ENVIRONMENTAL

Do it Right, Do it once

Per- and Polyfluoroalkyl Substances (PFAS) Remediation Webinar-Part 2

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April 25, 2018

Agenda
Part 2

- Introduction
- Quick Review of effective remedial options
- Adsorption / IX Case Studies
- In-situ Chemical Oxidation Case Study
- Wrap-Up / Summary of Current State of the Practice
- Questions and Answers

Remedial Options Overview

- Based on the physical – chemical properties of PFAS (at least the higher C PFAS)
  - High molecular weight = potential for sieving / filtration
  - High Koc = potential for adsorption
  - Charged group = potential for ion exchange
  - Low VP = not suitable for SVE at ambient temperatures
  - Low H = not suitable for stripping from groundwater at ambient temperatures
- Biodegradation
  - Very limited research to date showing definitive biodegradation of Pers
    - Evidence of transformations of Polys
    - Question on whether can treat to the proposed standards
- Oxidative / reductive technologies
  - Oxidative showing promise, but some unanswered questions
  - Common theme is high energy and / or diverse reactive species needed (e.g., electro-chemical, sonolysis)
- Thermal desorption / destruction (higher temperatures ~1000°C)
- Isolation
  - Excavation and landfilling
  - Stabilization

Filtration

Essentially "Sieving" of PFAS molecules

- Nano-Filtration (NF)
  - PFAS have molecular weight cutoff (MWCO) of approximately 300 - 500 Daltons
    - Measure of size restriction to pass through filter media
  - NF MWCO > 200 Daltons, therefore >90% effective most PFAS
  - Ultra and micro-filtration low effectiveness
- Reverse Osmosis
  - Polymers used have spaces on the order of 100 – 200 Daltons
  - >90% effective most PFAS
- Concentrated waste streams result / require treatment
  - Typically incineration at > 1100 oC
- Pretreatment needed due to potential for filter clogging
- PerfluorAd – not really filtration but coagulation - flocculation with sorbent polishing
  - Flocculant requires disposal / treatment

Adsorption/Ion Exchange

(most commonplace, non-destructive)

- Carbon-based systems
  - Ex-situ activated carbon systems (GAC or PAC)
  - Biochar (biomass and charcoal)?
  - In-situ injectable carbon-based systems
- Clays or blend of sorbent-based systems
  - e.g., Rembind™, MatCARE™
  - Part isolation?
- Synthetics resins – gaining traction due to capacity/effectiveness
  - Combination IX and adsorption
  - Faster kinetics
- Zeolites – R&D
- For in-situ applications questions exist on long term performance

Treatability studies are essential

Adsorption and IX Case Studies

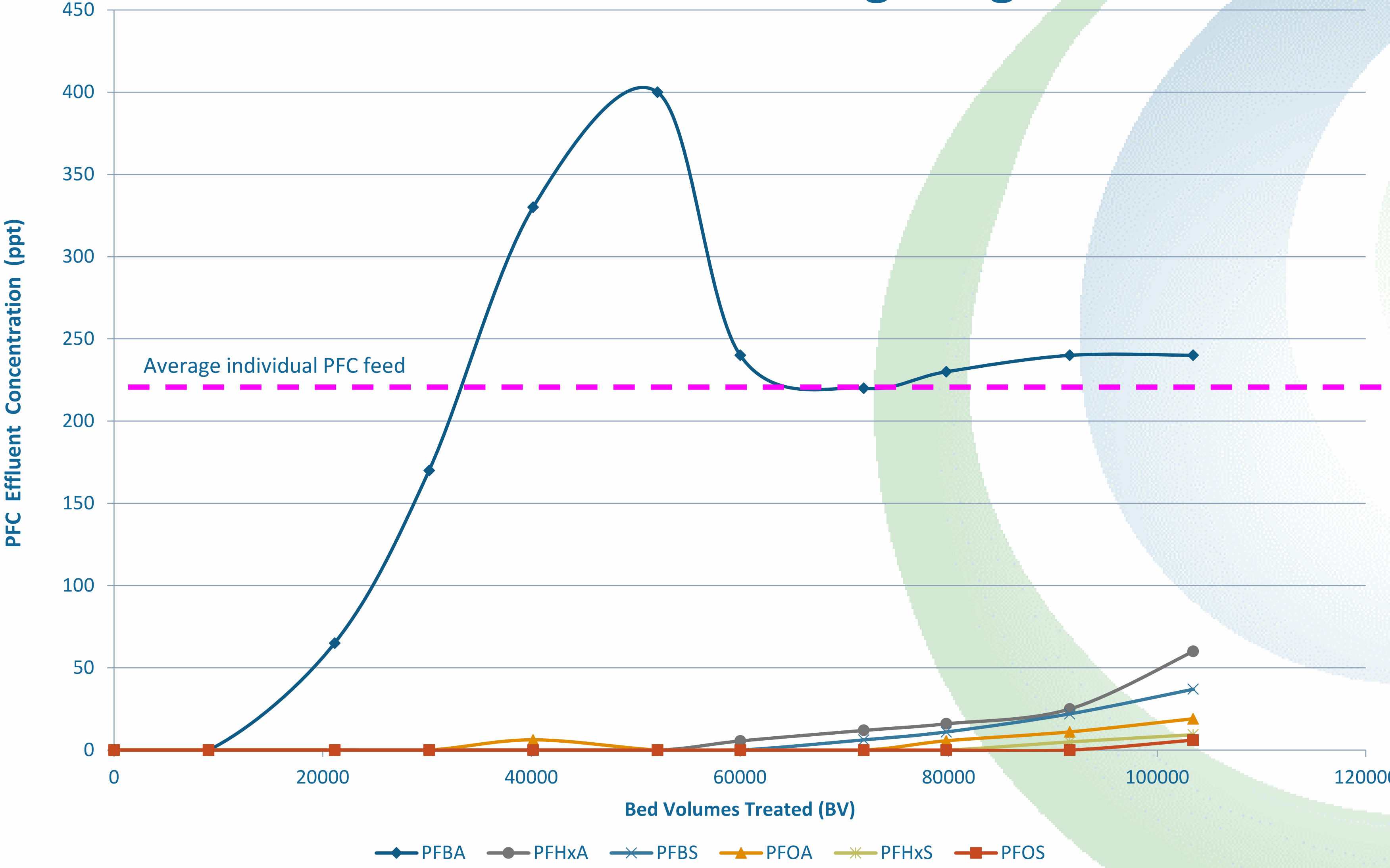
Comparison of Various GAC for PFAS Removal

- Multiple PFAS, variety of chain lengths
  - Each compounds spiked to approximately 200 ppt

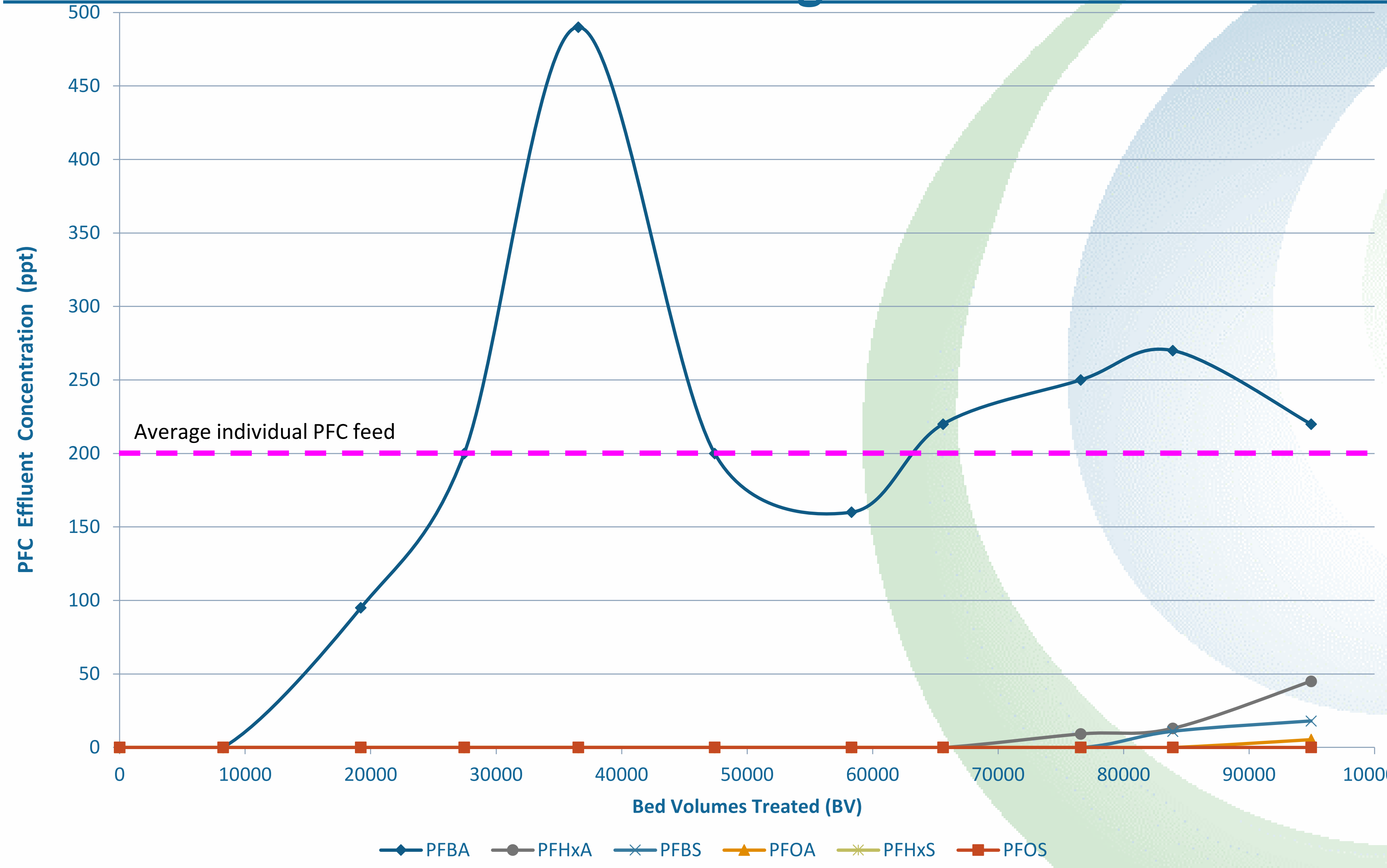
Name	Abbreviation	CAS Number	Carbon Chain Length	Molecular Weight (g/mol)
Perfluoro octanesulfonic acid	PFOS	1763-23-1	C8	500.13
Perfluoro octanioc acid	PFOA	335-67-1	C8	414.07
Perfluorohexanesulfonic acid	PFHxS	355-46-4	C6	400.11
Perfluoro hexanoic acid	PFHxA	307-24-4	C6	314.05
Perfluoro butanesulfonic acid	PFBS	375-73-5	C4	300.1
Perfluoro butanoic acid	PFBA	375-22-4	C4	214.04

- Background TOC – 0.16 ppm
- Simulated Empty Bed Contact Time (EBCT) – 10 minutes

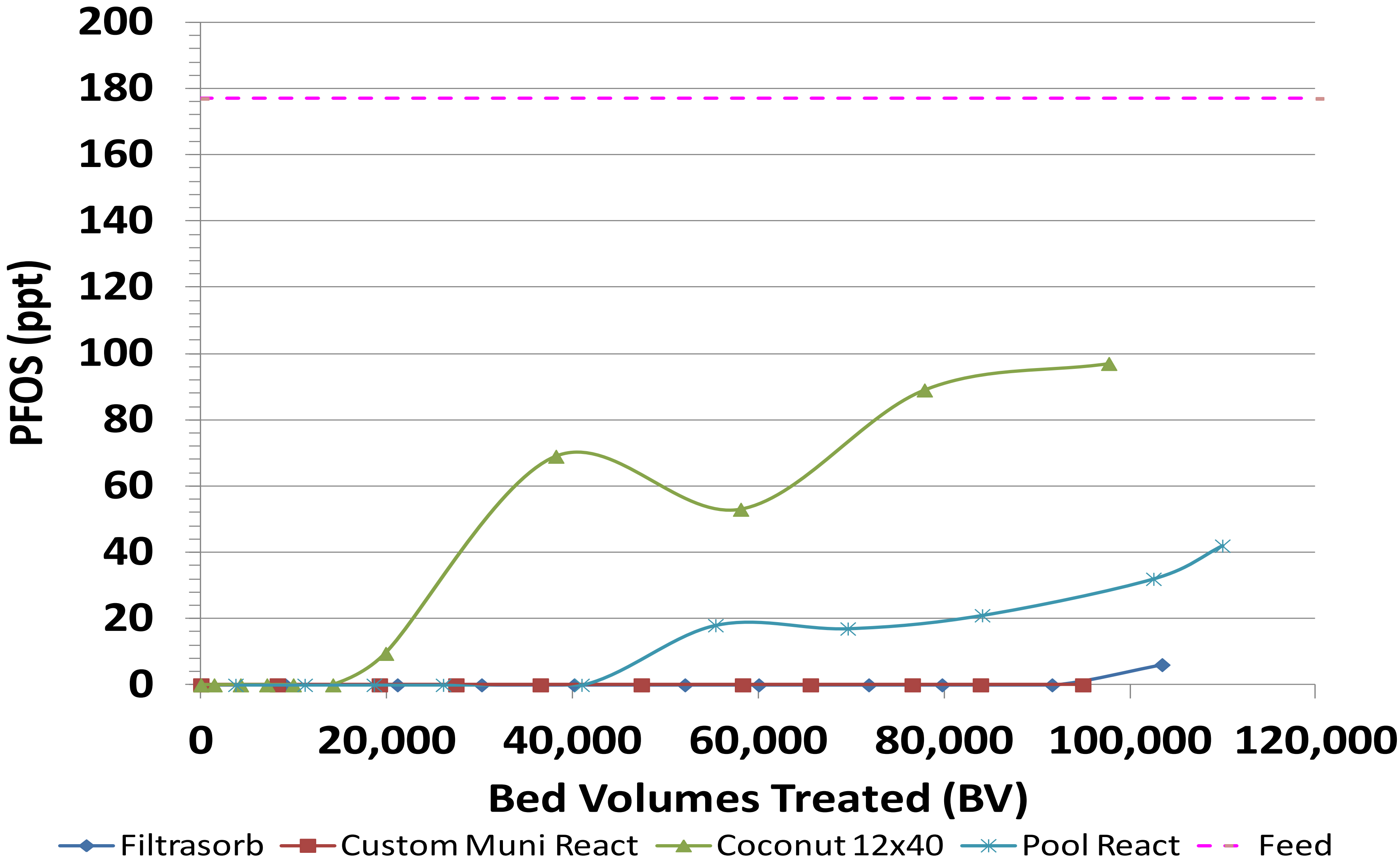
Removal of Various PFAS using Virgin Filtrasorb



Removal of Various PFAS using Reactivated Filtrasorb

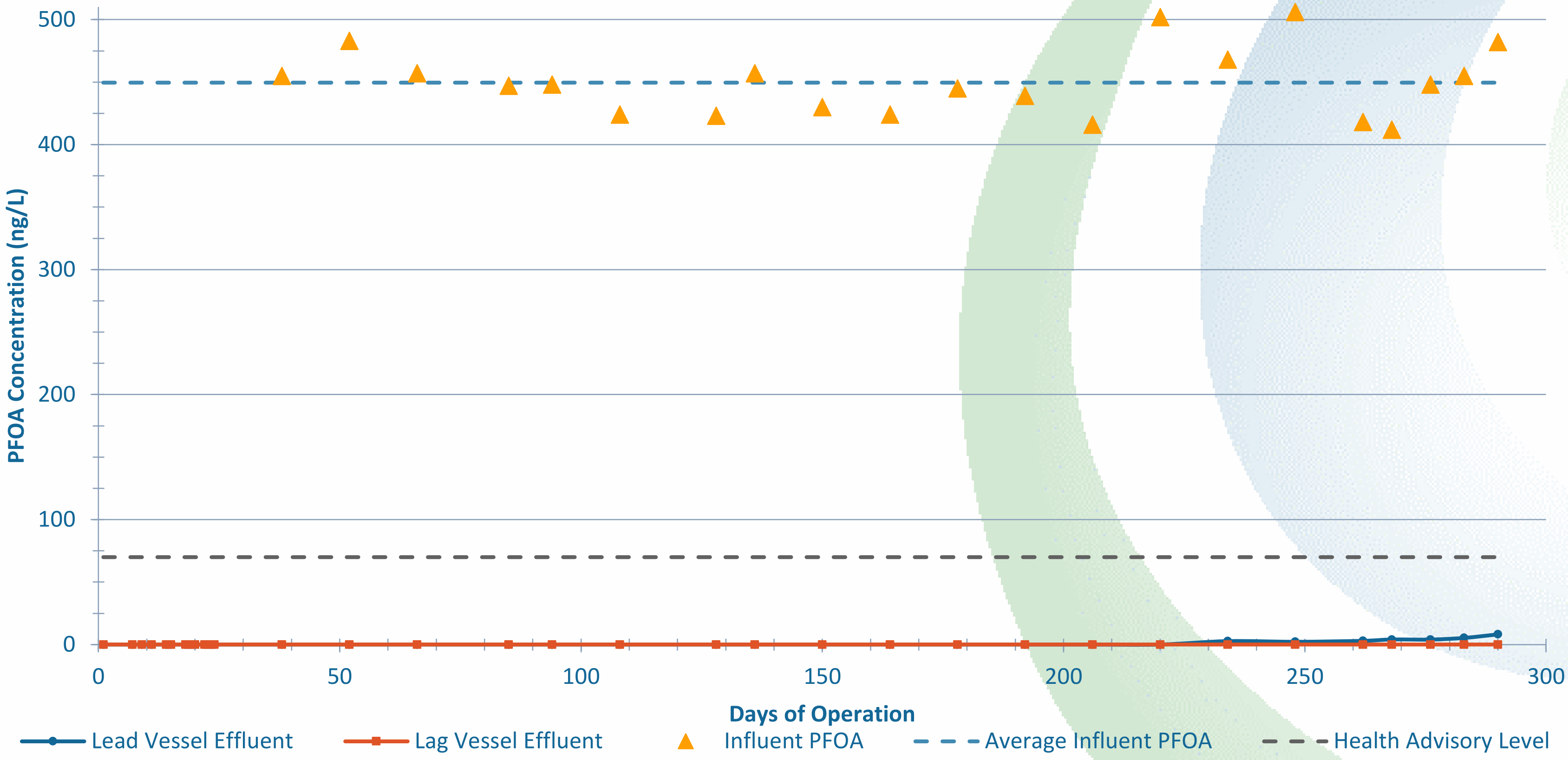


PFOS Breakthrough Comparison, EBCT 10 Minutes

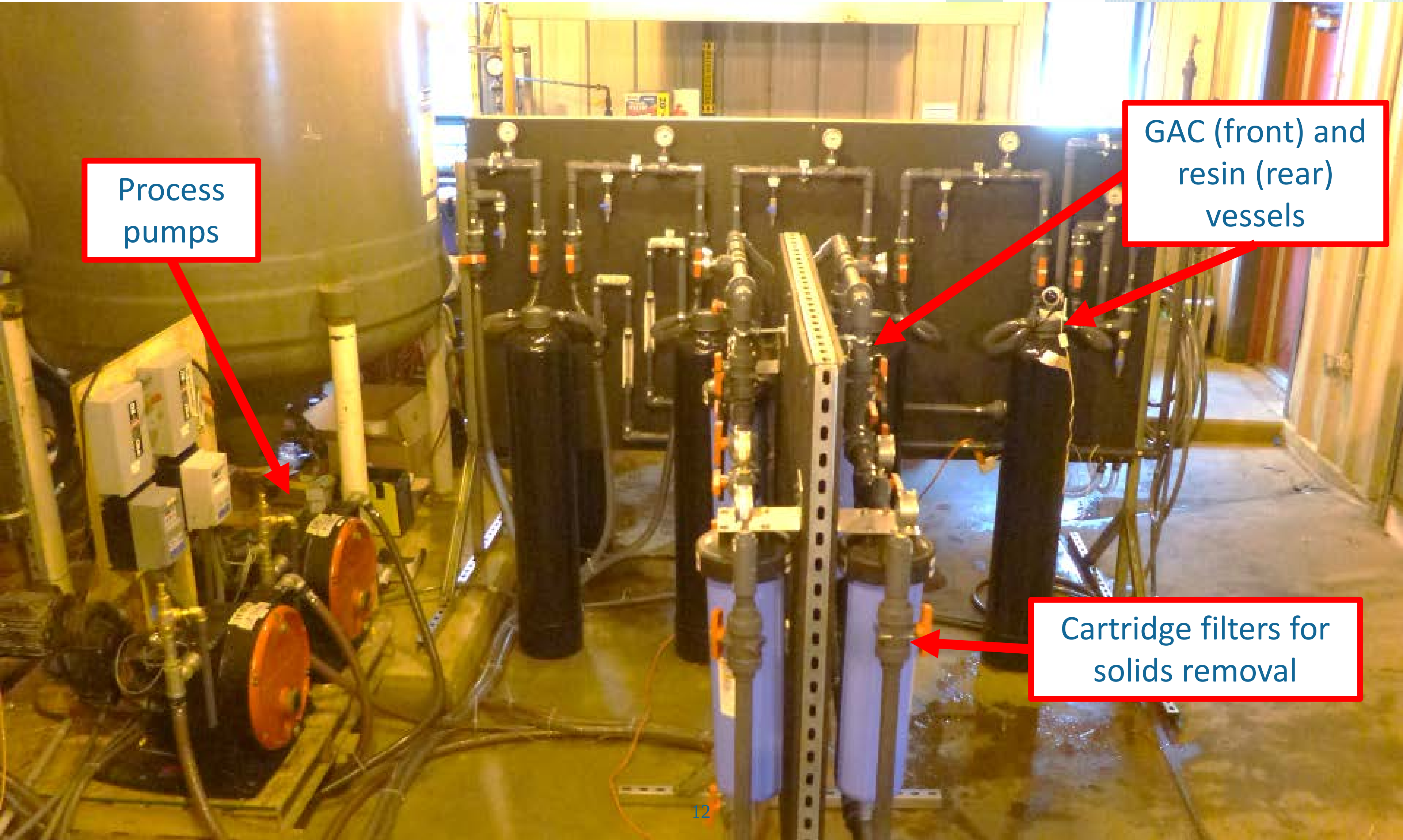


Customer Field Data

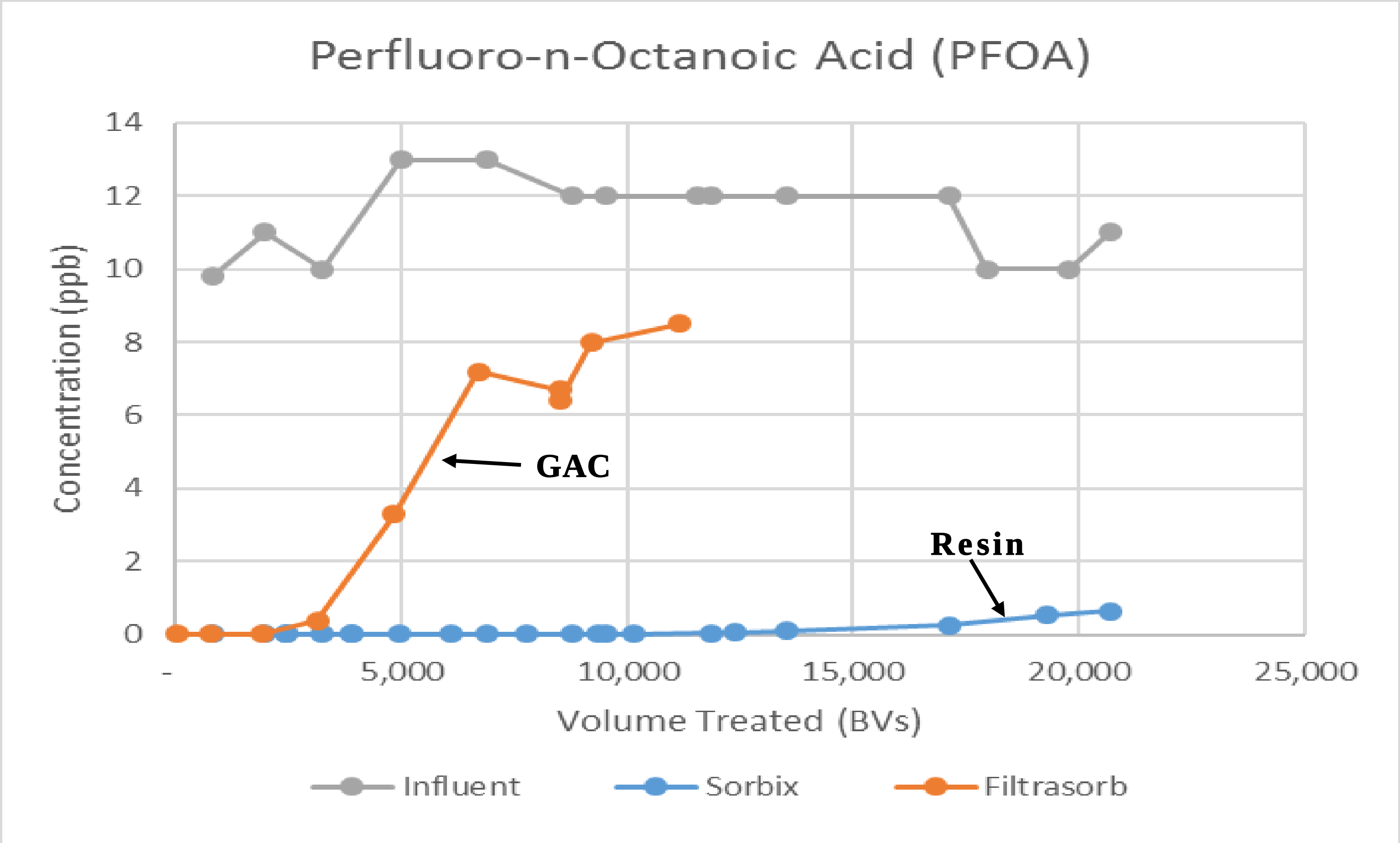
Temporary Model 10 System
10 minutes EBCT



Pilot Test: IX Resin vs. GAC

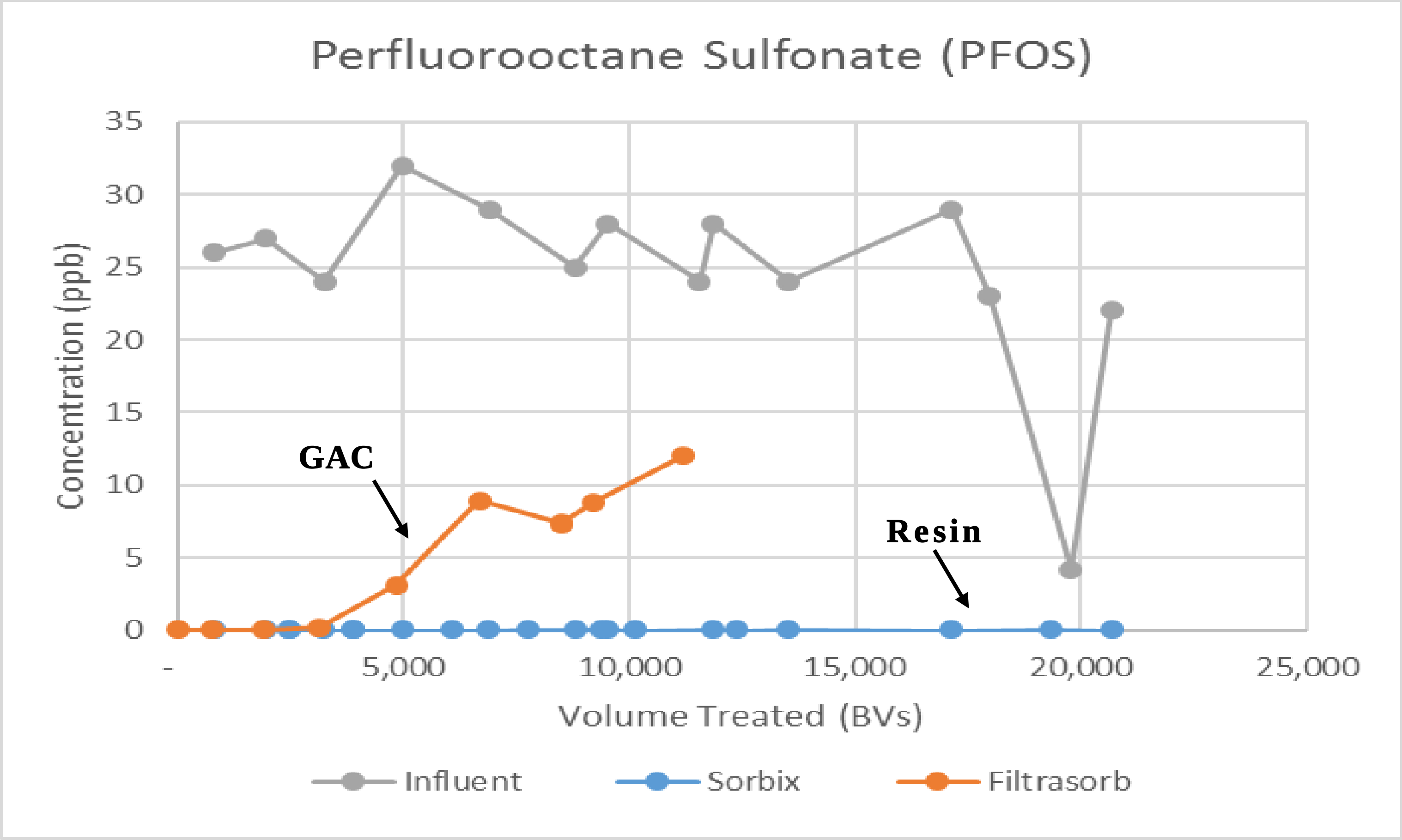


PFOA Breakthrough at 5-min EBCT



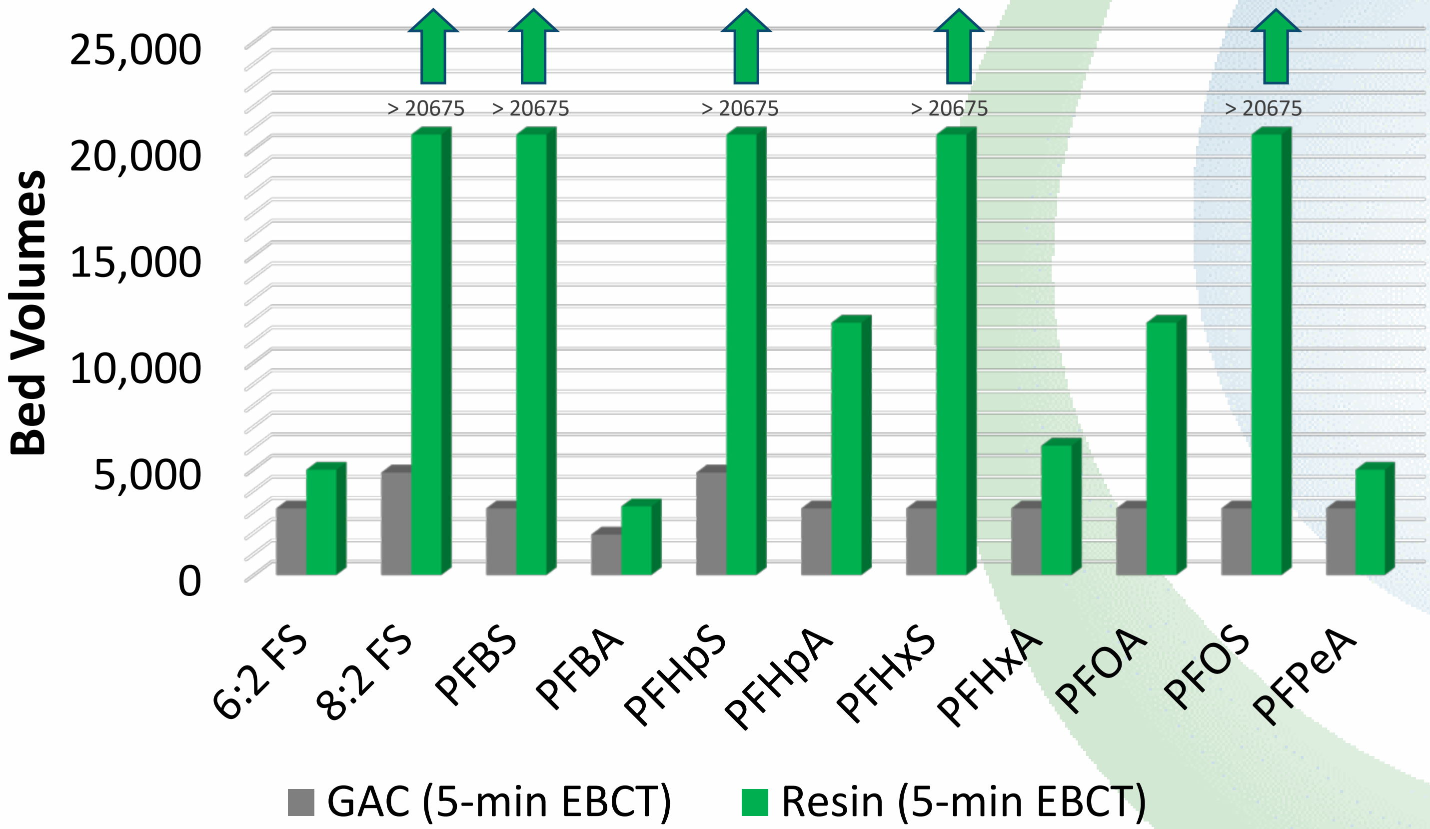
BV = bed volumes   EBCT = empty bed contact times

PFOS Breakthrough at 5-min EBCT



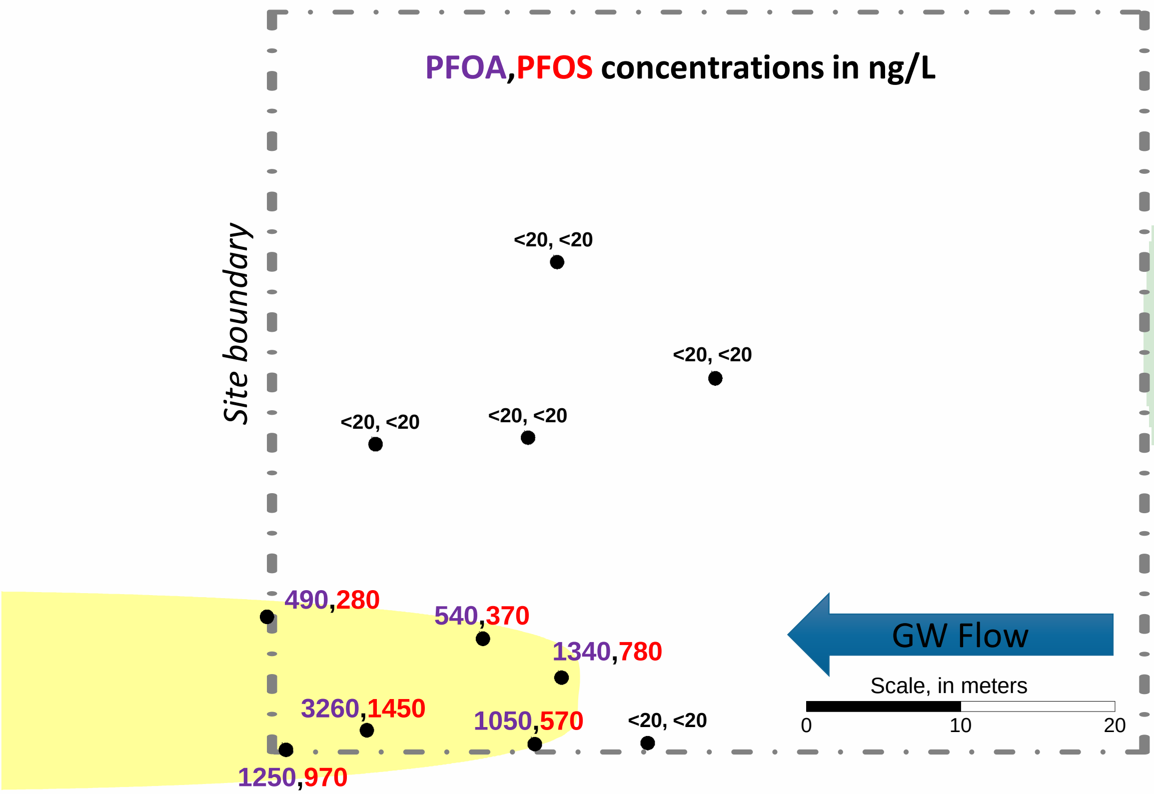
BV = bed volumes EBCT = empty bed contact times

Volume Treated Before Breakthrough



Regenesis Case Study - PLUME STOP

Liquid Activated Carbon



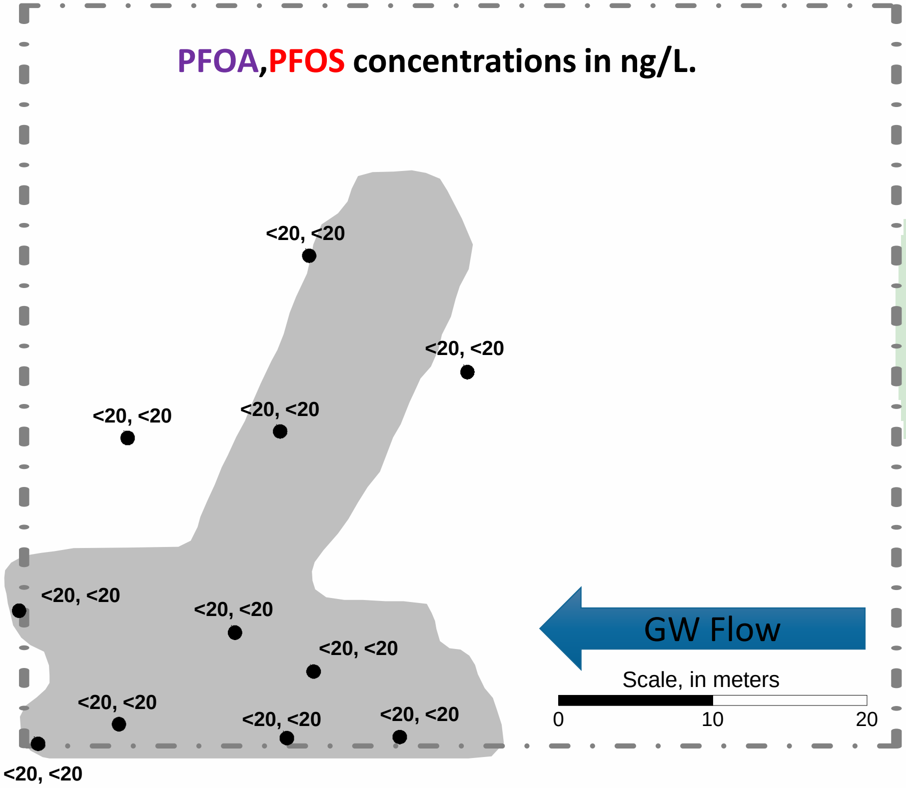
Location: Canada
Soil: Silty sand
DTW: 4 ft
GW velocity: 2 ft/day
History:

- Hydrocarbon spill
- Former fire training area

Baseline Contamination:
PFOS: 0.3 – 1.5 µg/L
PFOA: 0.5 – 3.3 µg/L

BTEX: <0.5 – 264 µg/L
TPH: <25 – 6,000 µg/L

Regenesis Case Study



Remedial Technology Used:

PLUME STOP
Liquid Activated Carbon

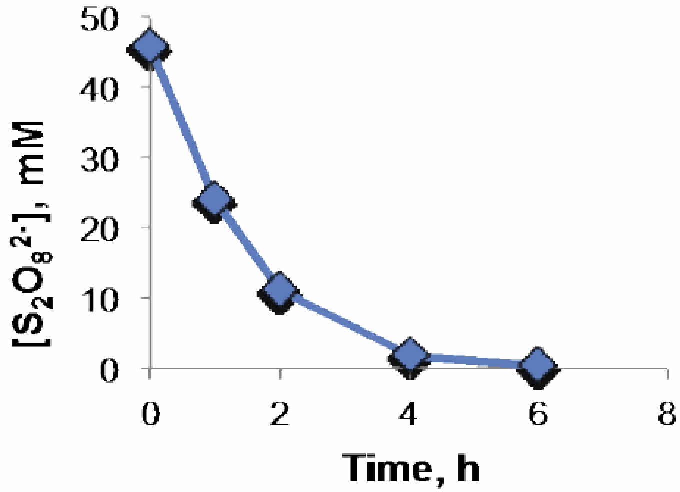
Results

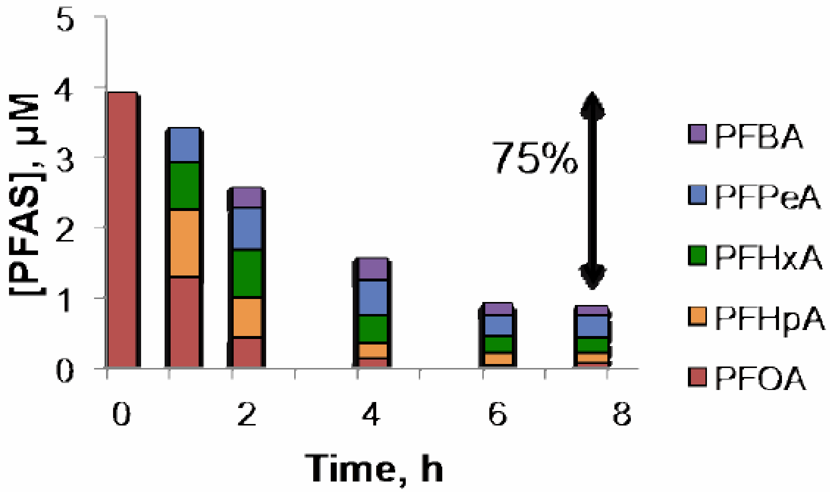
PFOS:	ND (<20 ng/L)
PFOA:	ND (<20 ng/L)
BTEX:	ND (<0.5 µg/L)
TPH:	ND (<25 µg/L)

Through 3, 6, and 15-month (May '17) monitoring events

Chemical Oxidation

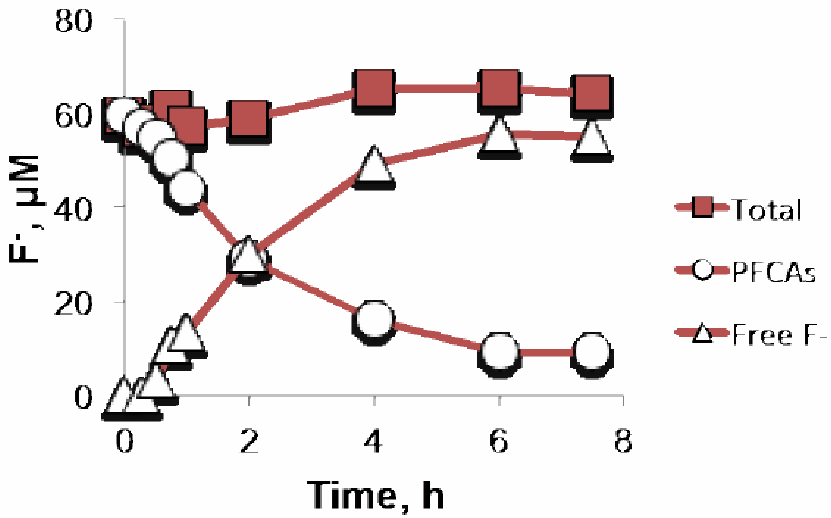
PFOA in Deionized Water





Conditions:
$[S_2O_8^{2-}]_0$ = 50 mM,
$[PFOA]_0$ = 4 µM
unbuffered (pH < 3) H_2O,
T = 85° C

Bruton and Sedlak, in review



Chemical Oxidation Case Study

Remediation of Mixed Organics and Per and Poly Fluoroalkyl Substances (PFAS) with OxyZone®, a Multi-Oxidant Blend

Raymond Ball, Ph.D., P.E., L.S.P.

www.en-chem.com

OxyZone® Chemistry

- Patented persulfate-based oxidant mixture
- Safe to apply under buildings
- Small site footprint, generation entirely enclosed
- Requires fresh water source and electrical hookup
- Equipment designed and built in-house
- Proven to be effective for in-situ treatment of conventional and emerging organic contaminants

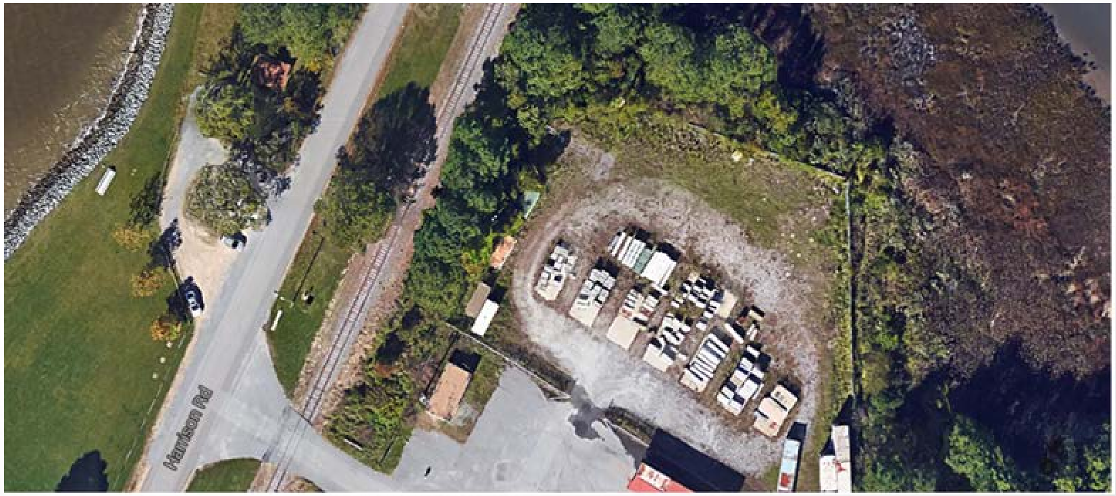
Field Demonstration Test of Mixed Organics Remediation

Summary

- Fire Training Area (FTA) at Joint Base Langley-Eustis (JBLE) in Hampton, VA
- Mixed organic wastes released and contaminated soil and GW
- 9 Month Field Demonstration
- OxyZone® Injection test cell of 20 feet by 30 feet
- Successful aromatic and chlorinated VOC treatment
- Groundwater PFAS Results showed statistically significant reduction
- PFAS destruction confirmed by laboratory bench scale testing

Field Demonstration

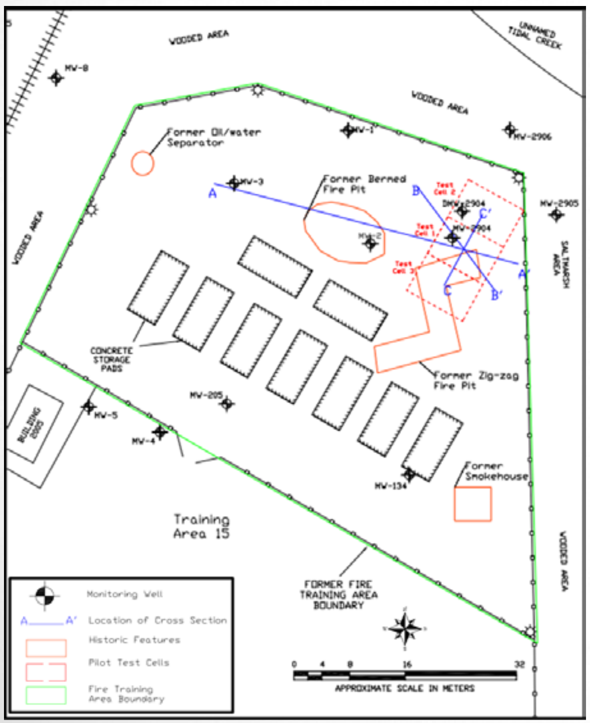
- Historical military FTA where Aqueous Film-Forming Foam (AFFF) released
- Complex geology, shallow GW (1-2'), low GW velocity, tidal influenced
- Surficial (shallow and intermediate) aquifer underlain by a clay confining unit
- Shallow (2-10' bg) – silty sands and organic silt (K=0.5 m/d)
- Intermediate (10-20' bg) - Highly permeable poorly sorted sands (K=4.9 m/d)

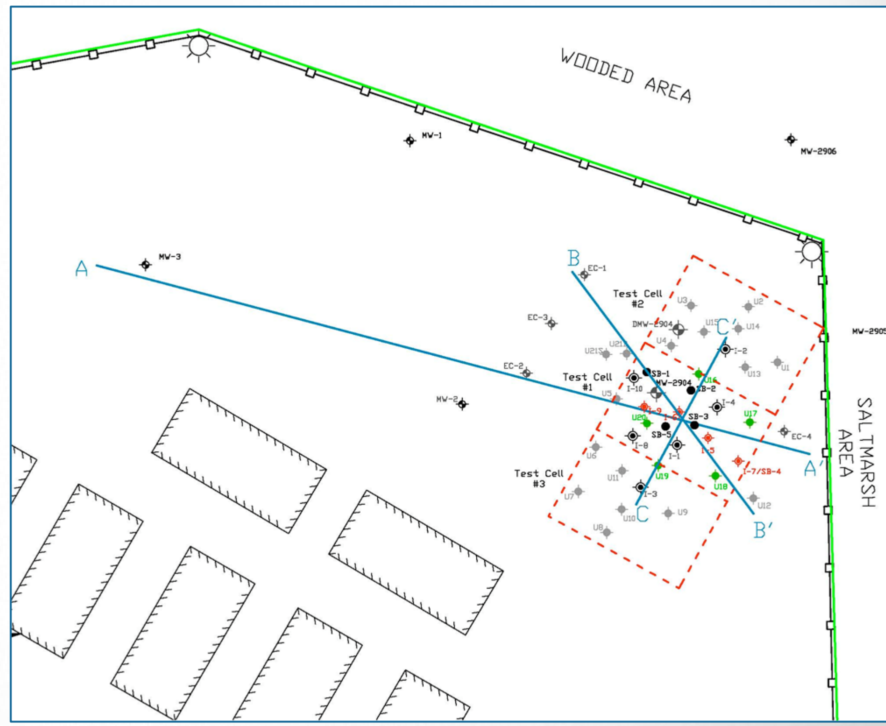


Field Demonstration – Subsurface Conditions

- Highest groundwater VOC concentrations were localized in some areas of the shallow zone.
- The highest VOC concentrations in deep groundwater were located directly below and down-gradient of the shallow source zone.
  - Mix of contaminants in site soil & GW at very high concentrations (NAPL)
    - Chlorinated solvents (PCE, 1,1,1-TCA, DCB): 10 – 250 mg/l (total)
    - Total Petroleum hydrocarbons (BTEX): 0.1 – 5 mg/l
    - Total SVOCs (mostly phenolics): 0.5 – 50 mg/l
    - Total of 9 detected PFAS: 28 – 280 ug/l
    - PFOS (the dominant PFAS): 7 – 200 ug/l
    - PFOS also dominant PFAS in soil: 1-150 ppb

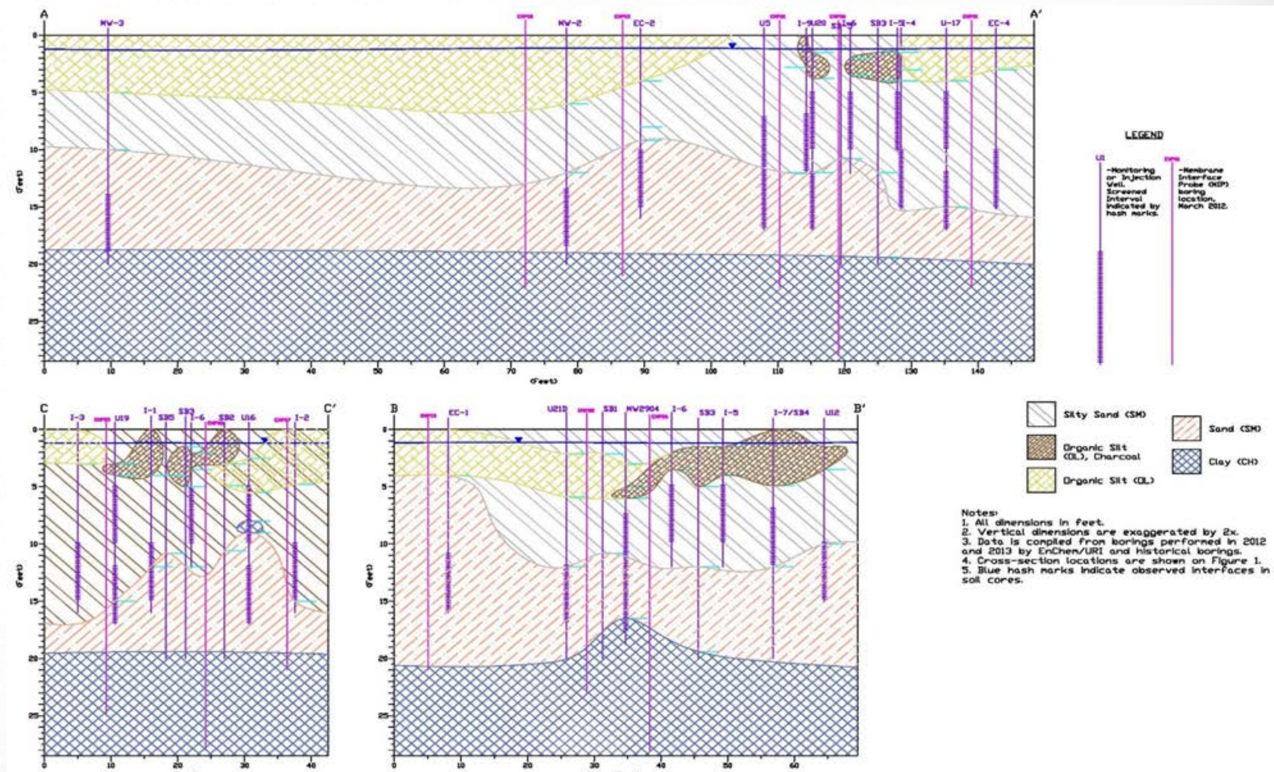
Field Demonstration – Test Cells





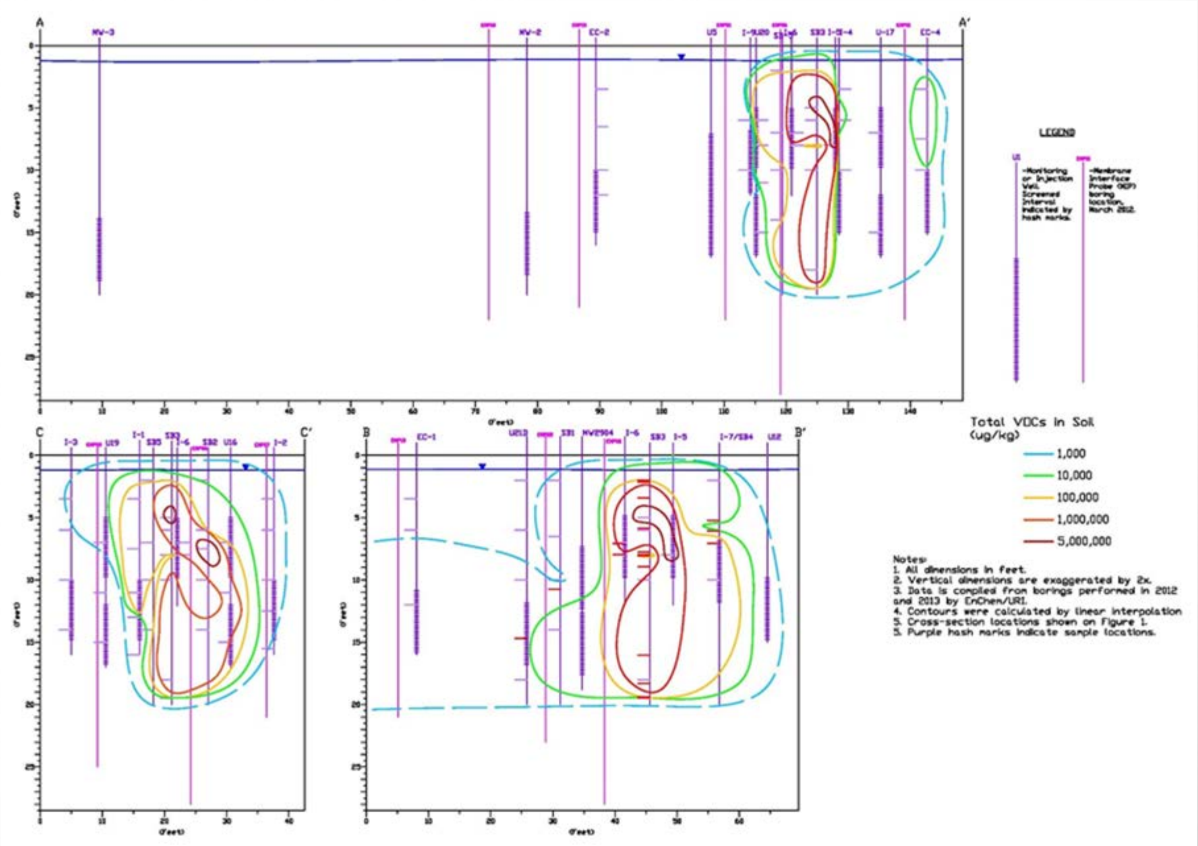
Field Demonstration

Geologic Cross-Sections



Field Demonstration – Cross Sections

Contamination Cross-Sections



Field Demonstration

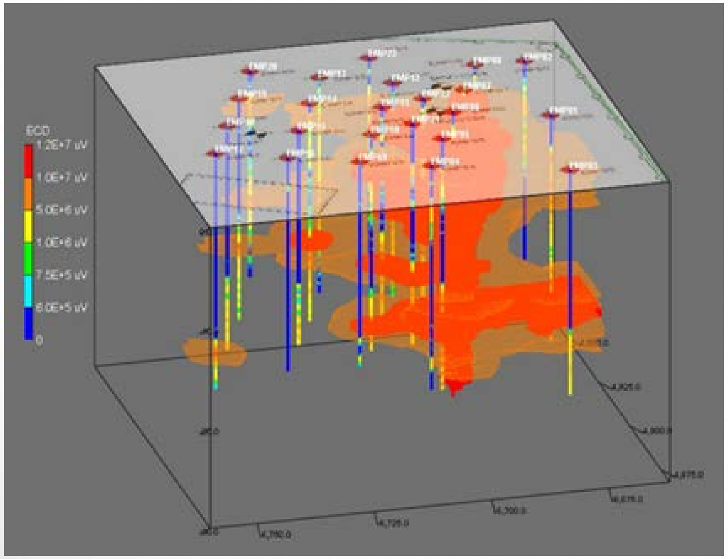
Study Approach

- Pre-injection MIP and soil investigation to fully define extent of VOC and SVOC contamination.
- Pre-injection bench testing of NAPL treatment
- Pre-injection PFAS soil and groundwater analysis
- Three XCT® and OxyZone® injection events completed in the Test Cell at the site
- Post injection soil and groundwater (2x) sampling, including PFAS
- Laboratory OxyZone® tests to confirm PFAS treatment

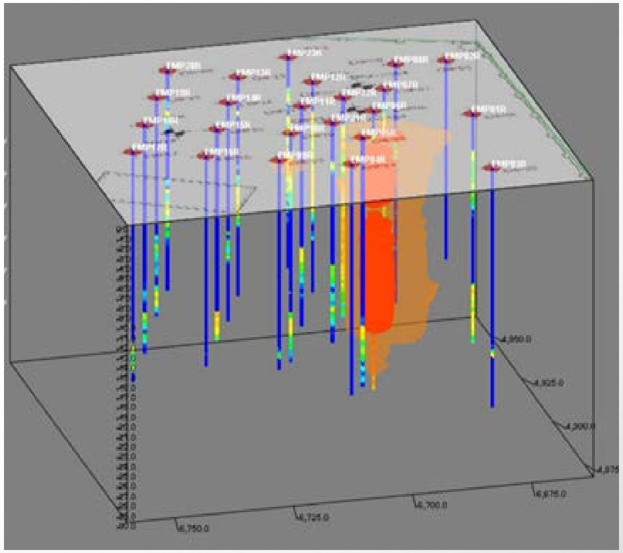
Field Demonstration Results for Chlorinated VOCs using Membrane Interface Probe (MIPs):

- Significant overall reduction in chlorinated VOCs
- PFAS concentrations too low to be detected by MIPS

Pre-injection

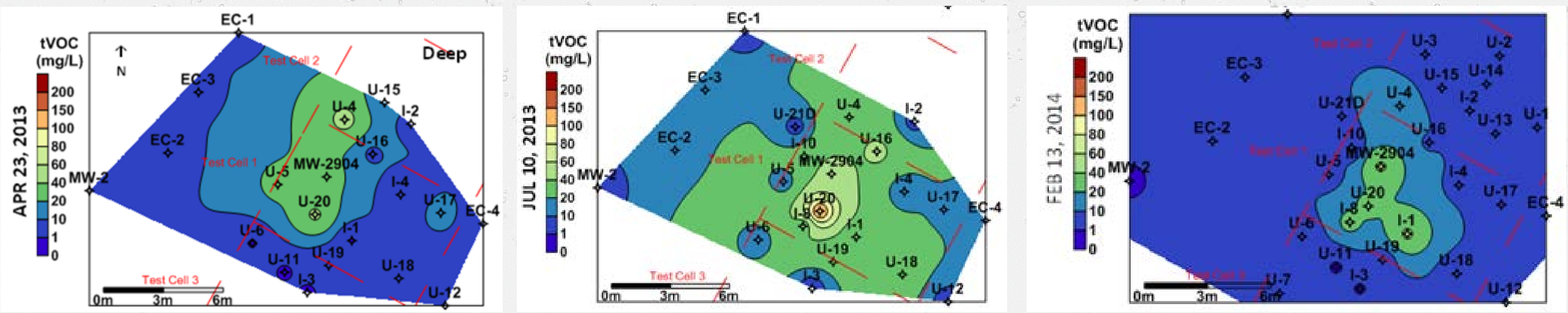


Post-injection



Impact of XCT® on Total VOC Concentration in Groundwater

XCT® is a patented biodegradable carbohydrate mixture to enhance the solubility of organic contaminants for subsequent efficient oxidation by OxyZone®



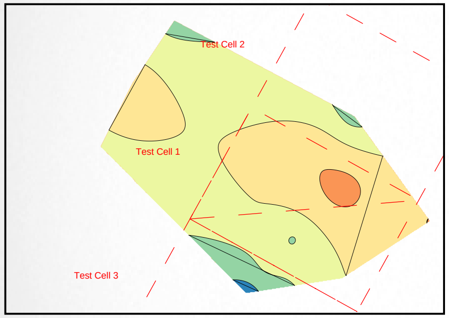
Baseline prior to injections

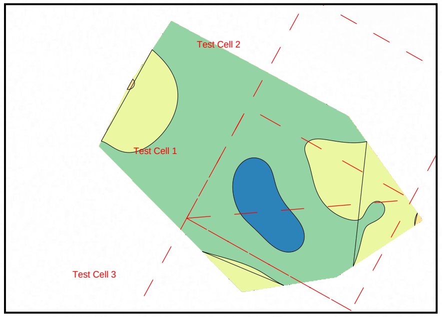
After 1st XCT® Injection (VOCs increased)

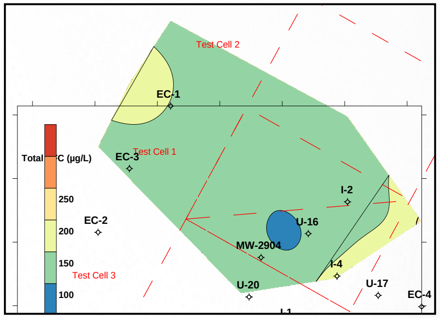
After 183 days of OxyZone® (VOCs decrease)

Field Demonstration Groundwater Results for PFAS

April 2013 | **October 2013** | **February 2014**

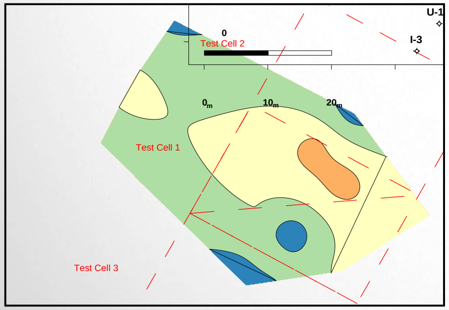


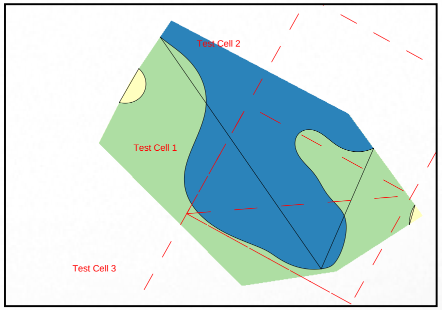


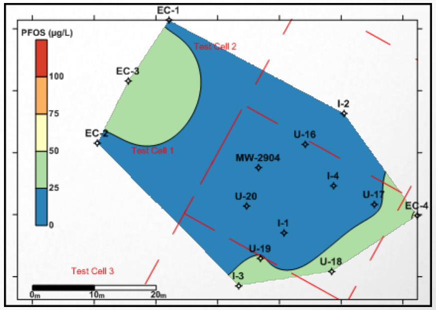


Total PFAS

OxyZone® Injections: May & July-August 2013







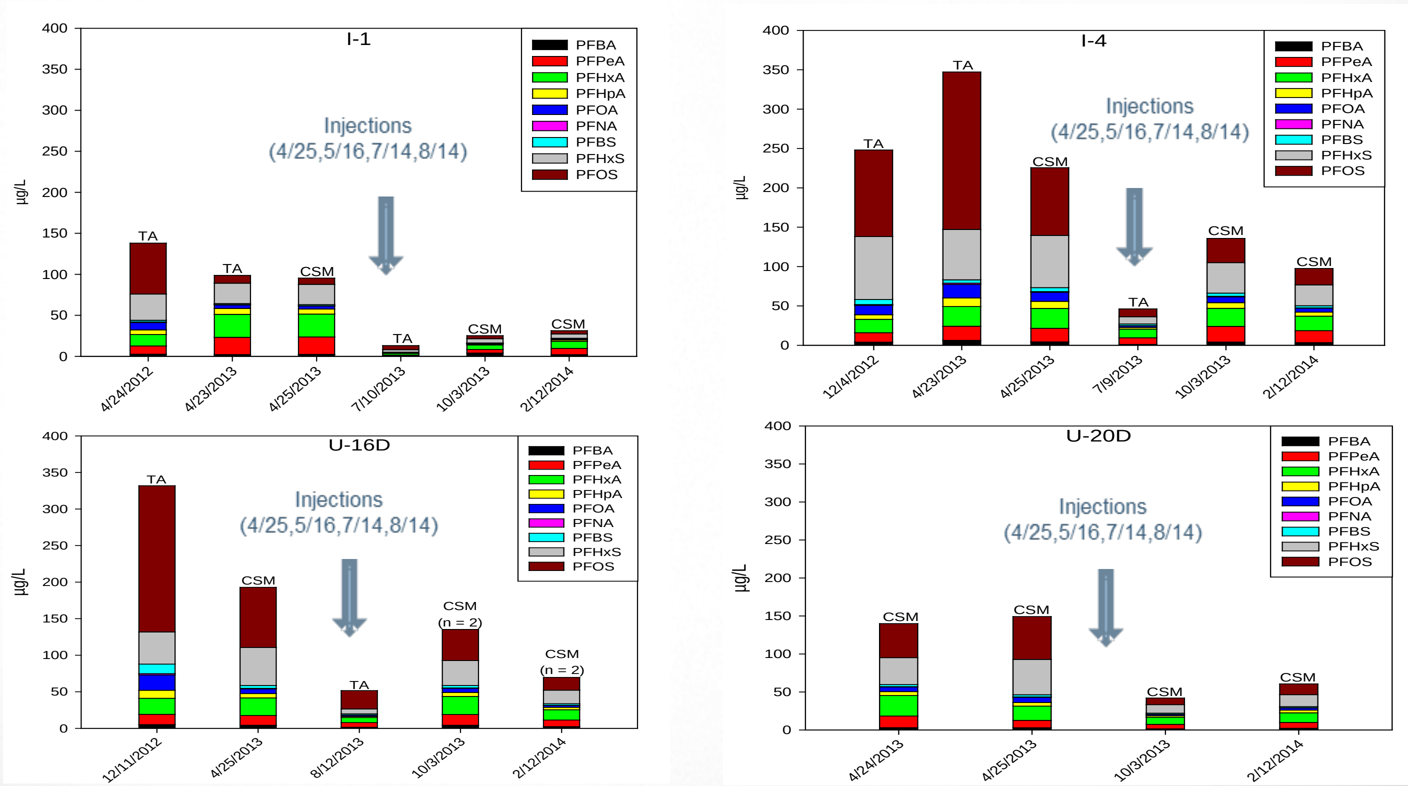
PFOS only

EnChem
Engineering, Inc.

Field Demonstration Results for PFAS

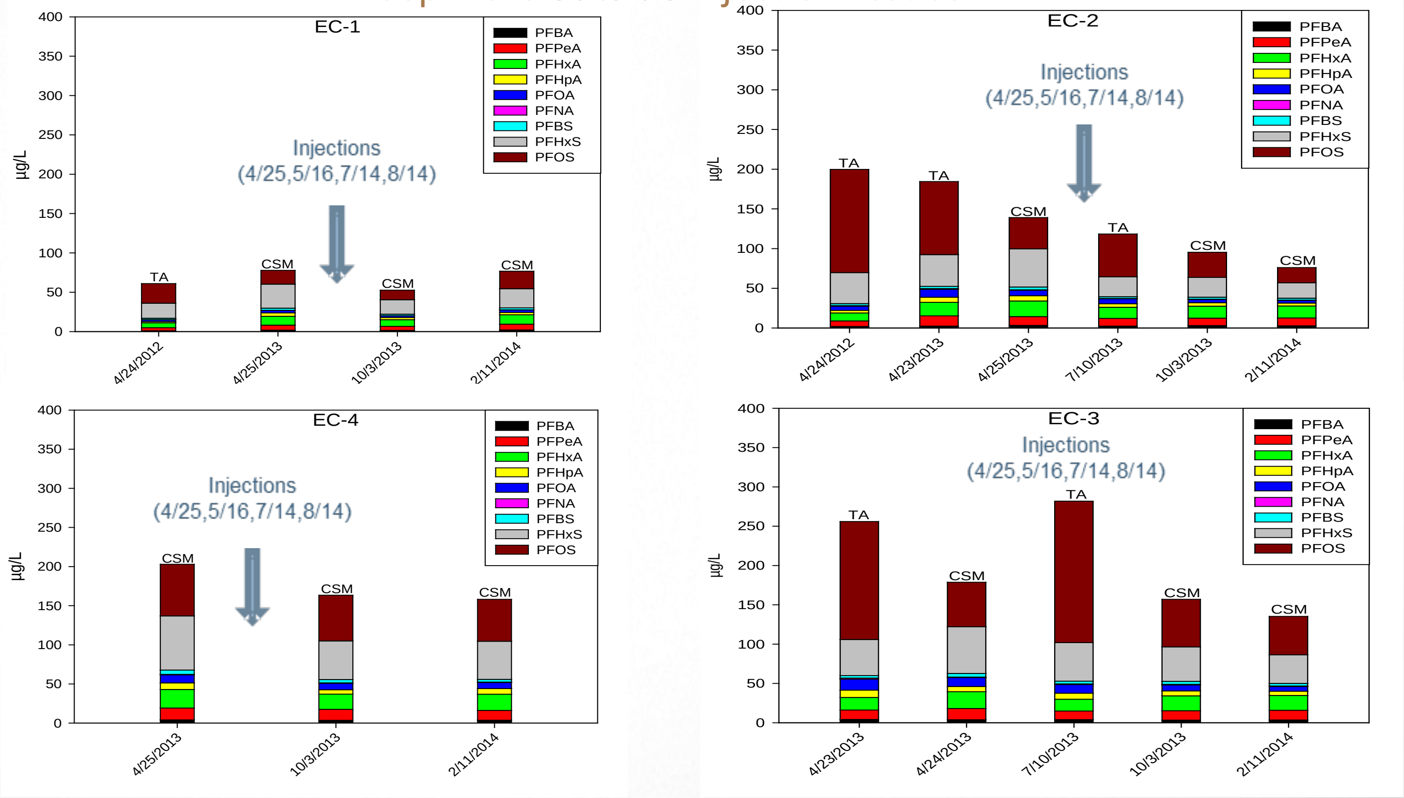
Deep wells **within** injection test cell

Statistically significant (p=0.005) decrease in PFAS concentrations after injections



Field Demonstration Results for PFAS

Deep wells **outside** injection test cell

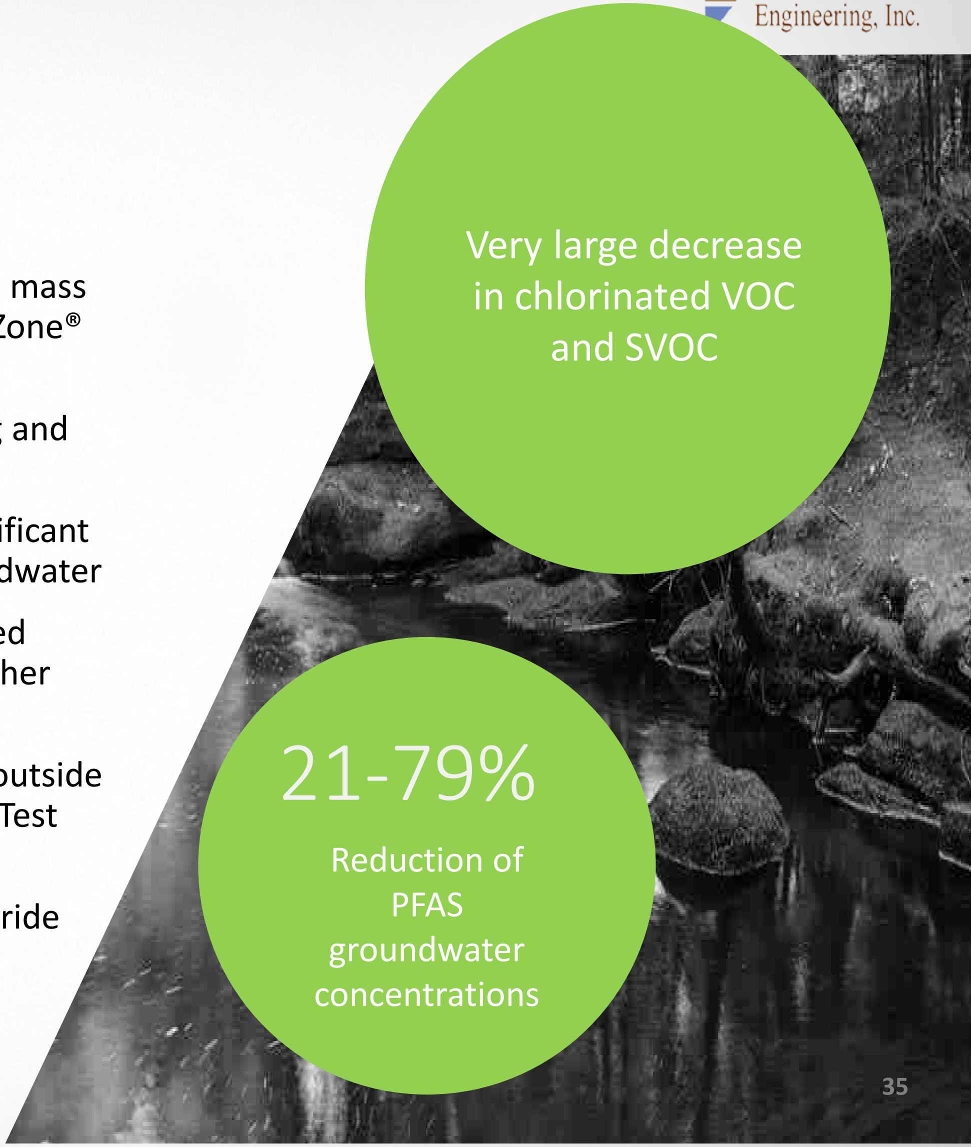


Not a statistically significant (p=0.005) decrease in PFAS concentrations after injections

EnChem Engineering, Inc.

Field Demonstration Results

- Based on MIPs data, overall VOC and SVOC contaminant mass significantly reduced in and around Test Cell where OxyZone® was injected
- 9 different PFAS were discovered during baseline testing and monitoring
- Groundwater data analysis supported a statistically significant reduction in PFAS concentrations (21% to 79%) in groundwater
- Indicative that OxyZone® processes successfully degraded PFAS in-situ in the presence of high concentrations of other organics
- Statistical comparison of wells within Test Cell to those outside Test Cell showed PFAS concentrations decreased within Test Cell, not outside
- Groundwater concentrations of conservative tracer chloride showed no (dilution) impact from injections



Confirmatory Bench Scale Treatability Testing of PFAS

OxyZone® process performed on:

- contaminated groundwater from the Fire Training Area
- distilled –deionized water
- Tested both unspiked & spiked PFOA & PFOS

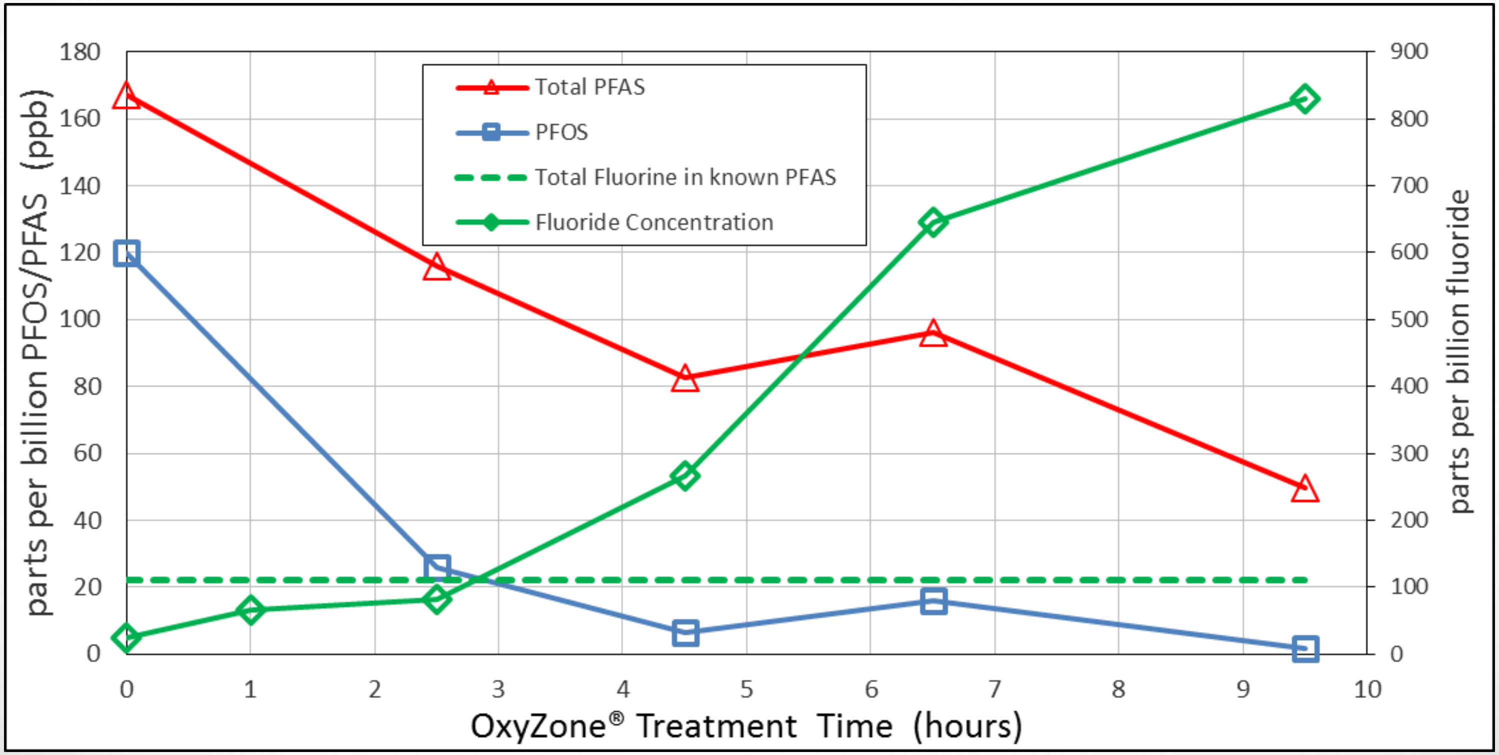
Bench Scale Treatability Testing on Spiked DI and Groundwater (JBLE)

Spiked Deionized Water (after 2 hours OxyZone® treatment)			
Specific PFAS	Initial concentration	Final concentration	Net Change
PFOS: (8 carbon sulfonate)	93 ppb	< 1 ppb	99% decrease
PFOA: (8 carbon acid)	83 ppb	< 1 ppb	99% decrease
PFHpS (7 carbon sulfonate)	4 ppb	< 0.4 ppb	99% decrease
PFHxA (6 carbon acid)	6 ppb	6 ppb	no change

PFAS Contaminated Site GW Spiked with Additional PFOS and PFOA (6 hrs. treatment)				
Specific PFAS	Initial concentration	Intermediate (3 hrs.) concentration	Final (6 hrs.) Concentration	Net Change
PFOS: (8 carbon sulfonate)	138 ppb	25 ppb	3 ppb	95% decrease
PFOA: (8 carbon acid)	33 ppb	22 ppb	6 ppb	97% decrease
PFHpS: (7 carbon sulfonate)	7 ppb	4 ppb	0.4 ppb	97% decrease
PFHpA: (7 carbon acid)	6 ppb	< 0.4 ppb	< 0.4 ppb	67% decrease
PFHxA: (6 carbon acid)	15 ppb	43 ppb	30 ppb	net increase
PFHxS: (6 carbon sulfonate)	68 ppb	99 ppb	14 ppb	79% decrease
PFPeA: (5 carbon acid)	11 ppb	< 2 ppb	< 2 ppb	91% decrease
PFBS: (4 carbon sulfonate)	9 ppb	14 ppb	10 ppb	no change
PFBA: (4 carbon acid)	3 ppb	6 ppb	5 ppb	small increase

Bench Scale Lab Results

Actual AFFF Site Contaminated Groundwater – High Undetected PFAS – 750% Fluoride Recovery



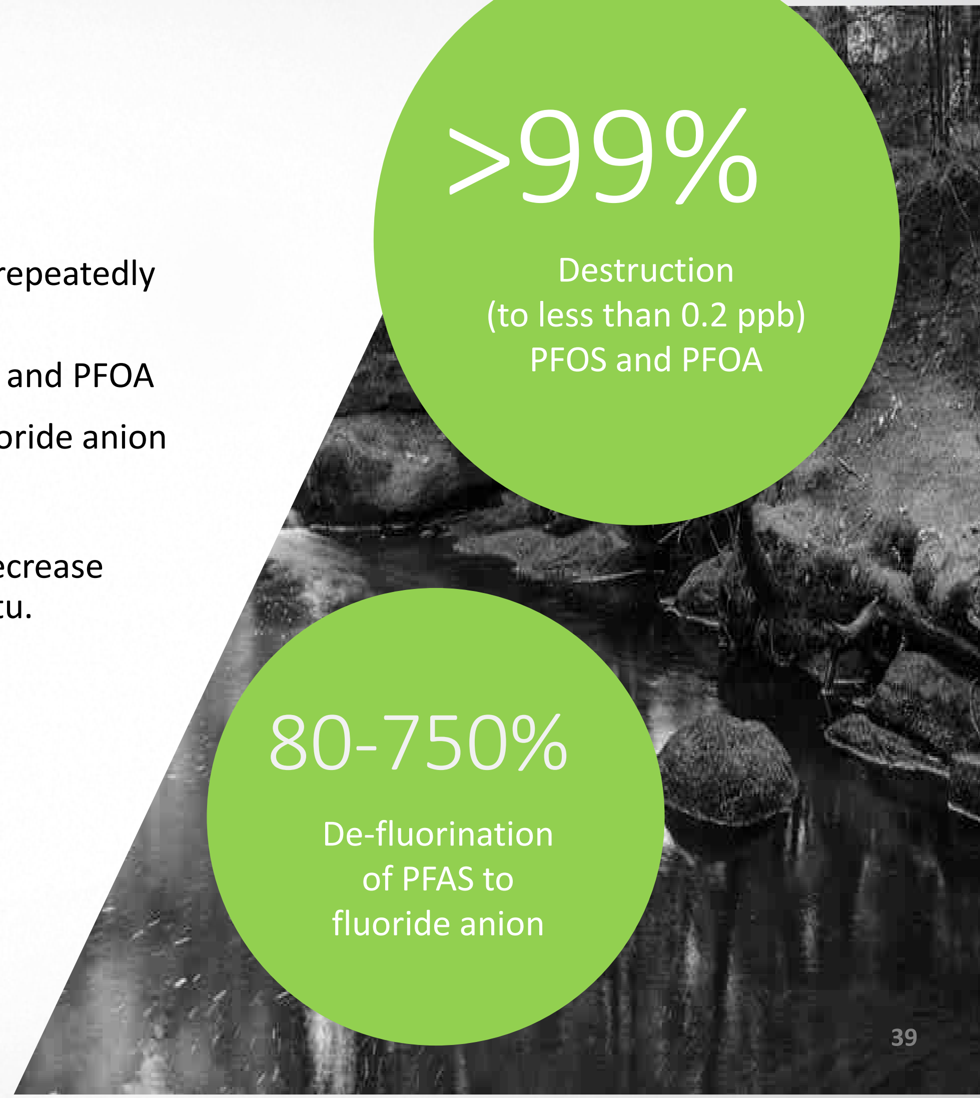
Case Study Results

Bench Scale Testing

- Subsequent evaluation of OxyZone® in the laboratory repeatedly confirmed PFAS destruction and de-fluorination
- Up to 99.9% destruction (to less than 0.2 ppb) of PFOS and PFOA
- 80 - 750% defluorination of PFAS organofluorine to fluoride anion

Conclusion

- Results indicate that OxyZone® has the capability to decrease PFAS to very low concentrations, either in-situ or ex-situ.



>99%

Destruction
(to less than 0.2 ppb)
PFOS and PFOA

80-750%

De-fluorination
of PFAS to
fluoride anion

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OxyZone® Field Demonstration

Acknowledgements

- Tom Boving, Ph.D., Co-Principal Investigator, and Dylan Eberle, Ph.D., University of Rhode Island (for Field Demonstration effort)
- AFCEC, for funding the Field Demonstration Project, FA8903-11-C-8804: Chemical Oxidation and Inclusion Technology for Expedited Soil and Groundwater Remediation

Last Thoughts

- PFAS on most people's radar for just a few years

- PFAS remediation very challenging:
  - Moving targets – which PFAS need to be remediated and to what concentrations?
  - Large number of chemicals with varying properties
  - Low concentrations of concern
  - Many data gaps and analytical difficulties
  - Complexity due to chemical transformations
  - Thin track record of many remediation technologies

Last Thoughts

- Technologies that are currently most promising
  - Filtration (Nano-filtration, reverse osmosis)
  - Adsorbents
  - Ion exchange / adsorption resins
  - Chemical oxidation

- Treatability studies can help:
  - Select the best technology(s)
    - Function of PFAS concentrations and many other factors
  - Optimize remediation design
    - e.g., dosing
  - Minimize the risk of unintended consequences
    - e.g., creating more PFOS/PFOA from precursors

Question and Answers

For any questions that we cannot get to during the Q/A period, please feel free to contact the presenters:

- Michael Marley (marley@xdd-llc.com)
- Ellen Moyer (ellenmoyer@em-green.com)
- Raymond Ball (rball@en-chem.com)