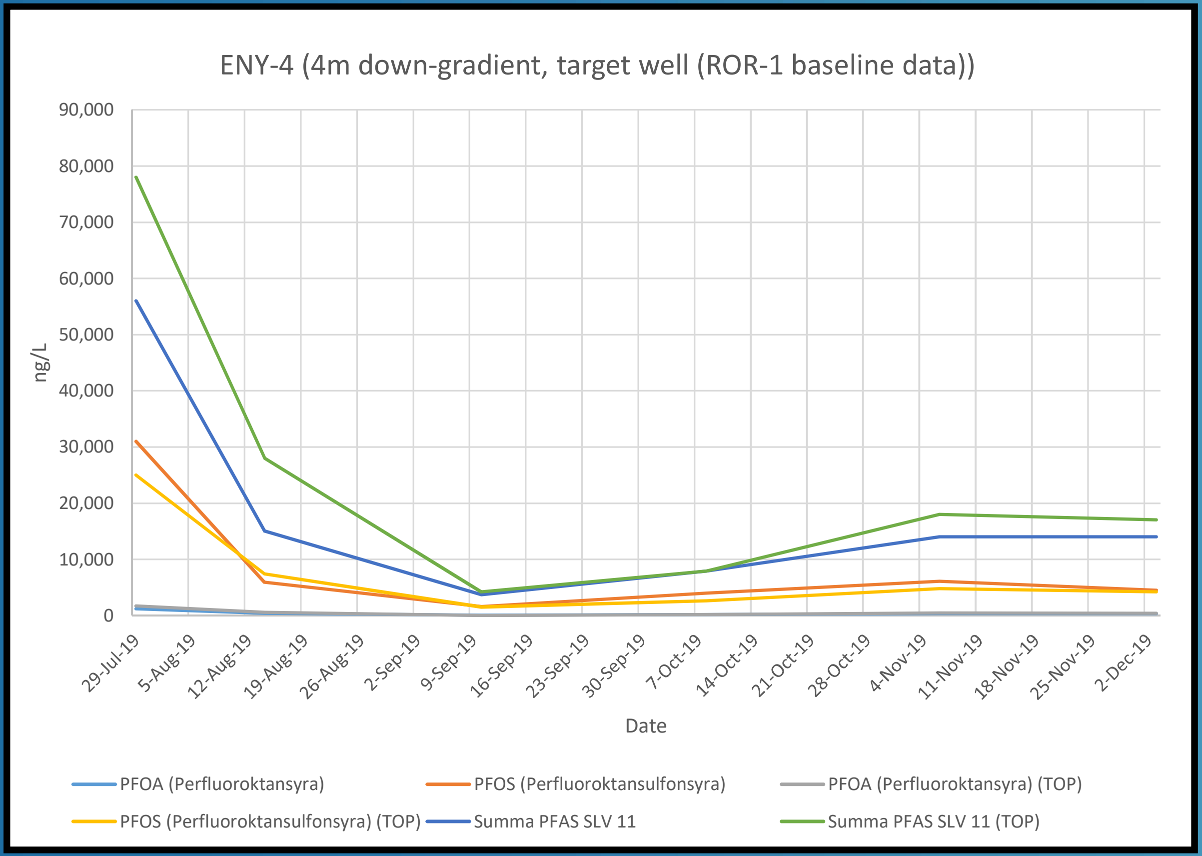


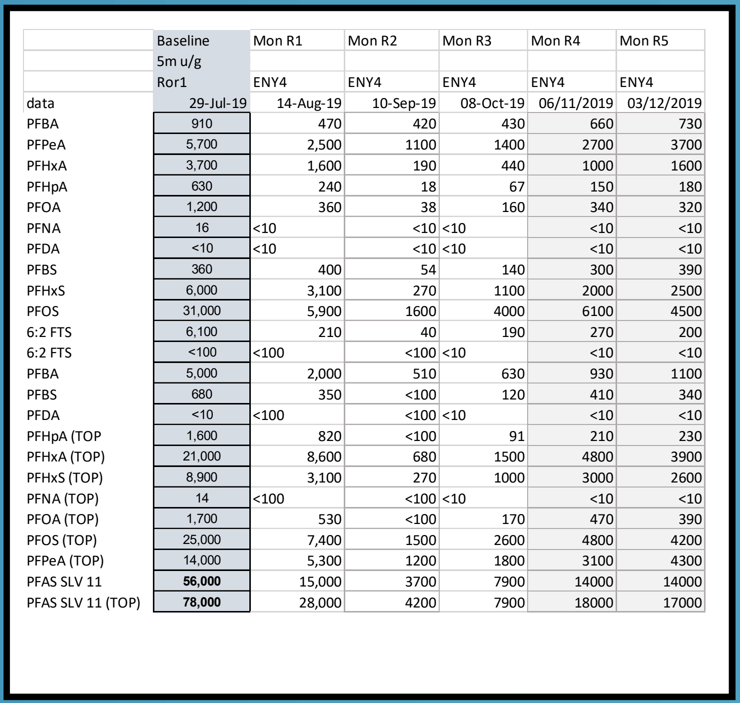


	Baseline	Mon R1	Mon R2	Mon R3	Mon R4	Mon R5
	in-barrier					
	Ror2	Ror2	Ror2	Ror2	Ror2	Ror2
	29-Jul-19	14-Aug-19	10-Sep-19	08/10/2019	06/11/2019	03/12/2019
DOC						
PFBA	920	380	650	500	1000	1000
PFPeA	5,200	970	1300	1400	2700	3800
PFHxA	3,700	76	61	76	190	700
PFHpA	690	<10	<10	<10	<10	44
PFOA	1,400	11	<10	<10	<10	40
PFNA	<10	<10	<10	<10	<10	<0,30
PFDA	<10	<10	<10	<10	<10	<0,30
PFBS	600	18	26	40	82	130
PFHxS	8,100	46	27	54	65	270
PFOS	26,000	1,400	320	250	460	510
6:2 FTS	2,700	27	<10	<10	<10	75
6:2 FTS	<100	<100	<100	<10	<10	<10
PFBA	5,300	1,400	820	450	890	1100
PFBS	950	<100	<100	30	86	140
PFDA	<100	<100	<100	<10	<10	<10
PFHpA (TOP	1,000	390	<100	16	<10	80
PFHxA (TOP)	17,000	3,600	800	220	400	1300
PFHxS (TOP)	10,000	320	<100	54	75	430
PFNA (TOP)	<100	<100	<100	<10	<10	<10
PFOA (TOP)	1,600	200	<100	13	17	91
PFOS (TOP)	22,000	3,300	1300	400	330	1700
PFPeA (TOP)	9,100	3,300	1800	1400	2900	4200
PFAS SLV 11	**49,000**	2,900	2400	2300	4500	6600
PFAS SLV 11 (TOP)	**67,000**	13,000	4700	2600	4700	9000

87% reduction in TOP∑11 PFAS compounds

Pilot results … so far





	Baseline	Mon R1	Mon R2	Mon R3	Mon R4	Mon R5
	5m u/g					
	Ror1	ENY4	ENY4	ENY4	ENY4	ENY4
data	29-Jul-19	14-Aug-19	10-Sep-19	08-Oct-19	06/11/2019	03/12/2019
PFBA	910	470	420	430	660	730
PFPeA	5,700	2,500	1100	1400	2700	3700
PFHxA	3,700	1,600	190	440	1000	1600
PFHpA	630	240	18	67	150	180
PFOA	1,200	360	38	160	340	320
PFNA	16	<10	<10	<10	<10	<10
PFDA	<10	<10	<10	<10	<10	<10
PFBS	360	400	54	140	300	390
PFHxS	6,000	3,100	270	1100	2000	2500
PFOS	31,000	5,900	1600	4000	6100	4500
6:2 FTS	6,100	210	40	190	270	200
6:2 FTS	<100	<100	<100	<10	<10	<10
PFBA	5,000	2,000	510	630	930	1100
PFBS	680	350	<100	120	410	340
PFDA	<10	<100	<100	<10	<10	<10
PFHpA (TOP	1,600	820	<100	91	210	230
PFHxA (TOP)	21,000	8,600	680	1500	4800	3900
PFHxS (TOP)	8,900	3,100	270	1000	3000	2600
PFNA (TOP)	14	<100	<100	<10	<10	<10
PFOA (TOP)	1,700	530	<100	170	470	390
PFOS (TOP)	25,000	7,400	1500	2600	4800	4200
PFPeA (TOP)	14,000	5,300	1200	1800	3100	4300
PFAS SLV 11	**56,000**	15,000	3700	7900	14000	14000
PFAS SLV 11 (TOP)	**78,000**	28,000	4200	7900	18000	17000

78% reduction in TOP∑11 PFAS compounds

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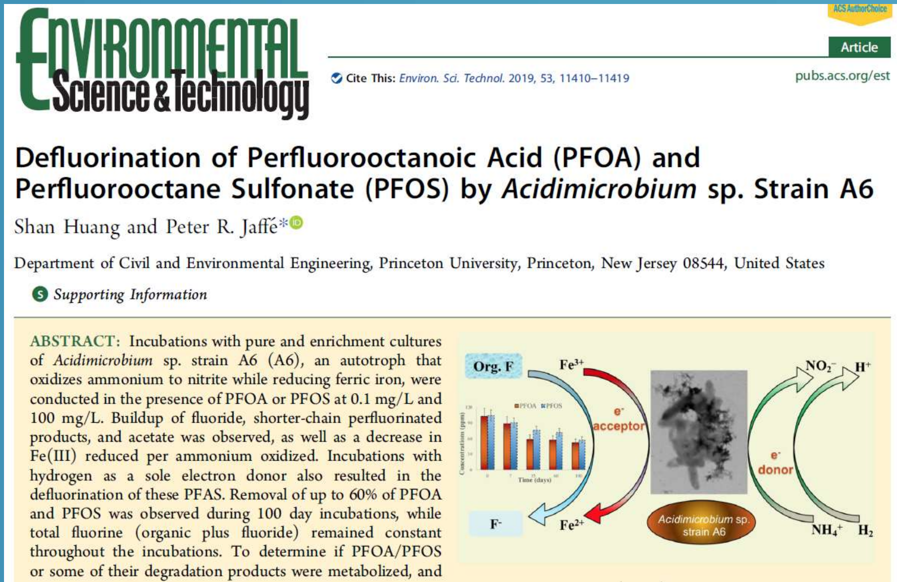
And when the barrier is finally spent…

- Be thankful you had a barrier
- Use new technology
  - We don't know what technology will be available within several decades.
  - Maybe it's biology that is the most promising.
- Put in some more PlumeStop
  - Compare it to painting a shed to stop them rotting.



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Article

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Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by *Acidimicrobium* sp. Strain A6

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Supporting Information

ABSTRACT: Incubations with pure and enrichment cultures of *Acidimicrobium* sp. strain A6 (A6), an autotroph that oxidizes ammonium to nitrite while reducing ferric iron, were conducted in the presence of PFOA or PFOS at 0.1 mg/L and 100 mg/L. Buildup of fluoride, shorter-chain perfluorinated products, and acetate was observed, as well as a decrease in Fe(III) reduced per ammonium oxidized. Incubations with hydrogen as a sole electron donor also resulted in the defluorination of these PFAS. Removal of up to 60% of PFOA and PFOS was observed during 100 day incubations, while total fluorine (organic plus fluoride) remained constant throughout the incubations. To determine if PFOA/PFOS or some of their degradation products were metabolized, and

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Thank You!

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