Do it Right, Do it once

Remedial Options for PFAS

Presented by:

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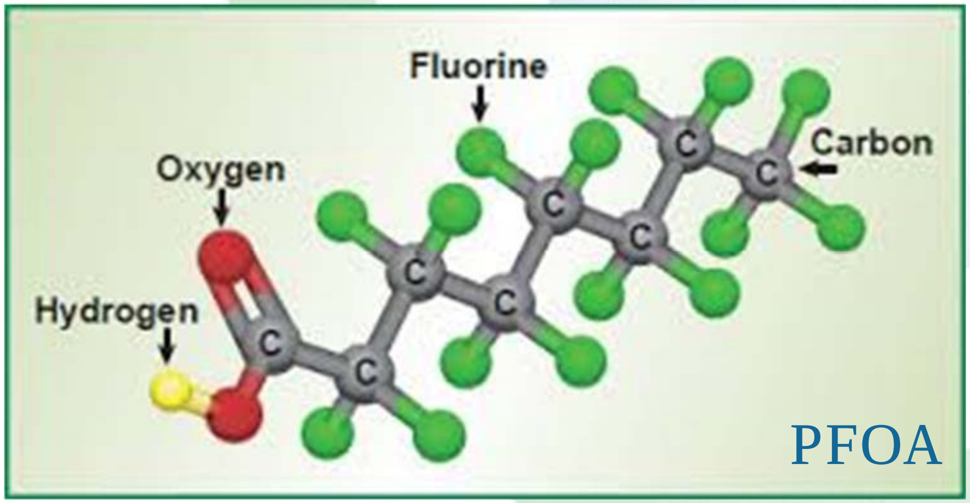
Agenda

- ❑ Overview of PFAS and Properties – Ellen Moyer
- ❑ Current State of Remedial Options – Mike Marley
- ❑ Resin/Carbon Case Study – Mike Marley
- ❑ Chemical Oxidation Case Study – Raymond Ball
- ❑ Questions/Answers

Overview of PFAS and Properties

What are PFAS?

- Per- and polyfluoroalkyl substances
- Diverse class of chemicals containing C-F bonds, which are extremely strong and stable
  - Definition of PFAS and which chemicals are included varies – there are dozens of PFAS
  - Many PFAS are carbon chains of varying lengths
    - Per FAS – all C in the chain are bonded to F
    - Poly FAS – not all C in the chain are bonded to F
  - Other atoms in PFAS can include atoms such as O, H, S, and/or N
- Most in the news:
  - Perfluorooctanoic acid - PFOA (C8)
  - Perfluorooctane sulfonate - PFOS (C8)
- PFAS properties:
  - Water soluble
  - Low volatility
  - Resistant to biodegradation?
- Certain chemicals can degrade to PFOA



NIEHS – National Institutes of Health

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Chemical/Physical Properties

Property	PFOA	PFOS	Benzene
Chemical Formula	$C_8HF_{15}O_2$	$C_8HF_{17}O_3S$	C_6H_6
Molecular Weight (g/mol)	414.09	500.13	78.11
Boiling Point (^oC)	192.4	259	80
Vapor Pressure (mm Hg at 25 ^oC)	0.525	~0.002	86
Henry's Law Constant @ 25^{o}C (unitless)	Not measurable	Not measurable	0.225
K_{oc} (temperature as specified)	115	371	79 (at 25 ^oC)
Solubility in Water (mg/L)	~9,500 (at 25 ^oC)	680 (temp. not stated)	1,780 (at 25 ^oC)
	USEPA 2016	USEPA 2016	

Uses

- PFAS resist heat, oil, grease, and water
- Used in industry and consumer products worldwide since the 1950s – products contain a mix of carbon lengths and impurities
- Waterproof clothes, non-stick cookware, take-out containers
- Wire insulation
- Paper and paints
- Fire-fighting foams
- Carpet
- Furniture

https://commons.wikimedia.org/w/index.php?curid=31071118

https://commons.wikimedia.org/w/index.php?curid=2390636

Occurrence

- Found worldwide in the environment, wildlife, and humans
  - Including the Arctic and Antarctic
- 2015 study by U.S. National Health and Nutrition Examination Survey:
  - PFAS found in 97 percent of human blood samples
- 2013-2015 Safe Drinking Water Act testing:
  - PFAS found in 66 water supplies serving more than 16 million Americans in 33 states with at least one sample at or above EPA drinking water health advisories
- Tendency for large dilute plumes
- Difficult to sample
  - Cross-contamination issues
- Difficult to laboratory analyze
  - Some PFAS not detected by commercial labs

https://commons.wikimedia.org/wiki/File:Antarctic,_adelie_penguins_(js)_19.jpg

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Concerns

- Most concern with longer-chain PFAS (C8 or greater – e.g., PFOA, PFOS)
- Persist, travel long distances, and bioaccumulate
- Potential health effects (debated):
  - Affect developing fetus and child – including learning and behavior
  - Decrease fertility
  - Disrupt hormones
  - Increase cholesterol
  - Suppress immune system
  - Increase cancer risk

Concerns

- EPA established health advisories for PFOA and PFOS at 70 ng/L (individually and combined, for lifetime exposure from drinking water) (ng/L = ppt)
  - Based on lab studies of effects on rats and mice and epidemiological studies of exposed human populations
  - EPA has no plans to establish Maximum Contaminant Levels
  - EPA plans to develop Regional Screening Levels for site cleanup
- State requirements vary widely
  - Some states are looking at more than PFOA and PFOS

Current State of Remedial Options

Remedial Technologies with "Success" in PFAS Treatment

- Physical treatment/removal
  - Filtration/reverse osmosis*
  - Adsorption/ion exchange (IX)*
  - Excavation + disposal
  - In-situ stabilization
- Chemical Oxidation
  - Various high energy oxidant systems
  - Sonolysis
  - Photolysis
- Biotransformation
  - Partial
    - Not for C-F bond?
    - Possible in time?
- "Other"
  - High temperature > 1,100 ^{o}C
  - Electrochemical

* typical component of pump and treat

Summary of Ex Situ Water Treatment Options

Compound	Acronym	Molecular Weight (g/mole)	Aeration	Coagulation Dissolved Air Floatation	Coagulation Flocculation Sedimentation Filtration	Conventional Oxidation (MnO_4, O_3, ClO_2, CLM, UV-AOP)	Anion Exchange (Select Resins Tested)	Granular Activated Carbon	Nano Filtration	Reverse Osmosis
Perfluorobutanesulfonic Acid	PFBS	300	(red)	(red)	(red)	(red)	(yellow)	(green)	(green)	(green)
Perfluoroheptanoic Acid	PFHpA	364	(red)	(red)	(red)	(red)	(yellow)	(green)	(green)	(green)
Perfluorohexanesulfonic Acid	PFHxS	400	(red)	(red)	(red)	(red)	(green)	(green)	(green)	(green)
Perfluorooctanoic Acid	PFOA	414	(red)	(red)	(red)	(red)	(yellow)	(green)	(green)	(green)
Perfluorononanoic Acid	PFNA	464	(red)	unknown	(red)	(red)	assumed (green)	assumed (green)	(green)	(green)
Perfluorooctane Sulfonate	PFOS	500	(red)	(yellow)	(red)	(red)	(green)	(green)	(green)	(green)

Table modified from E. Dickenson and C. Higgins 2016

(green) > 90% removal; (yellow) >10%, < 90% removal; (red) < 10% removal

E. Dickenson and C. Higgins, “Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances,” Water Research Foundation, 2016.

Filtration

Essentially “Sieving” of PFAS molecules

- Nano-Filtration (NF)
  - PFAS have molecular weight cutoff (MWCO) of approximately 300 - 500 Daltons
  - NF MWCO > 200 Daltons
  - >90% effective most PFAS
  - Ultra and micro-filtration low effectiveness
- Reverse Osmosis
  - Polymers 100 – 200 Daltons
  - >90% effective most PFAS
- Concentrated waste streams result

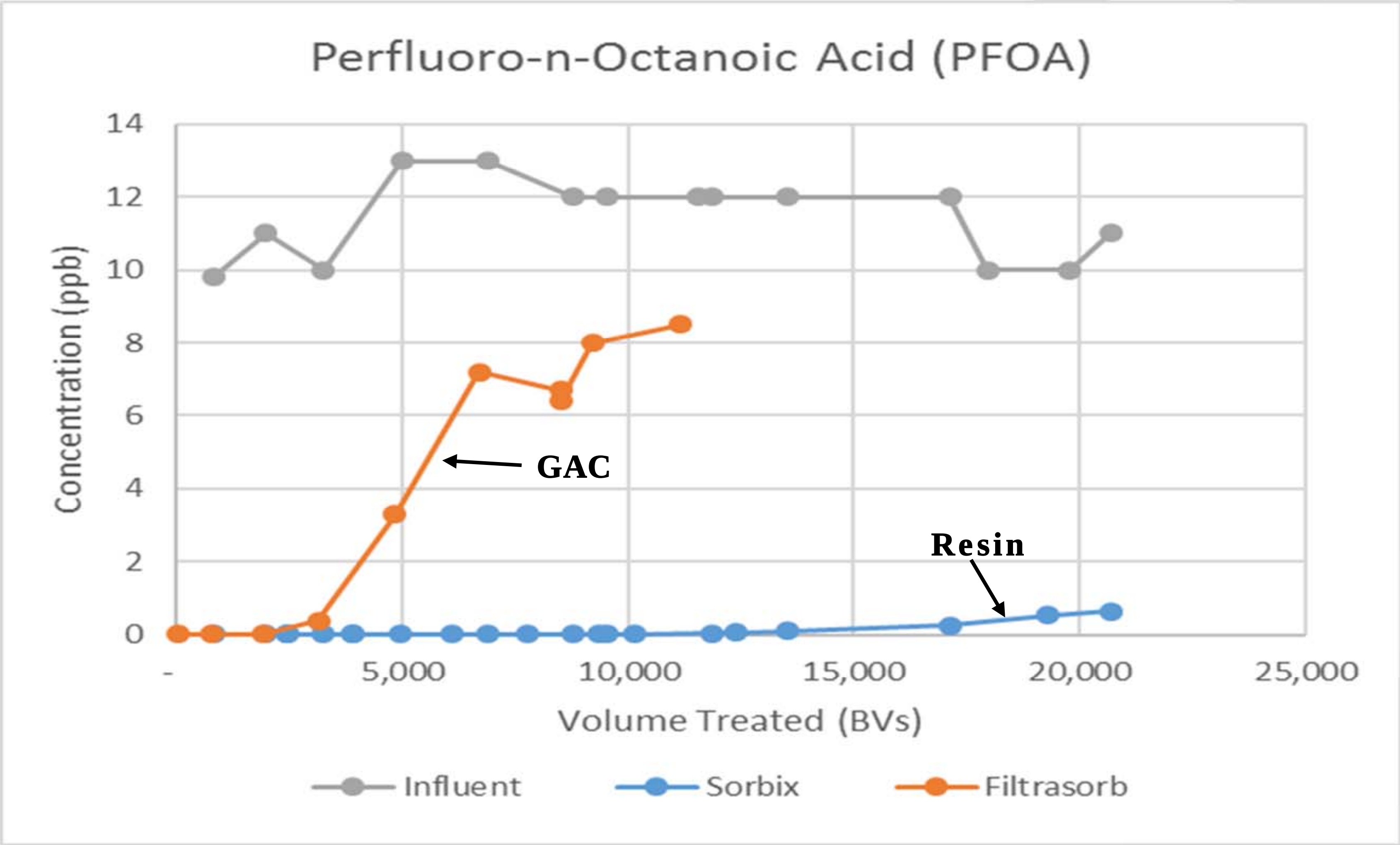
Adsorption/Ion Exchange (n0n-destructive)

- Carbon-based systems
  - Ex situ activated carbon systems / GAC (current go to approach)
  - In situ injectable carbon-based systems
- Clays (or blend of sorbent-based systems)
  - e.g., RemBind or MatCare
- Zeolites? – in R&D
- Synthetics resins – gaining traction due to capacity/effectiveness

Carbon versus IX Resins

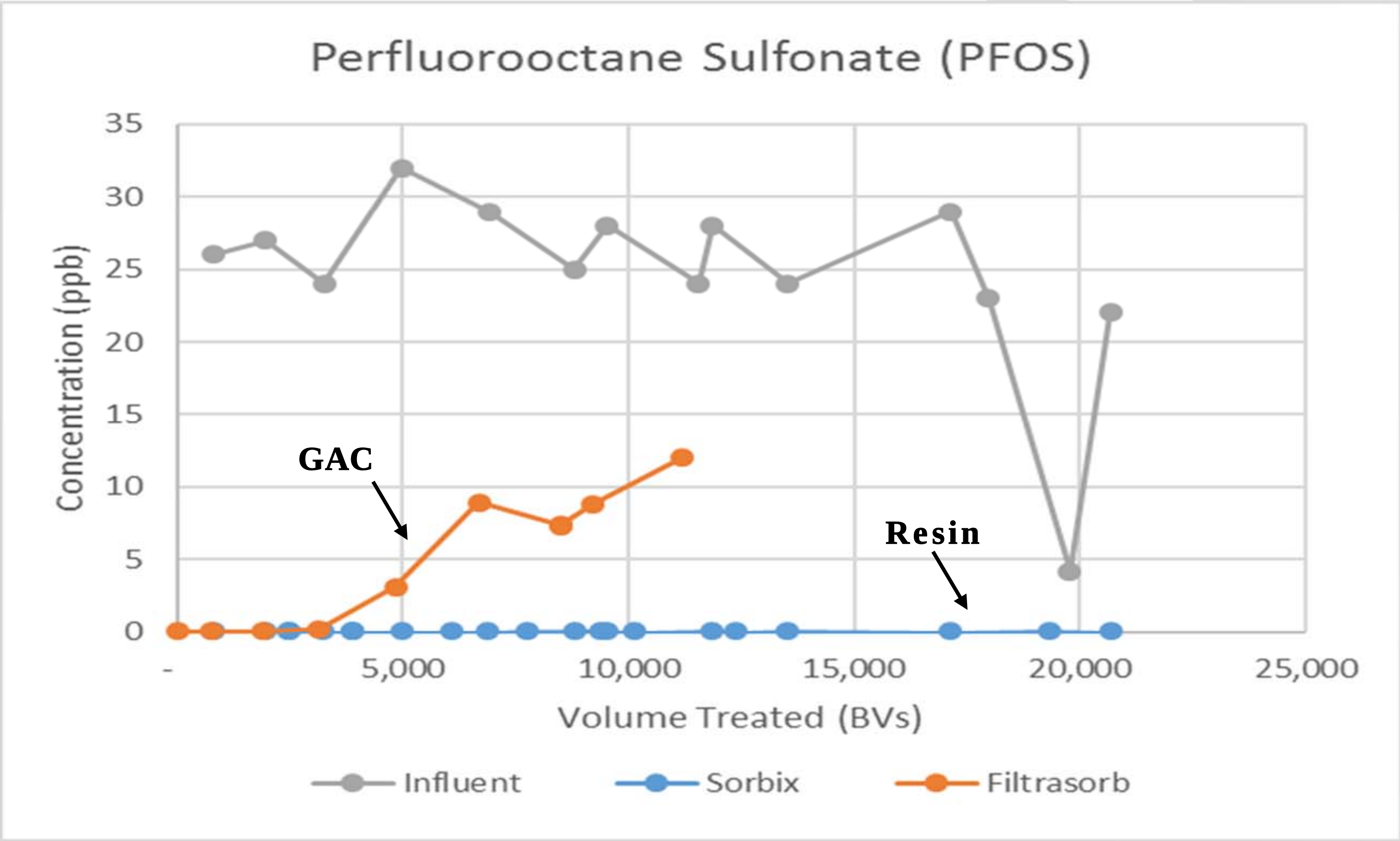
- Carbon (not all carbons created equal)
  - Proven effective multiple sites and >1000 point of entry treatment (POET) systems
  - Regeneration, at high temperature: “destroys” PFAS but may reduce capacity
  - Lower capacity than IX
  - May be ineffective on short chain PFAS
  - Still evaluating the level of concern on short chain PFAS?
  - Can be more cost-effective, but site-specific analysis required
    - If shorter duration operations, lower PFAS concentrations, and less natural organic matter
- IX
  - Number case studies increasing
  - High capacity for PFAS adsorption
  - Working on resins for improving short chain PFAS removal
  - Can be more cost-effective, but site-specific analysis required
  - Regeneration and PFAS destruction research/demonstration is ongoing
- Treatability studies are essential for design, etc.

PFOA Breakthrough at 5-min EBCT



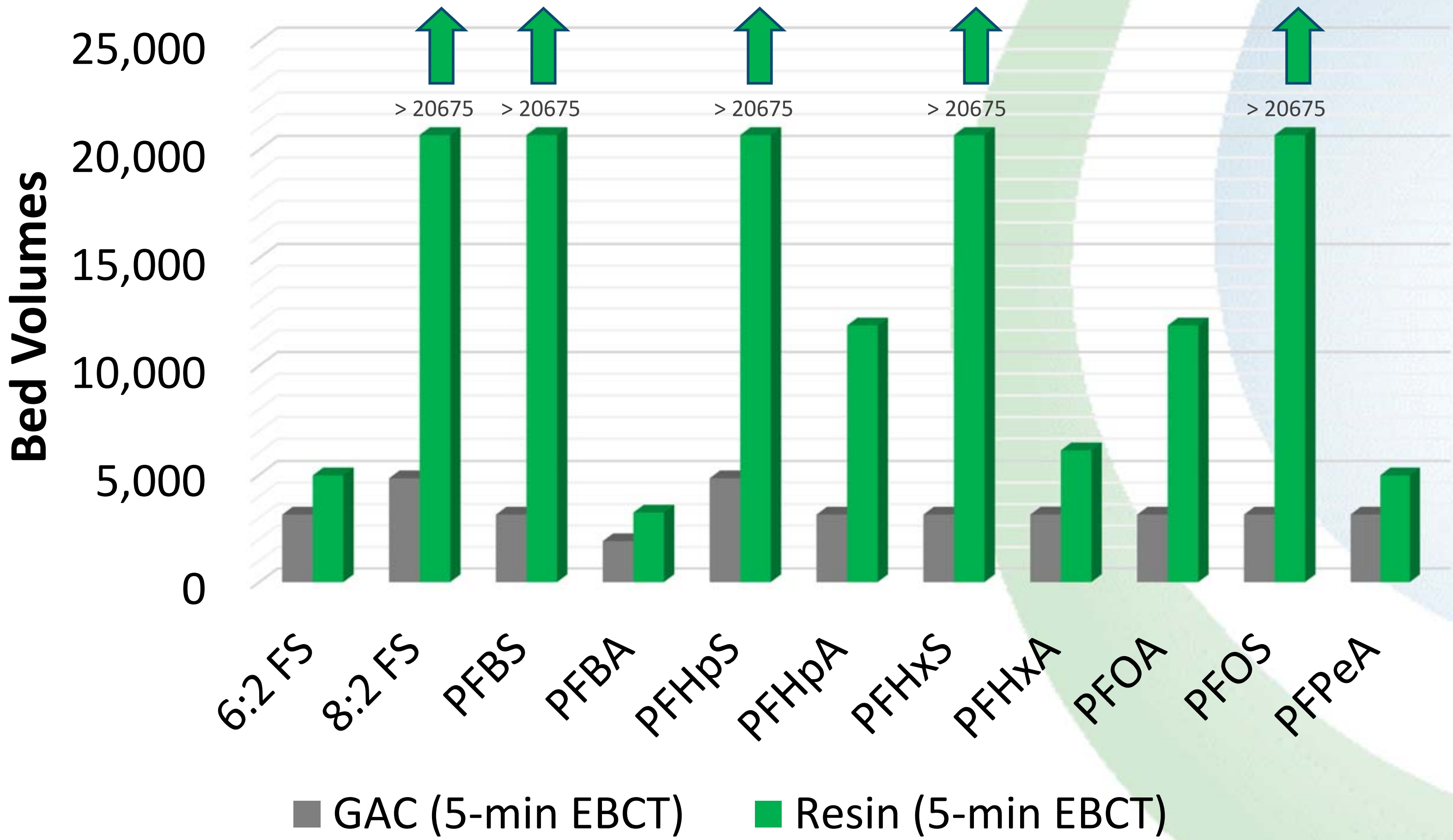
BV = bed volumes   EBCT = empty bed contact times

PFOS Breakthrough at 5-min EBCT

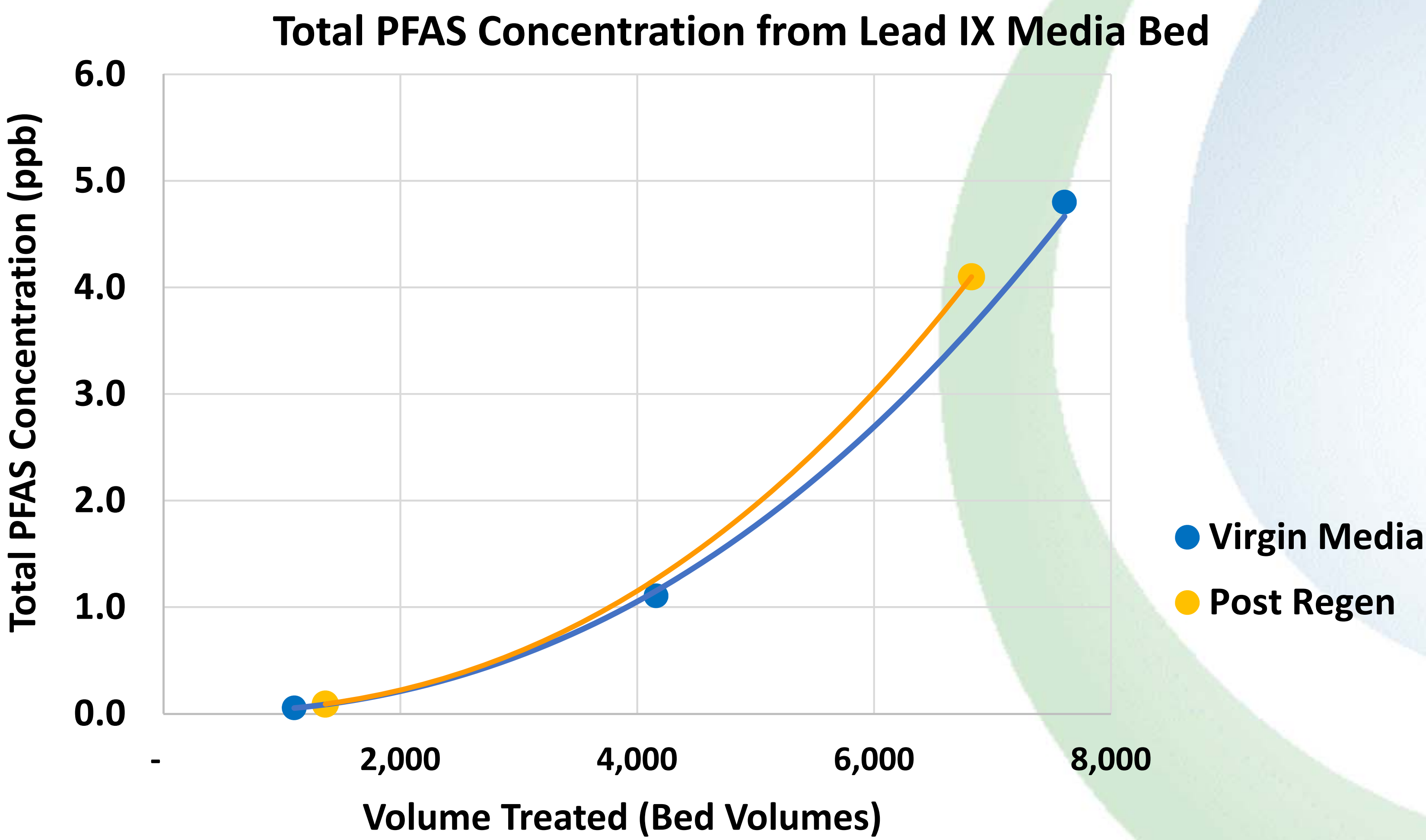


BV = bed volumes   EBCT = empty bed contact times

Volume Treated Before Breakthrough



Regeneration of IX Resin at Pilot Scale



Chemical Oxidation In Situ or Ex Situ

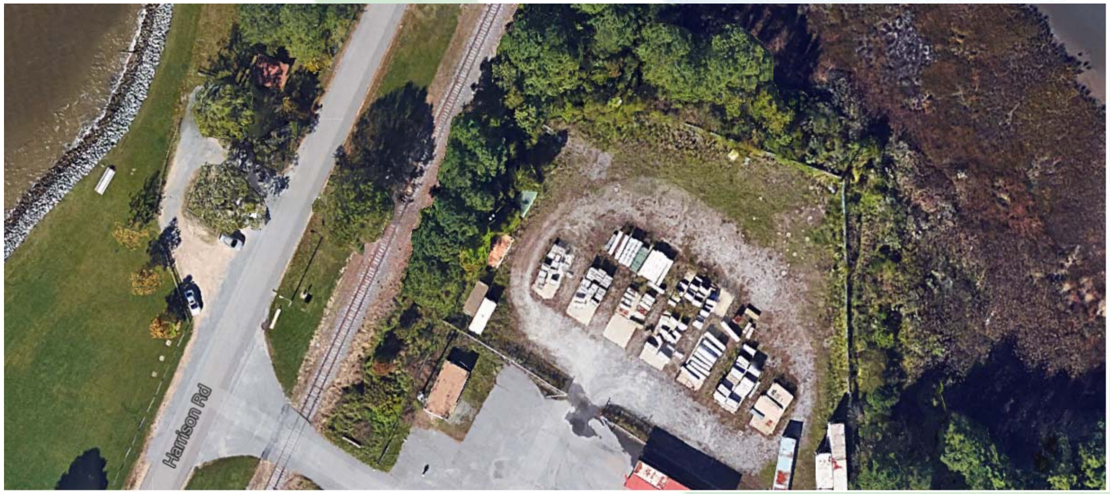
- Several bench studies / few pilots performed over last several years showing partial to full destruction of PFAS
  - Focus has typically been on PFOA and PFOS
- Common theme observed in chemical oxidation approaches is success when creating complex chemistries / radical mixtures
  - Creating reductive and oxidative radicals
- Also success under high temperature / pressure conditions – practical?
  - E.g. high temperature permanganate
- Following slides provide examples of bench and pilot studies

OxyZone®

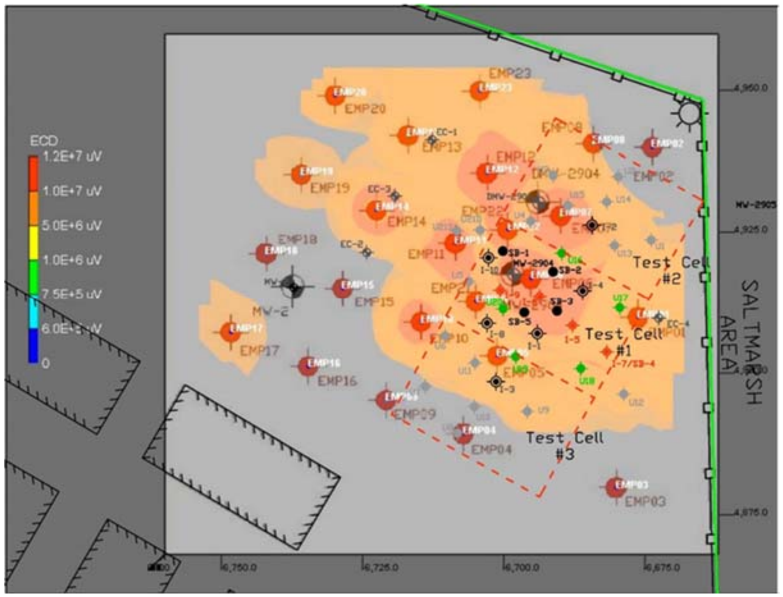
- Patented persulfate-based oxidant mixture
- Safe to apply under buildings
- Small site footprint, generation entirely enclosed
- Proven effective for in-situ treatment of a wide range of traditional and emerging organic contaminants
- Applicable to *in-situ* remediation and/or *ex-situ* treatment in an above-ground reactor
- Selected by the Air Force for a field demonstration in Virginia to treat mixed organic waste ***in-situ***
- PFAS discovered during field demonstration

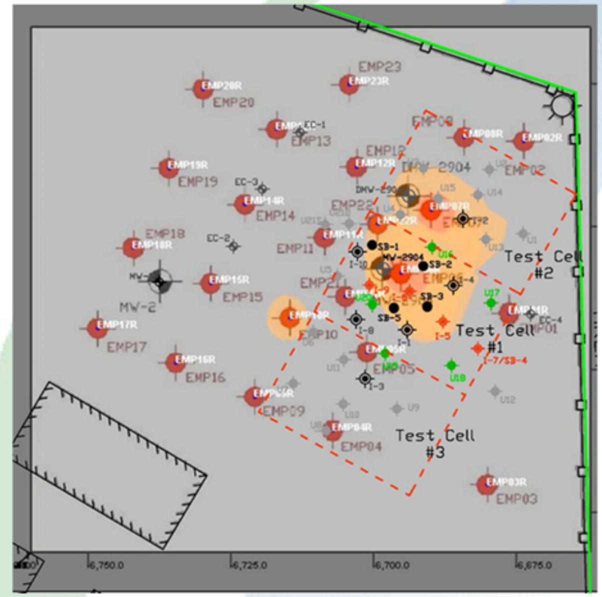
Field Demonstration at the JBLE Fire Training Area (FTA) in Hampton, VA

- Historical military FTA – aqueous film-forming foam (AFFF) released
- Mix of contaminants in site soil & GW at high concentrations
  - Total chlorinated solvents (PCE, TCA, DCB): 10 – 250 mg/l
  - BTEX: 0.1 – 5 mg/l
  - Total SVOCs (mostly phenolics): 0.5 – 50 mg/l
  - Total of 9 detected PFAS: 28 – 280 µg/l
  - PFOS (dominant PFAS): 7 – 200 µg/l
- DNAPL present
- Complex geology

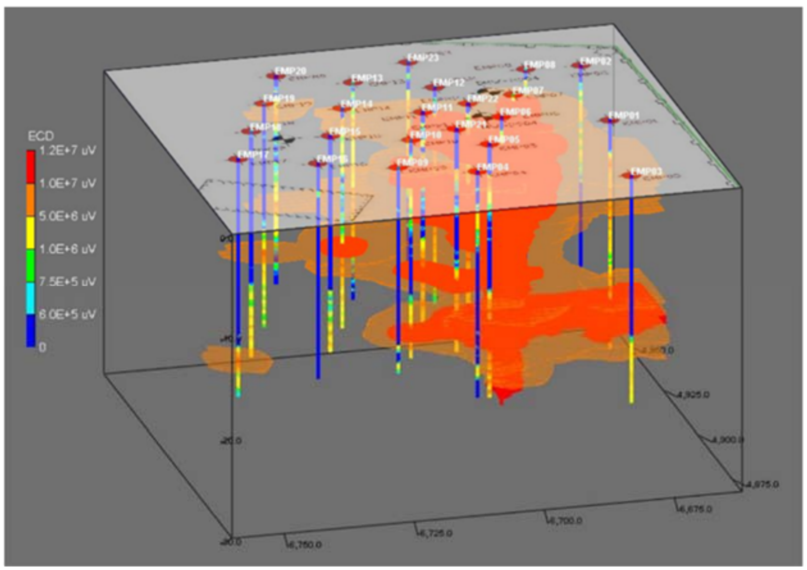


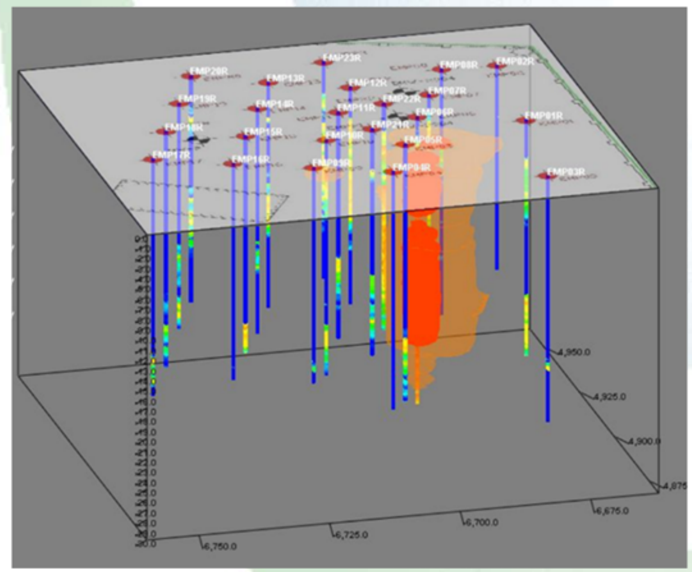
Field Demonstration for CVOCs: Saturated Zone





MIPs Data – Plan View





MIPs Data – Isometric View

Pre-injection

Post-injection

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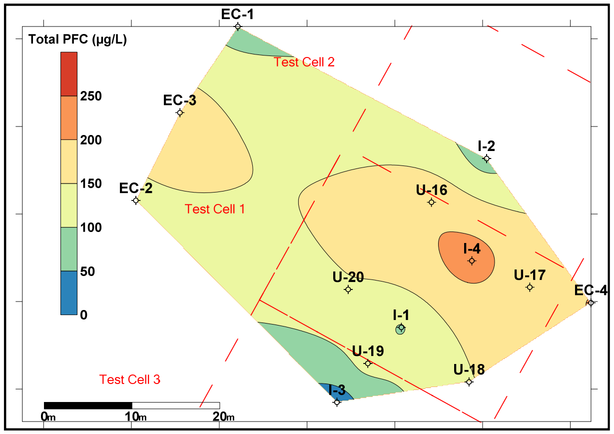
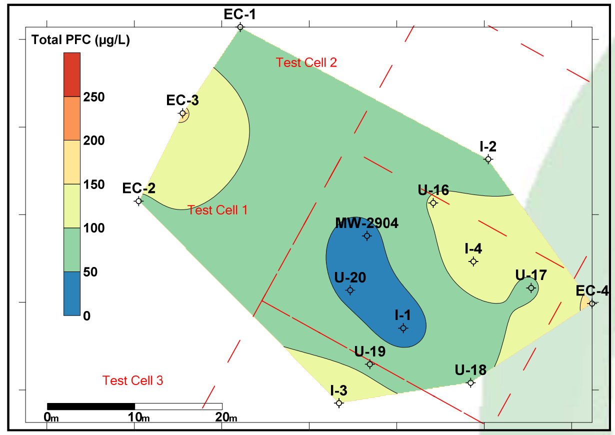
Field Demonstration Results for PFAS

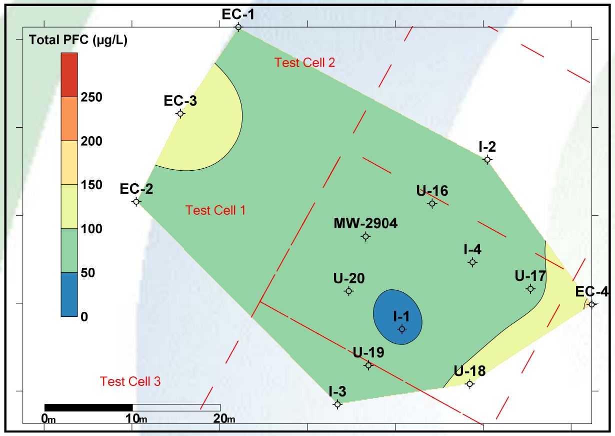
Pre-Injection
April 2013



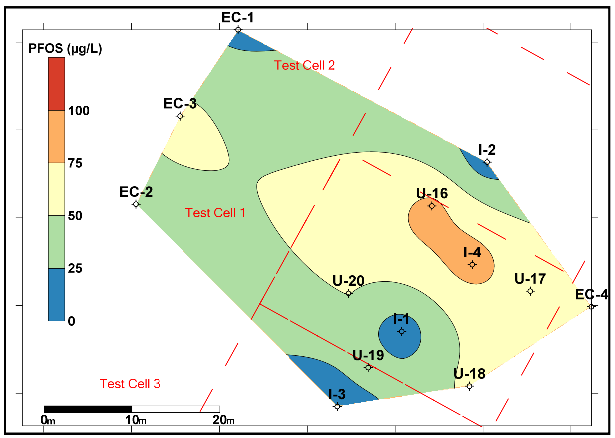
Post-Injection
October 2013

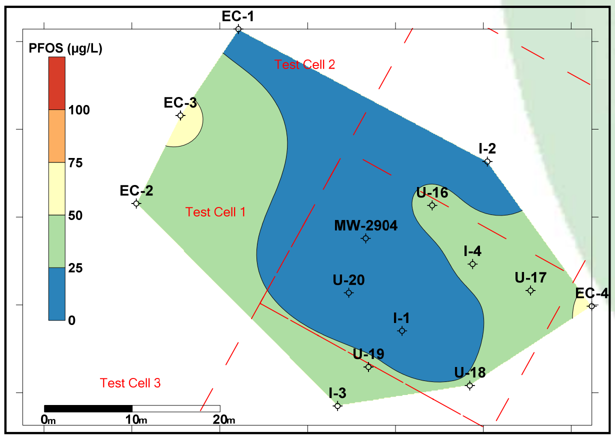


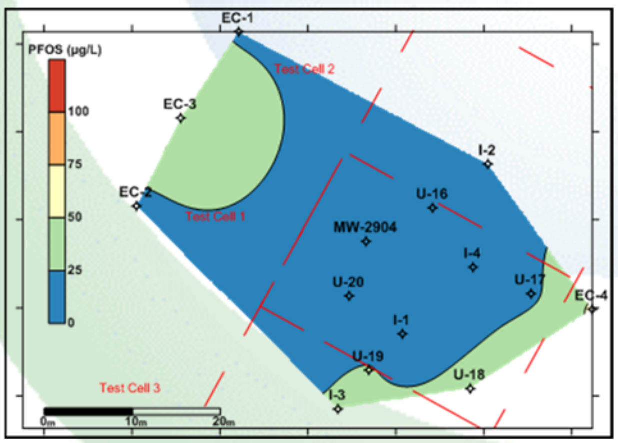
Post-Injection
February 2014



Total of all 9 detected PFAS (µg/l)







PFOS only (ug/l)

OxyZone® Injections: April-May & July-August 2013

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Field Demonstration Results for PFAS

Overall OxyZone® Impact on PFAS:

Lines of Evidence Approach

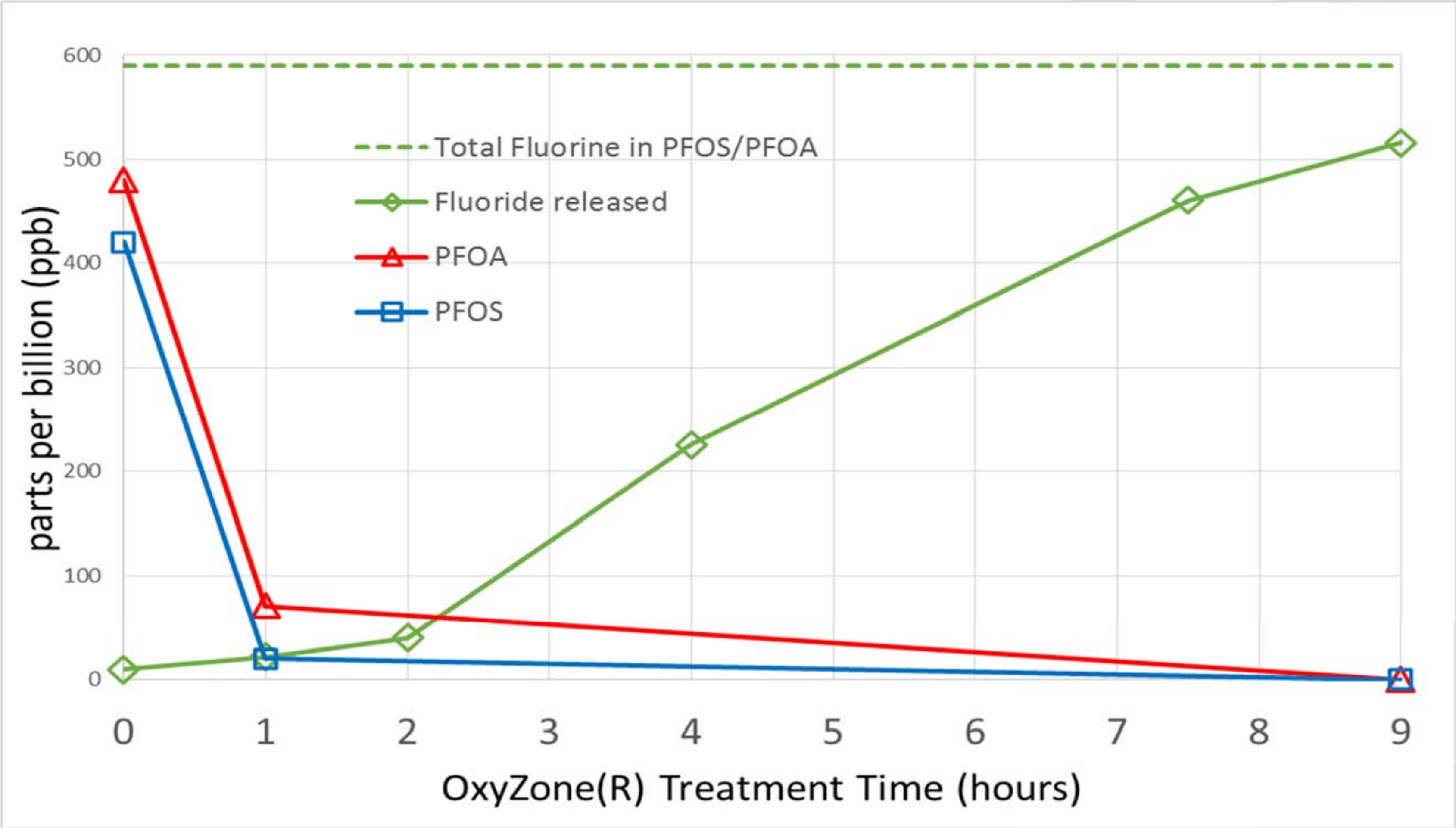
- 21-79% decrease in total groundwater concentration of the 9 detected PFAS in the Test Cell
- PFOS:
  - Had the greatest reduction in groundwater concentration of all PFAS
- Statistical comparison of wells within the Test Cell to those outside the Test Cell showed PFAS concentrations decreased within Test Cell, not outside
- Groundwater concentrations of conservative tracer chloride showed no (dilution) impact from injections

Field Demonstration Site: Bench-Scale Test Results

Spiked Deionized Water (after 2 hours OxyZone® treatment)			
Specific PFC	Initial concentration – ppb	Final concentration – ppb	% removal
PFOS: (8 carbon sulfonate)	93	1	99%
PFOA: (8 carbon acid)	83	1	99%
PFHpS (7 carbon sulfonate)	4	0.4	90%
PFHxA (6 carbon acid)	6	6	no change
Total of 4 PFAS	186	8.4	95%

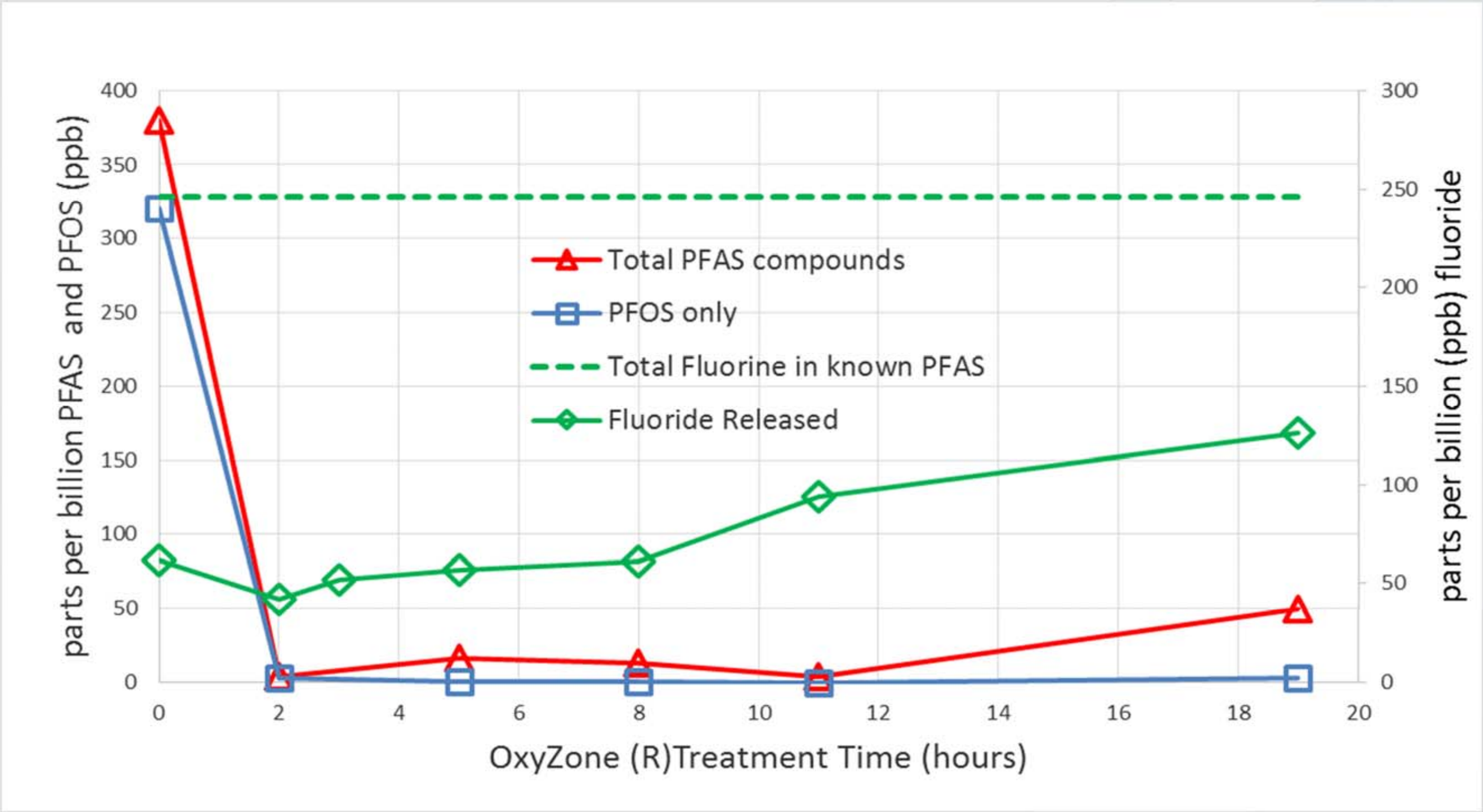
PFAS Contaminated Site GW spiked with additional PFOS and PFOA – 6 hrs. OxyZone®				
Specific PFAS	Initial concentration - ppb	Intermediate (3 hrs.) concentration - ppb	Final (6 hrs.) Concentration - ppb	% removal
PFOS: (8 carbon sulfonate)	138	25	3.6	97%
PFOA: (8 carbon acid)	33	22	1.6	95%
PFHpS (7 carbon sulfonate)	6.7	3.9	2.3	65%
PFHpA (7 carbon acid)	5.5	< 0.4	< 0.2	96%
PFHxA (6 carbon acid)	15	43	< 8.5	44%
PFHxS (6 carbon sulfonate)	68	99	< 0.2	99.7%
PFPeA (5 carbon acid)	11	< 2.0	< 0.9	92%
PFBS (4 carbon sulfonate)	8.7	14	< 0.4	95%
PFBA (4 carbon acid)	3.0	5.5	< 0.4	86%
Total of 9 PFAS	289	127	18	94%

Additional Bench-Scale Testing



- Distilled water spiked with PFOS and PFOA
- Results: 99.9% reduction of PFOS, PFOA; 86% fluoride released

Additional Bench-Scale Testing



- AFFF groundwater sample #1
- Results: 99% reduction of PFOS; 39% fluoride released

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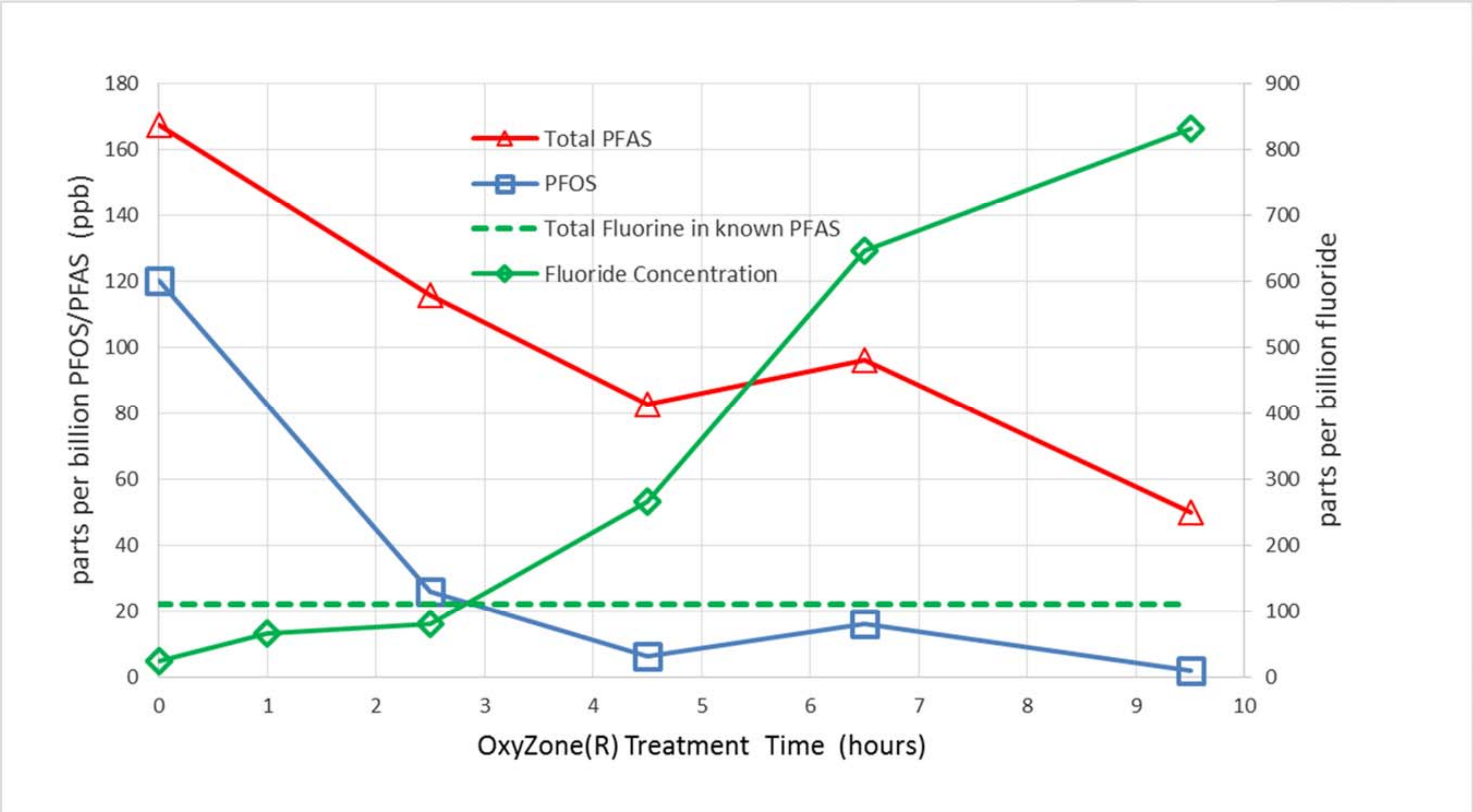
Additional Bench-Scale Testing



- AFFF groundwater sample #2
- Results: 99% reduction of PFOS; 750% fluoride released

Summary

- **Field Demonstration**
  - Based on MIPs data, overall VOC and SVOC contaminant mass significantly reduced in and around Test Cell where OxyZone® was injected
  - PFAS were discovered during base line testing and monitored
  - Groundwater data analysis supported a statistically significant reduction in PFAS concentrations in groundwater, indicating that OxyZone® processes successfully degraded PFAS in-situ in the presence of mixed organic NAPL waste
- **All Bench-Scale Testing**
  - Subsequent evaluation of OxyZone® in the laboratory repeatedly confirmed PFAS decrease 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 ion
- **Conclusion**
  - Results indicate that OxyZone® has the capability to decrease PFAS to very low concentrations, either in situ or ex situ.

Delivery Options

- Recirculation System:
  - In-situ OxyZone® treatment of soil and groundwater
  - Ex-situ OxyZone® reactor
  - Could supplement existing pump and treatment system

- Other Options:
  - Horizontal injection wells on plume transect
  - Vertical injection wells on plume transect

Last Thoughts

- PFAS on most people's radar screen for just a few years
- Many data gaps:
  - ID of PFAS chemicals and their breakdown products
  - Analytical – chemical ID and low-level quantification
  - Physical properties of less common PFAS chemicals
  - Health effects and appropriate cleanup levels
  - Biodegradability
  - Dealing with residuals containing fluorine/fluoride
- Low concentrations of concern present challenges for sampling, analysis, and remediation
- Common technologies that can work well for PFAS in water
  - Filtration (nano filtration, reverse osmosis)
  - Granular activated carbon
  - Ion exchange resin
  - Chemical oxidation

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)
- Dr. Ellen Moyer (ellenmoyer@em-green.com)
- Dr. Raymond Ball (rball@en-chem.com)

The presentation slides will be made available for registrants within a few days of the webinar