Per- and Polyfluoroalkyl Substances (PFAS) Remediation Workshop

Presented at:

Presented by:

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Moderated by Dennis Keane, P.G., XDD Environmental

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October 16, 2018 **Amherst, Massachusetts**

Agenda

- ❑ Introduction to Workshop and Objectives – Dennis Keane
- ❑ Properties, Uses, Occurrence and Concerns with PFAS – Ellen Moyer
- ❑ PFAS Remedial Options for Source and Plume Areas – Mike Marley
- ❑ Break
- ❑ Integrating Key Data in the Characterization Phase + Treatability Studies – Mike Marley
- ❑ Non–Destructive - Adsorption Case Studies – Mike Marley
- ❑ Destructive - Chemical Oxidation Case Study – Raymond Ball
- ❑ R&D Update – Mike Marley
- ❑ Wrap-Up / Summary of Current State of the Practice – Mike Marley
- ❑ Additional Discussion

Overview

- New and fast-changing targets
  - Which PFAS?
  - Which cleanup levels?
  - Can we measure all PFAS?
- PFAS remediation challenges
  - Low cleanup levels
  - Diverse physical – chemical properties
  - Numerous PFAS chemicals – are all being or need to be remediated?
  - Transformation vs. destruction/mineralization
  - Risk of making things worse – formation of Pers and lower C PFAS
- To help address issues
  - Collect appropriate site characterization data
  - Perform treatability and/or pilot testing

Properties, Uses, Occurrence and Concerns

What are PFAS?

- Per- and polyfluoroalkyl substances
- A diverse class of synthetic chemicals with at least one C-F bond
- C-F bonds are extremely strong
- Believed to be ~6,000 PFAS so far
- For nomenclature/acronyms, see ITRC PFAS fact sheet
  - Avoid using term PFC, perfluorinated compounds
    - Includes unrelated chemicals

What are PFAS?

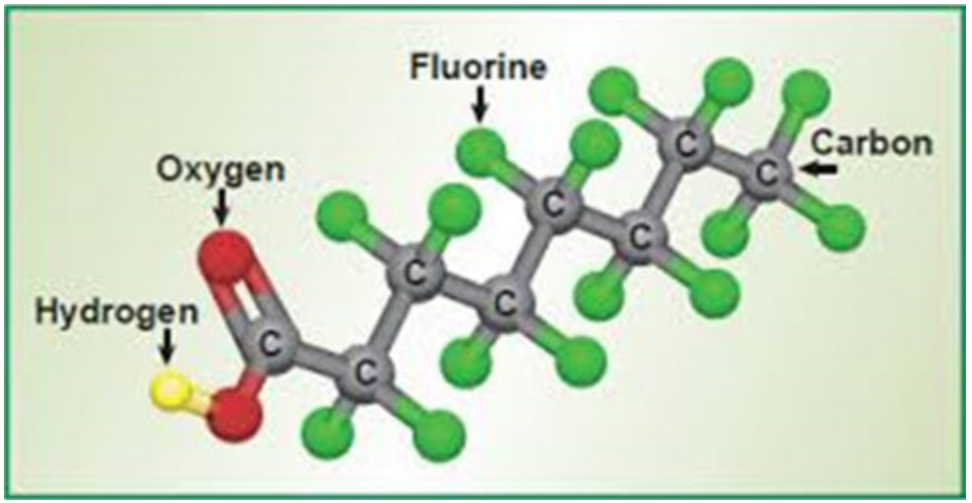
- Carbon chains with attached F
  - 2 to 18 C
  - Per FAS – all C in the chain are bonded to F
    - Most desired manufactured chemicals are per
  - Poly FAS – not all C in the chain are bonded to F
    - Most polys are unintended byproducts of manufacturing
    - Many are “precursors” to pers
- Other atoms can include O, H, S, N, others

What are PFAS?

– Produced in the largest amounts in the US:
  - Perfluorooctanoic acid - PFOA (C8)
  - Perfluorooctane sulfonate - PFOS (C8)

– Typical PFAS properties:
  - Moderate water solubility
  - Low volatility
  - Resist biodegradation
    - C-F bond
  - Properties vary

PFOA



NIEHS – National Institutes of Health

Resource: Physicochemical Properties table in Appendix 2 of https://www.concawe.eu/wp-content/uploads/2016/06/Rpt_16-8.pdf

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

Physical-Chemical 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 (°C)	192.4	259	80
Vapor Pressure (mm Hg at 25 °C)	0.525	~0.002	86
Henry's Law Constant @ 25°C (unitless)	Not measurable	Not measurable	0.225
K_{oc} (temperature as specified)	115	371	79 (at 25 °C)
Solubility in Water (mg/L)	~9,500 (at 25 °C)	680 (temp. not stated)	1,780 (at 25 °C)

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

For other properties of other PFAS, try: https://clu-in.org/contaminantfocus/default.focus/sec/Per-_and_Polyfluoroalkyl_Substances_(PFASs)/cat/Chemistry_and_Behavior/#3

Physical-Chemical Properties of Select Short-Chain PFAS

Property	CAS	Water solubility (mg/L)	Mp/Bp (°C)	Vapour pressure (Pa)	Log Pow	Log Koc
PFOS, perfluorooctane sulfonic acid	1763-23-1	519-570		3.31x10-4	5.5-7.03	2.57-3.3
PFOA, perfluorooctanoic acid	335-67-1	3400		12.1	3.6	2.11
PFHxS, perfluorohexane sulfonic acid	355-46-4	243.4	190/452	1.08x10-6	2.2	3.36/2.14
PFHxA, perfluorohexanoic acid	307-24-4	29.5 <<29		121	2.51 3.12-3.26	
PFHxA, perfluorohexanoate, sodium salt	2923-26-4	29.5		~ 0	0.70	
PFPeS, perfluoropentane sulfonic acid	2706-91-4					
PFPeA, perfluoropentanoic acid	2706-90-3	120			1.98	
PFBS, perfluorobutane sulfonate, potassium salt	29420-49-3	4340	188/447	1.49x10-6	0.26	2.25/1.07
PFBA, perfluorobutanoic acid	375-22-4	447			1.43	
8:2 FTOH, fluorotelomer alcohol	678-39-7	0.2 – 0.3		1.64	5.58	4.13
6:2 FTOH, fluorotelomer alcohol	647-42-7	19		22.1	4.54	2.43
4:2 FTOH, fluorotelomer alcohol	2043-47-2	97	-44/113	1330	3.07/3.30	2.34/2.83
6:2 FTS, fluorotelomer sulfonamide	27619-97-2				3.47-3.98	
6:2 FTAC, fluorotelomer acrylate	17527-29-6	0.38		44.3	5.2	

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https://www.researchgate.net/publication/299230070_Short-chain_Polyfluoroalkyl_Substances_PFAS_A_literature_review_of_information_on_human_health_effects_and_environmental_fate_and_effect_aspects_of_short-chain_PFAS

Physical-Chemical Properties of Select Short-Chain PFAS Acronyms

- CAS = Chemical Abstract Service number
- Mp = melting point
- Bp = boiling point
- Pow = octanol/water partitioning coefficient (aka Kow)
- Koc = organic carbon/water partitioning coefficient

PFAS – Historical Timeline

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

When	What Happened
1950s	3M was first to produce PFOS and higher homologues
1969	AFFF was patented as a method for extinguishing liquid hydrocarbon fires and implemented by the DoD in 1969
1980s – 90s	**First LCMSMS instruments with ppm to ppb detection capabilities**
1990s	A handful of commercial labs developed propriety methods to meet client needs
2002	Global manufacturers began to replace LC PFCs with SC PFCs
2005	$235Mil class action lawsuit brought by citizens against DuPont over PFC contamination in the Ohio river
2000s	**LCMSMS technology advancements lead to ppt and ppq DLs.**
2008, 09	**EPA published Method 537 and ISO published Method 25101**
2012	UCMR3 was signed by the EPA administrator
2014	**ASTM Published Method D7968-14 for PFC in Soil by LC/MS/MS**
2015	**ASTM Published Method D7979-15 for PFC in Water, Sludge, Influent, Effluent and WW by LC/MS/MS**
2017	DoD/DOE QSM 5.1 Table B-15 was developed to include PFAS

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Primary Sources – Point or Direct

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- Released in large quantities from primary manufacturing facilities
- Secondary Manufacturing – incorporation of PFC raw materials into industrial and consumer products
- The use of AFFFs to fight fires is a direct pathway to the environment – **(Connection to DoD)**

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Secondary Sources - Indirect

TestAmerica
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- Commercial and consumer products have a finite lifetime.
  - Dispose to landfills
  - WWTP
  - Air emissions
- **Trace chemistry – transformation mostly degradation by-products (TOP Assay)**

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Occurrence

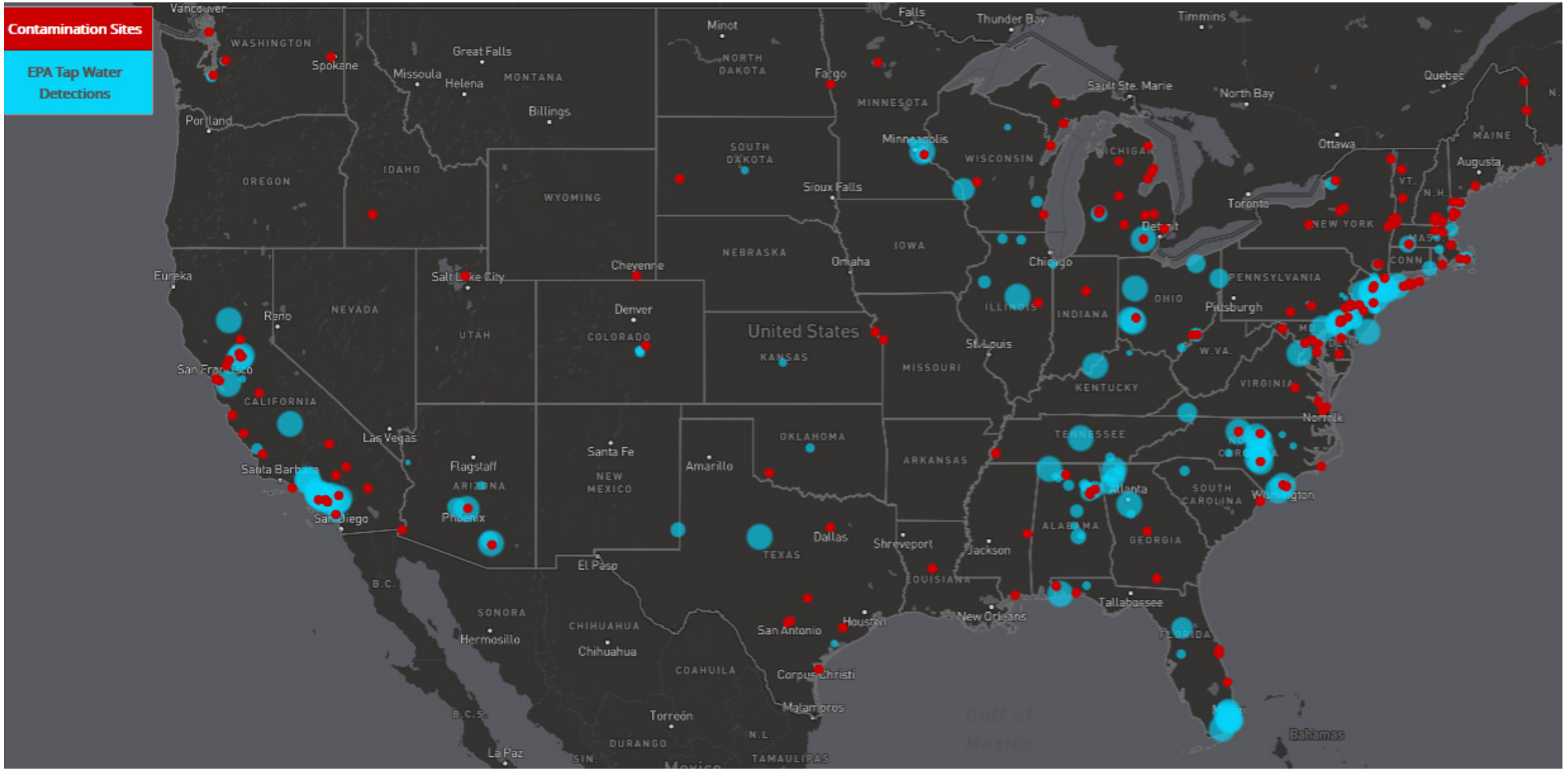
- Found worldwide in soil, air, water, wildlife, and humans
  - Including the Arctic and Antarctic
- 2015 study by U.S. National Health and Nutrition Examination Survey:
  - PFOA, PFOS, PFHxS, and PFNA were detected in 97%–100% of the blood samples
  - Blood levels of some PFAS have declined as production and use declined
- 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

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4483690/

https://www.wateronline.com/doc/study-finds-that-millions-of-americans-get-water-from-pfas-laced-sources-0001

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

PFAS in Tap Water and at Industrial and Military Sites



https://www.ewg.org/interactive-maps/2017_pfa/#.W6vqLvZRdPY accessed 9/26/2018

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Concerns

- Most attention to longer-chain PFAS (C8 or greater – e.g., PFOA, PFOS)
- Persist, travel long distances, and bioaccumulate
- PFOA/PFOS health effects
  - Decrease fertility
  - Disrupt hormones
  - Increase cholesterol
  - Suppress immune system
  - Reduced birth weight
  - Increase cancer risk (PFOA)
- Some info for other PFAS
- ITRC doc in draft will
  - Pull together risk/health effects info for PFAS
  - Final expected in 2019

Standards and Guidelines

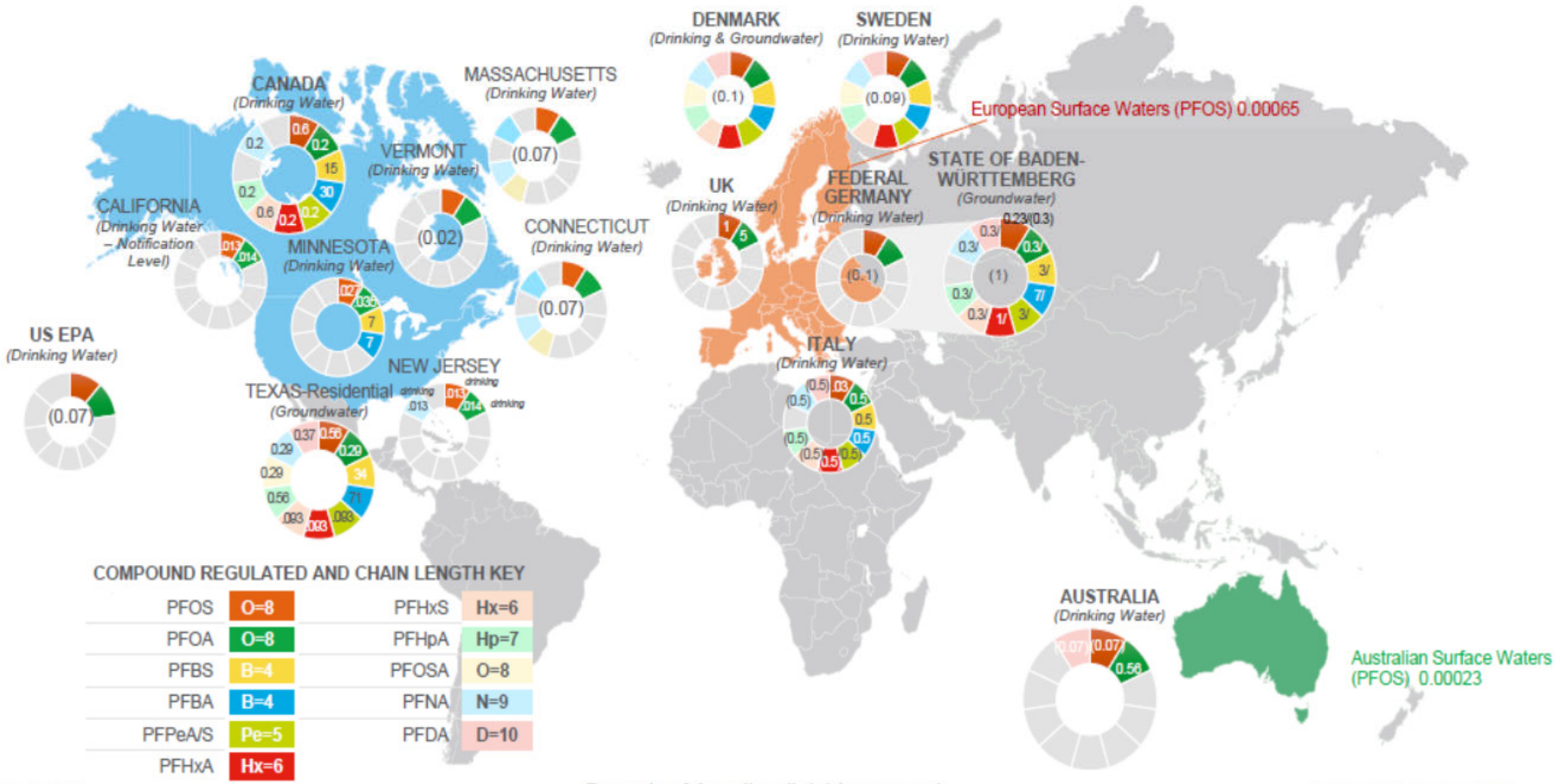
- EPA established health advisories for PFOA and PFOS
  - 70 ng/L or ppt (individually and combined)
  - For lifetime exposure from drinking water)
  - Based on lab studies of effects on rats and mice and epidemiological studies of exposed human populations
- EPA has established no Maximum Contaminant Levels for PFAS
  - Is currently evaluating the need for PFOA and PFOS MCLs
  - Is under pressure to develop MCLs
- CDC ASTDR Toxicological Profile - June 2018 – Rec'd Limits for Drinking Water
  - PFOA 11 ppt
  - PFOS 7.4 ppt
- Other requirements vary widely and change with time
  - Some states and countries are looking at more than PFOA and PFOS

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

Evolving Regulatory PFAS Values

ARCADIS Design & Consultancy for natural and built assets

Drinking Water, Surface Water and Groundwater (µg/l)



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Updated September 2018

Helpful Resources for Standards

- Regional Screening Level calculator (for user-calculated PFOA and PFOS tap water and soil RSLs): https://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search
- July 2018 ITRC table of PFAS water and soil standards, guidance, advisories, etc. (updated approximately monthly): https://pfas-1.itrcweb.org/wp-content/uploads/2018/08/ITRCPFASFactSheetSect4TablesJuly18.xlsx
- Good resource for state standards and other PFAS information: Interstate Technology and Regulatory Cooperation https://pfas-1.itrcweb.org/fact-sheets/

Air Transport – A Significant Pathway

- PFAS released to the air – readily adsorb to particles and settle to the ground
- PFOA deposited on soil can be transported to and contaminate groundwater
- Two sites in NH contaminate 30 square miles above standard via air emissions
  - Merrimack NH – Saint-Gobain Performance Plastics – releases at its Merrimack facility contaminated portions of three other towns above the 70 ng/L standard
- North Bennington VT
  - Bennington College delineated a plume of contaminated soil downwind of the Saint-Gobain Performance Plastics facility in N. Bennington
  - 10 miles long, covering ~120 square miles

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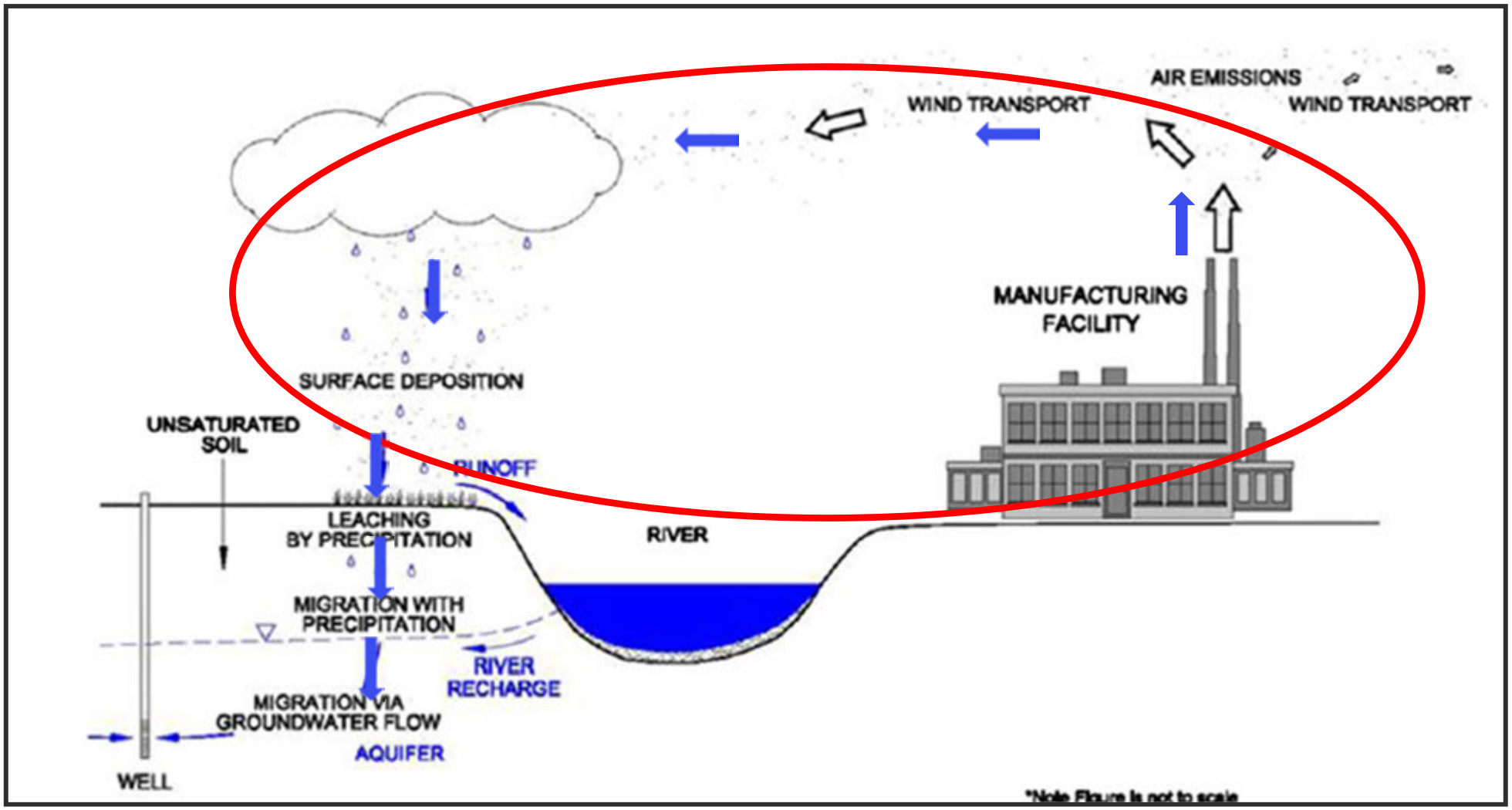
The New Hampshire PFCs/PFAS Investigation – Squarespace
NHDES Letter to Saint Gobain re: Review of Draft Site Investigation ...
https://www.bennington.edu/center-advancement-of-public-action/environment-and-public-action/understanding-pfoa

Air Emission Source



Davis et al., 2007, *Chemoshpere*

Question 1

Which of the following things in this room are highly likely to contain PFAS?

- ❑ Carpet
- ❑ Chairs
- ❑ People
- ❑ White board
- ❑ Air
- ❑ Projector
- ❑ Clothing
- ❑ Water
- ❑ Lights
- ❑ Everything….everything contains PFAS

Dante's Inferno: Entrance into the first circle of hell

Analytical Challenges

- Low detection limits required
- Cross-contamination
- Deciding which analytes to quantify of the many that exist
- Standards not available for many analytes
- Widely varying chemical/physical characteristics of PFAS
- Fast-changing regulatory requirements and analytical methods

PFAS Analysis – "Standard" Method

- Primary methodology
  - Method 537 rev1.1 Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction (SPE) and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Sept,2009
- EPA Technical Advisory 815-B-16-021
  - PFAS compounds can exist as linear & branched isomers
  - Method 537 addresses both for PFOS but not PFOA
    - Discrepancies in PFOA analysis addressed in Tech Advisory
- Drinking water method
  - Amenable to a specific 14 cmpd PFAS target list

EPA Method 537 - List of 14 Compounds

Perfluorooctanoic acid (PFOA)
Perfluorooctane Sulfonate (PFOS)
Perfluorobutanesulfonic acid (PFBS)
Perfluoroheptanoic acid (PFHpA)
Perfluorohexane Sulfonate (PFHxS)
Perfluorononanoic acid (PFNA)
Perfluorohexanoic acid (PFHxA)
Perfluorodecanoic acid (PFDA)
Perfluoroundecanoic acid (PFUdA)
N-methyl perfluorooctanesulfonamidoacetic acid (MeFOSAA)
Perfluorododecanoic acid (PFDoA)
N-ethyl perfluorooctanesulfonamidoacetic acid (EtFOSAA)
Perfluorotridecanoic acid (PRTrDA)
Perfluorotetradecanoic acid (PFTeDA)

Other LC/MS/MS Methodologies

- Method 537 not amenable to expanded list of compounds
  - 500 series DW methods not supposed to be modified

(DW = drinking water)

- "Laboratory proprietary methods" to address longer compound lists / sample matrices other than DW
  - May incorporate isotope dilution approach
  - May be different or multiple SPE cartridges
  - May utilize direct aqueous injection rather than SPE

(SPE = solid-phase extraction)

- EPA plans - additional methods for comments
  - For non-potable water and soil

ALPHA ANALYTICAL World Class Chemistry

Fluoride and Total Organic Fluorine Analysis

- Fluoride analysis – can be used to:
  - Evaluate extent of biological or chemical remediation that releases fluoride from PFAS
  - A drawback is high detection limits of ~20 ug/L
  - Drinking water standards/guidelines:
    - U.S. Public Health Service recommends 0.7 mg/L to prevent cavities
    - EPA MCL 4.0 mg/l and secondary MCL 2.0 mg/L
    - Concerns about thyroid, brain, and other impacts
- Total organic fluorine – an emerging technique – could help
  - Locate PFAS plumes
  - Provide sense of total mass of PFAS present
  - Verify remediation is complete
- Sensitivity is not sufficient with either analysis
  - Test America and others are working on TOF methods
    - Test America may have a commercial TOF method available in 2019

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3728443/

Transformation and Precursors

- Perfluorinateds don't naturally transform
- Oxidizable polyfluorinateds should eventually transform to perfluorinateds
  - Biotic or abiotic transformation
  - Polys cleave at a weak spot (i.e., a carbon not fully fluorinated)
- Total Oxidizable Precursors (TOP) analysis quantifies precursors to help assess the total mass of PFAS present

What is the TOP Assay?

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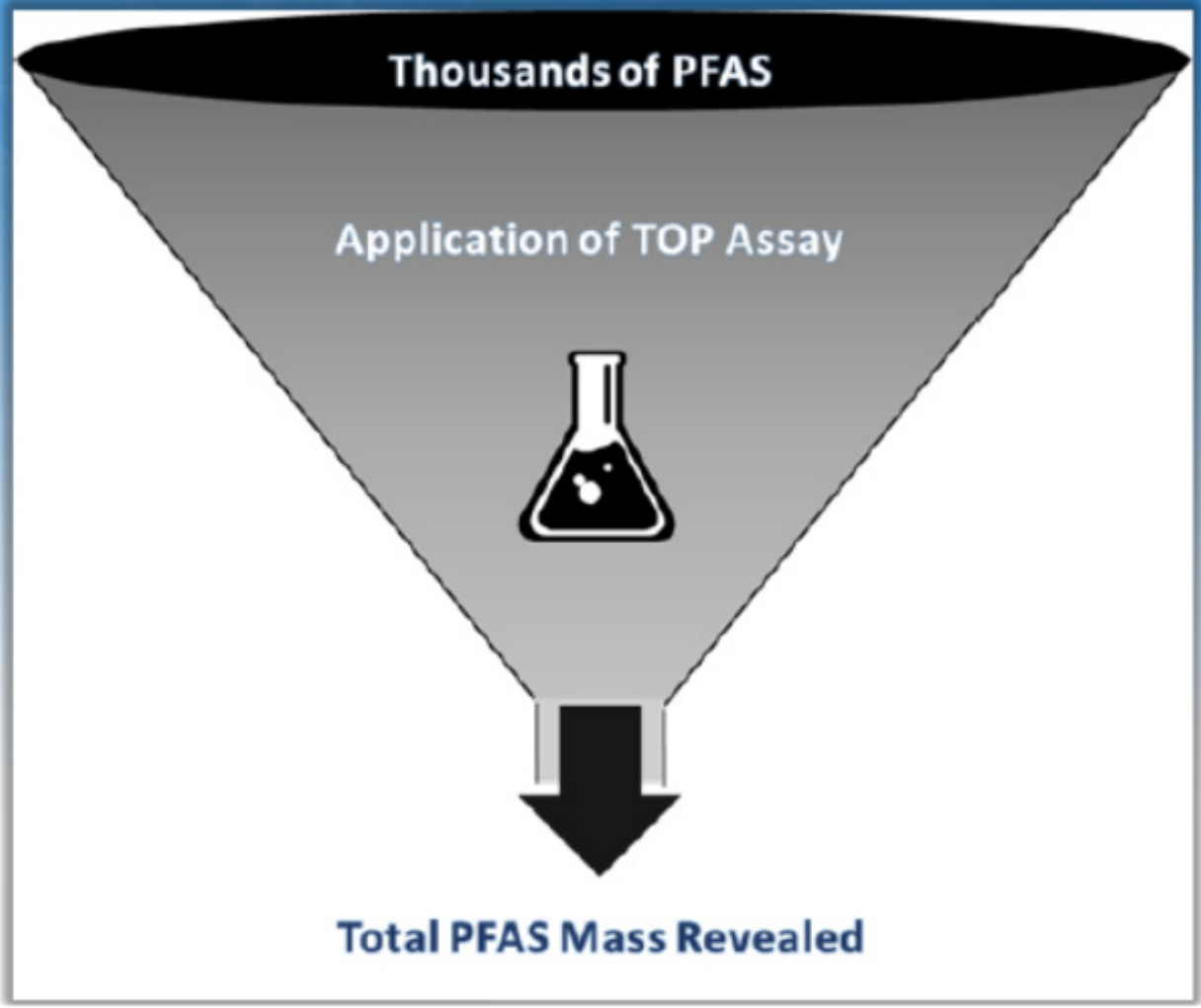
- A new PFAS sample preparation technique
- Conceptually simple chemistry
- Used in conjunction with 537M (Not 537) – combines pre and post oxidation results
- Indicates presence of unidentified PFAS in water, sediment and soil



Houtz, Erika, and David L. Sedlak. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science and Technology* 46: 9342-9349.

Image provided by Arcadis 2016

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Estimates total mass of precursors that oxidize to analytes measured by Method 537M

Possible Sources of Contamination
"*refer to EPA, regulatory agencies*"

OK

- Field Equipment
  - HDPE bottles, silicon tubing, loose paper, aluminum/Masonite clipboards, Alconox / Liquinox®, nitrile gloves
- Clothing / PPE
  - "Well laundered", preferably cotton
- Personal care products
  - None, see "allowable" sun screens & insect repellants

NOT OK

- Field Equipment
  - LDPE bottles, PTFE caps, PTFE tubing, waterproof field books, plastic clipboards/binders, sticky notes, chemical ("blue ice")
- Clothing / PPE
  - No fabric softener, water repellent clothing, protective suits
- Personal care products
  - No cosmetics, moisturizers, etc. as part of personal cleaning/showering routine on morning of sampling
  - Verify allowable sun screens / insect
  - Food packaging

Site Management Strategy

- ❑ Protect receptors from immediate exposure
- ❑ Complete site assessment to ID
  - All sources
  - All contaminants
  - Contaminant nature and extent in all media
- ❑ Control Source Area
- ❑ Remediate dissolved plume
- ❑ Monitored natural attenuation

Question 2

Which of the following types of sites would be least likely to have PFAS contamination?

- ❑ Airports
- ❑ Department of Defense facilities
- ❑ Manufactured gas plants
- ❑ Landfills
- ❑ Dry cleaners
- ❑ Gas stations
- ❑ Fire stations
- ❑ Websites

PFAS Remedial Options for Source and Plume Areas

Topics Covered

- Physical – Chemical Properties
- Non-Destructive Technologies
  - Sorption / Ion-Exchange
  - Filtration / Separation
  - Isolation
- Destructive Technologies
  - Chemical
  - Biological
  - Thermal

Physical-Chemical Properties

(widely ranging across all PFAS)

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 (°C)	192.4	259	80
Vapor Pressure (mm Hg at 25 °C)	0.525	~0.002	86
Henry's Law Constant @ 25°C (unitless)	Very Low	Very Low	0.225
K_{oc} (temperature as specified)	115	371	79 (at 25 °C)
Solubility in Water (mg/L)	~9,500 (at 25 °C)	680 (temp. not stated)	1,780 (at 25 °C)

USEPA 2016 USEPA 2016

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Overview

Based on the physical – chemical properties of PFAS (higher C PFAS)

- High molecular weight = potential for sieving / filtration / separation
- High Koc = potential for adsorption
- Charged head = potential for ion exchange (IX)
- Low VP = not suitable for SVE at ambient temperatures
- Low H = not suitable for stripping from groundwater at ambient temperatures

Non-Destructive Technologies

Adsorption/Ion Exchange

(most commonplace, produces concentrated PFAS waste)

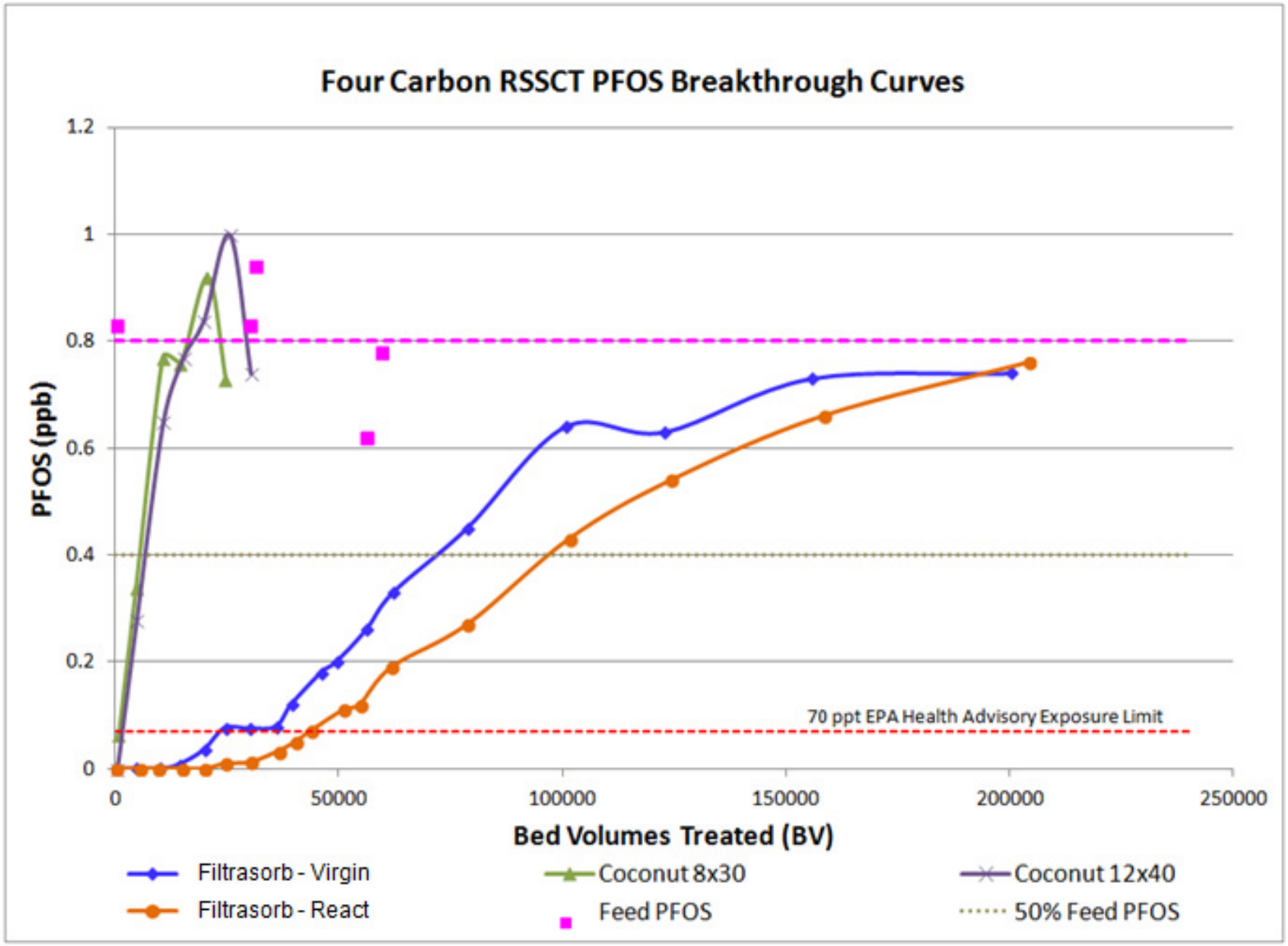
❑ Carbon-based systems

- Ex-situ activated carbon systems (GAC or PAC)
- Biochar (biomass and charcoal) – less consistent and kinetically slower?
- In-situ injectable carbon-based systems – * gaining interest *
- Competition with organics for sorptive sites – may require pretreatment

❑ Clays or blend of sorbent-based systems

- e.g., Rembind™, MatCARE™
- Part isolation?

Treatability studies are needed



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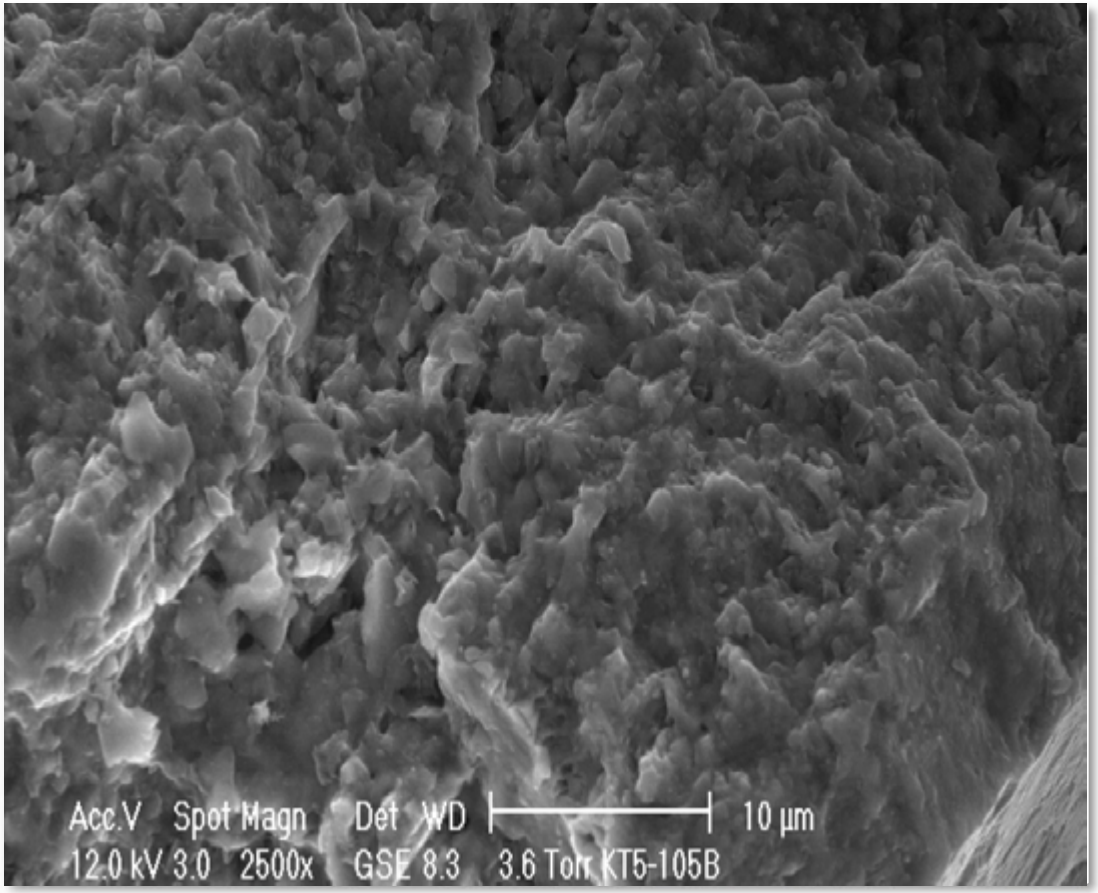
In-Situ Injectable Carbon-Based Systems

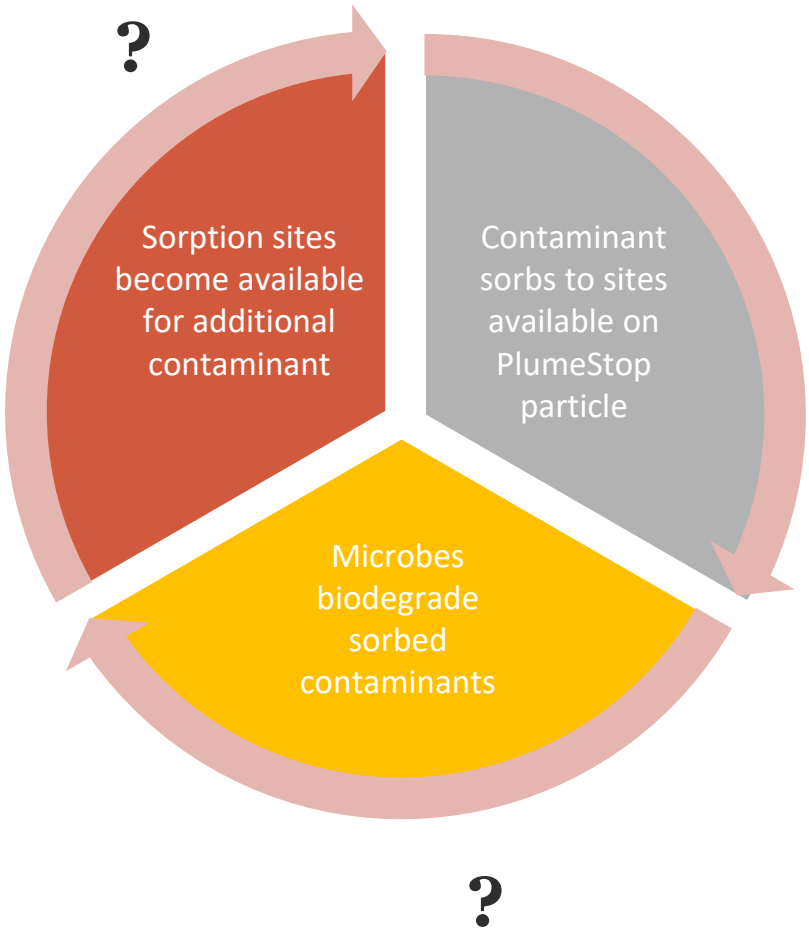
PLUME STOP Liquid Activated Carbon – what is it?

- A highly dispersive, injectable sorbent and microbial growth matrix
- Colloidal activated carbon (1 – 2 µm)
  - Size of a bacterium – suspends as 'liquid'
  - Huge surface area – extremely fast sorption
- Proprietary anti-clumping / distribution supporting surface treatment (patent applied for)
  - Core innovation
  - Enables wide-area, low-pressure distribution through the soil matrix without clogging

Courtesy Regenesis

Mode of Action - PFAS





Courtesy Regenesis

? Added

Longevity?

- Loading can be designed, based on non-destruction of PFAS, to theoretically provide long term control
- Questions to consider
  - Will carbon degrade and bleed PFAS?
  - Will competition for sorption sites occur?
  - Will geochemical changes occur to affect sorption?

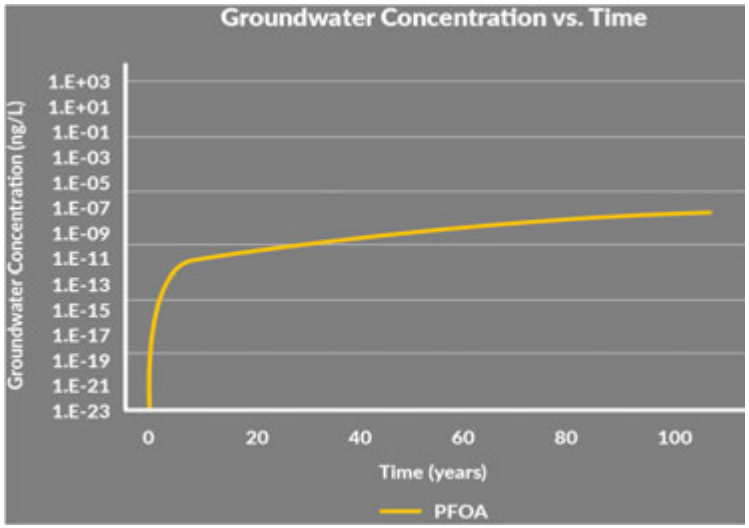
Long Term Results

❑ Modeled

Grant Carey, PhD

Porewater Solutions
Expertise • Experience • Innovation

- Conservative Analytical Solution
  - Mass flux 161 ug/m²/day
  - Source half life 30 years
- Source Zone PFOA
  - Strongly adsorbed
  - ~100 years 1x10-⁶ ng/L
- Source Zone PFOS
  - Not as strongly adsorbed
  - ~100 years ~24 ng/L



❑ Principal Inputs:

- Source zone PFOA concentration = 4,000 ng/L
- Groundwater velocity = 0.8 m/d
  - K = 2.6 m/d, i = 0.06, effective porosity = 0.2

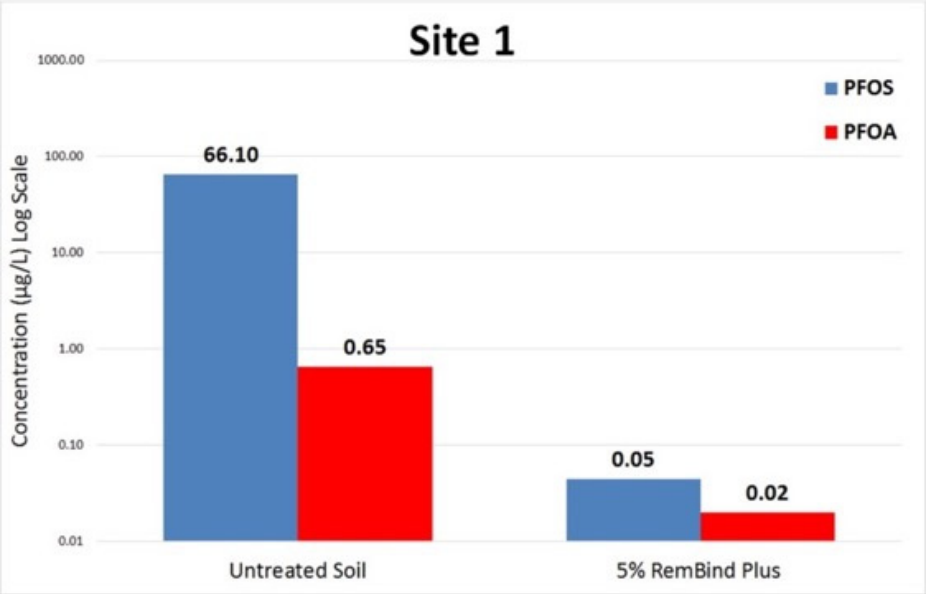
What is *RemBind*®?

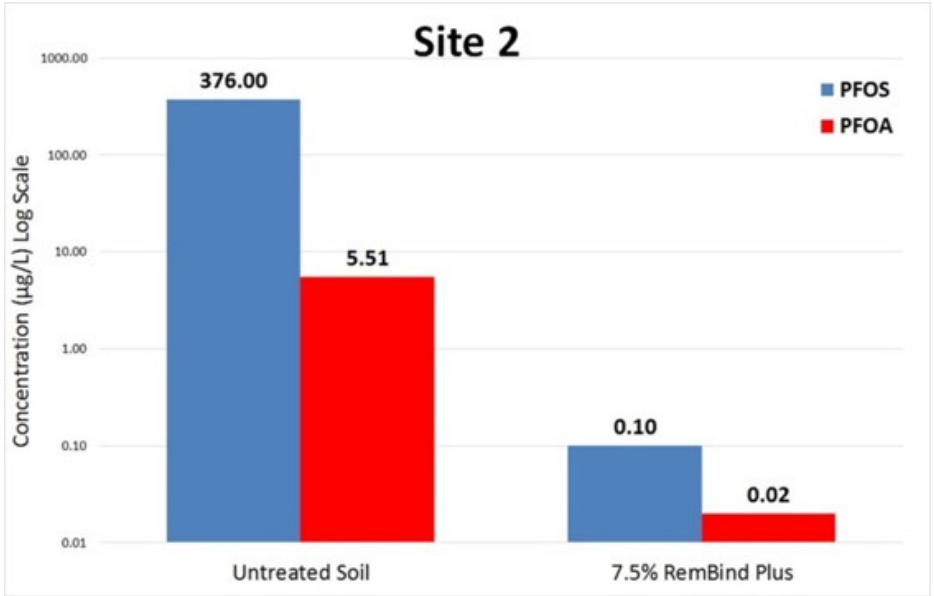
- Powdered reagent that binds to organic contaminants in soil/water to prevent leaching
- Chemical fixation or immobilization
- Binds to range of contaminants including TPH, PAH, and PFASs
- US Patent 8,940,958

How Does *RemBind*® Work?

- Main ingredients:
  - Activated carbon
  - Aluminium hydroxide (amorphous)
  - Organic matter and additives
- Large surface area with mixed charges
- Chemical and physical interactions

PFOS and PFOA Soil Results





* Soil leachates prepared using the Toxicity Characteristic Leaching Procedure (TCLP)

Adsorption/Ion Exchange
(also produces concentrated PFAS waste)

- Synthetics resins – gaining traction due to capacity/effectiveness
  - Combination IX and adsorption
  - Faster kinetics and higher capacities = smaller reactor size
  - Higher product cost – requires site specific cost-benefit analysis
  - Ongoing work on single use IX and shorter chain PFAS sorption

Treatability studies are essential

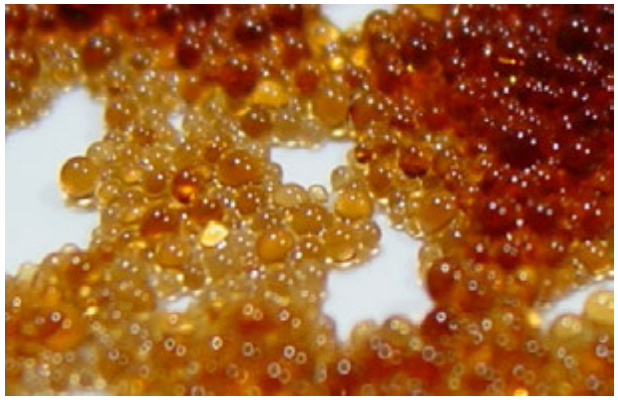
Adsorption/Ion Exchange
(also produces concentrated PFAS waste)

- Other natural materials or modified natural materials (mainly R&D)
  - Modified natural mined materials
    - Surface charge
    - Surface area
- Organically modified silicas – flexible pore structure OSorb® or PuraSorb®
  - Potential for greater applicability over range of PFAS
  - OSorb® for higher concentration PFAS
  - PuraSorb® for lower concentration PFAS

Treatability studies are essential

Resins

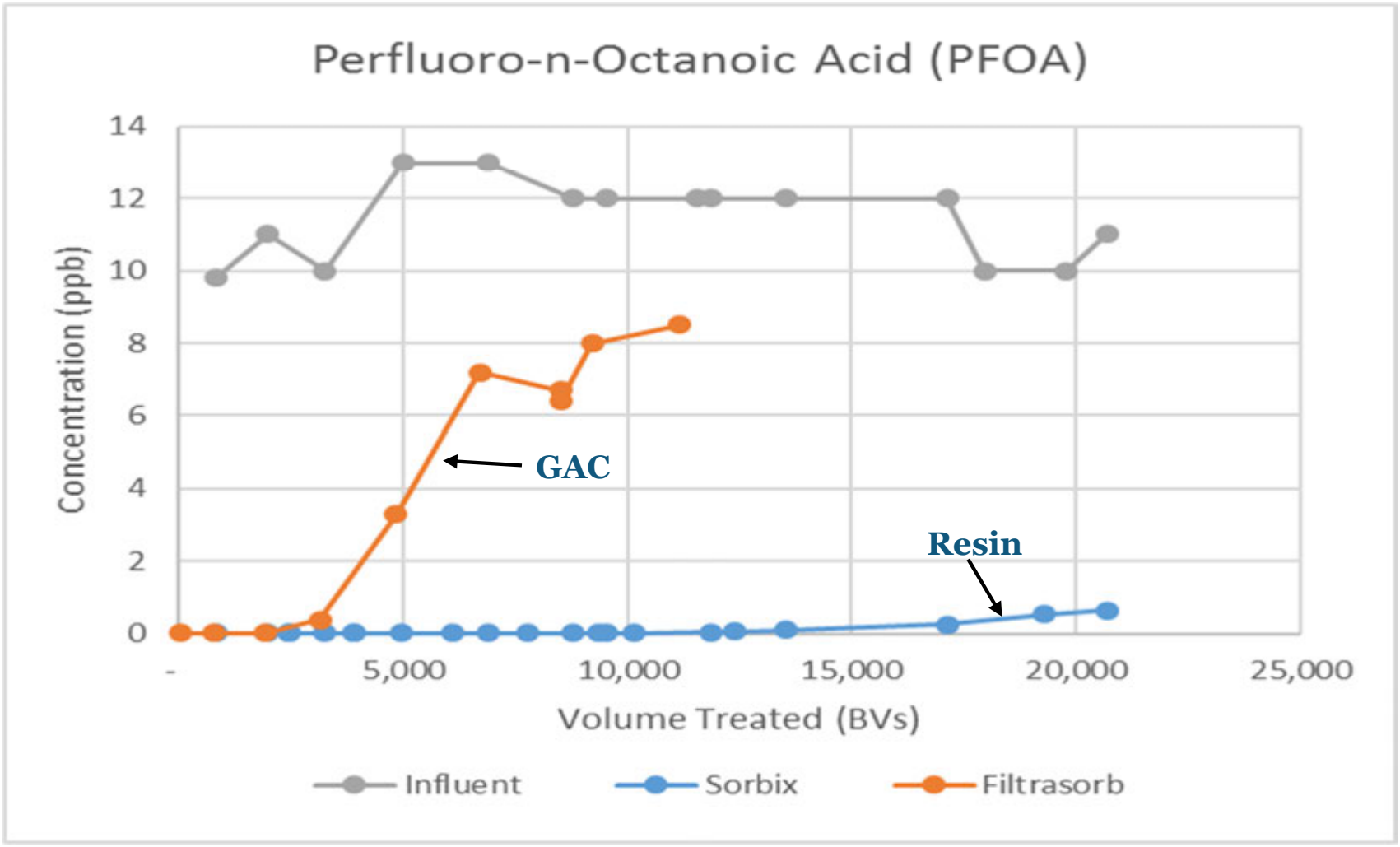
- Synthetic Media can be engineered / used to collect various contaminants from liquids, vapor or atmospheric streams and be reused indefinitely



Overview Sorbix

- Sorbix is essentially an adsorbent with IX functionality
- Dual mechanism of removal takes advantage of properties of PFAS compounds
- Capacity is 5-6X greater than GAC for PFOA and > 8X greater for PFOS.
- Successful resin regeneration has been demonstrated
- Distillation and PFAS destruction maximize sustainability
- New resins are being tested: i.e., removal of shorter chain compounds

PFOA Breakthrough at 5-min EBCT



BV = bed volumes EBCT = empty bed contact times

Carbon vs. IX Resins

- Carbon
  - Proven effective multiple sites and >1000 point of entry treatment systems
  - Regeneration, at high temperature: “destroys” PFAS but may reduce capacity
  - Lower capacity than IX
  - Still evaluating short chain PFAS, but some success
  - Can be more cost-effective
    - If shorter duration operations, lower PFAS concentrations, and less natural organic matter
- Resins
  - Number case studies increasing
  - Higher capacity for PFAS adsorption / IX
  - Working on engineering resins for improving short chain PFAS removal
  - Can be more cost-effective
  - On-site regeneration and PFAS destruction research/demonstration ongoing
- Treatability studies are essential for design, etc.

Filtration / Separation

(Also produces concentrated PFAS waste)

- Nano-Filtration (NF)
  - PFAS have molecular weight cutoff (MWCO) of approximately 300 - 500 Daltons
    - Dalton is ~one twelfth of the mass of an atom of carbon-12
    - 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
- Thermal Desorption
  - Lower temperatures (e.g. 450°C)

Filtration / Separation

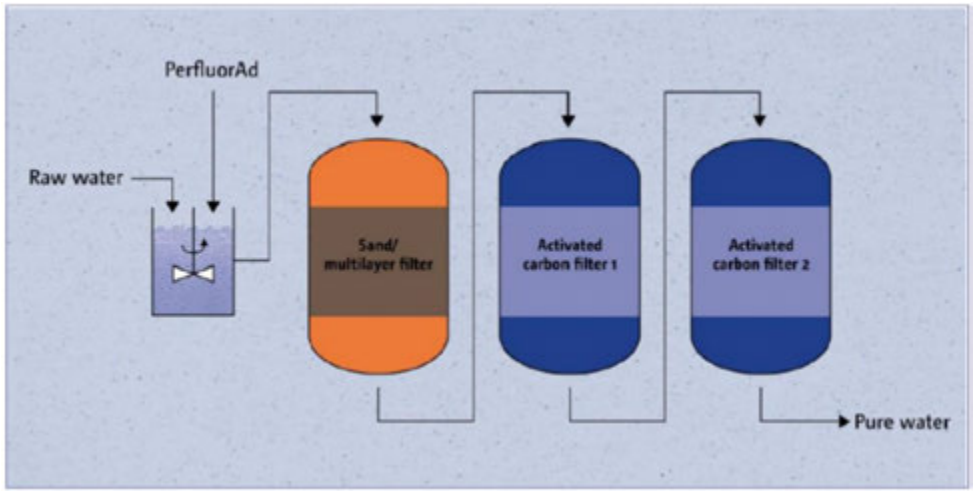
(Also produces concentrated PFAS waste)

- Pretreatment maybe needed due to potential for filter clogging
  - PerfluorAd – not really filtration but coagulation - flocculation
    - Electro-coagulation as alternate
  - Ozofractionation – separation on ozone / air microbubbles (as foam) due to PFAS surfactant properties
    - Ozone may treat co-contaminants and reduce Poly's to Per's
  - May not be effective for all PFAS or to reach ppt (ng/L) target
- Treatment trains are likely needed to achieve ppt levels cost-effectively
  - Pretreatment > filtration > polishing / sorption

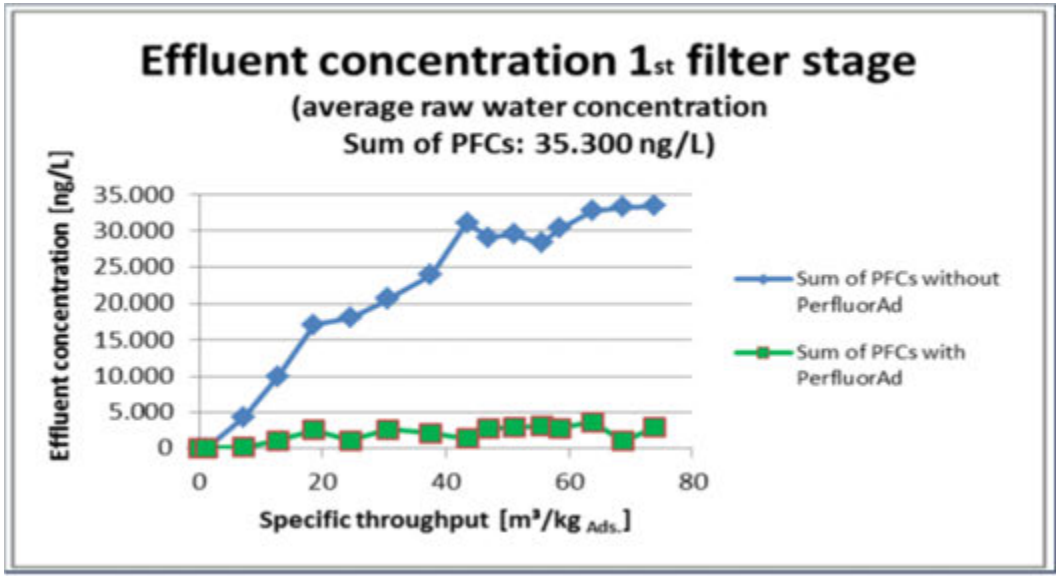
Treatability studies are needed

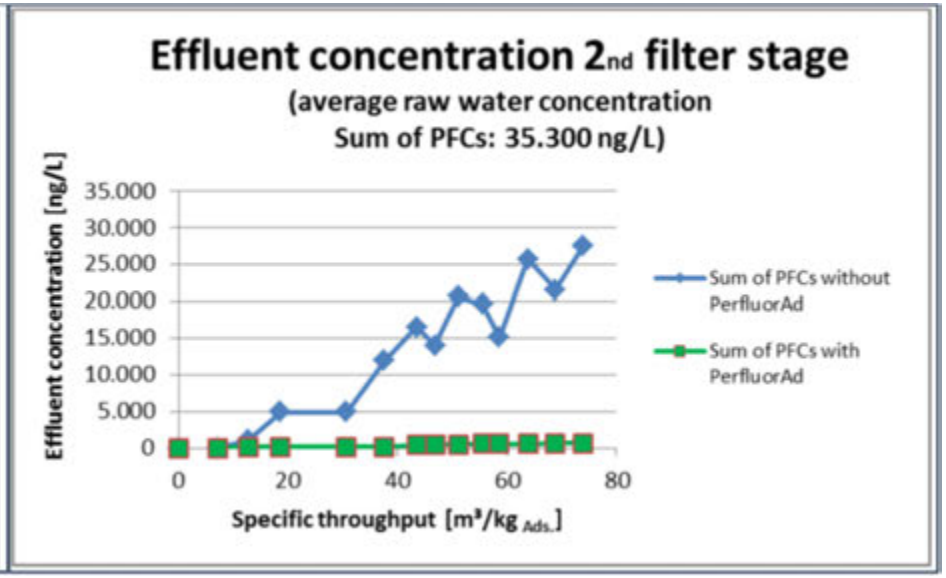
PerfluorAd Principle of Operation

- Added to PFASs contaminated water in stirring reactor
- Dosing rate adjustable to PFASs concentration or target
- Micro-flocs are generated
- Flocs removable by precipitation & filtration
- 95%+ PFASs removal attainable
- Non-detect concentrations with GAC/PAC polishing



Treatment with / without PerfluorAd





Concentrated PFAS Waste Require Treatment

(typically high mg/L level PFAS + salts + other organics)

- Typically incineration at > 1100 ^{o}C
- Applied research into other treatment options
  - Electrochemical
  - lower energy thermal
- R&D – SERDP current funding primary focus on waste stream treatment (described later in presentation)
- Reaction times can be long – up to hours
  - less suited for low level PFAS impacted waters

Question 3

What is the most common active remedial technology currently being used for PFAS?

- ❑ Bioremediation
- ❑ Adsorption/filtration
- ❑ Soil vapor extraction
- ❑ Pump and Treat
- ❑ Dig and Haul
- ❑ Isolation by injection of the 50's B-movie monster "The Blob"

Isolation

- Stabilization via Soil Mixing
  - Typically sorbents
- Landfill
- Capping
- Holding Cells

Applied Destructive Technologies

Destructive Technologies

- Oxidative / reductive technologies – redox manipulation
  - Showing promise, but many unanswered questions
  - Can treat many of the co-contaminants
  - Common theme is high energy and / or diverse reactive species needed and reaction time (e.g., electrochemical, plasma, photolysis)
    - UV photolysis generate aquated / hydrated electron with EV = 2.9V
    - Electrochemical using Boron Doped Diamond Electrode some success with PFAS, but not fully with sulfonates

      Other effective mixed metal electrodes are being evaluated e.g. Titanium suboxides Ti_4O_7
    - ZVI at high temperature and pressure or with catalyst has some success with PFOS

Treatability studies are needed

Destructive Technologies

- SERDP recent focus / R&D on PFAS Investigation–Derived Wastes (not complete set below)
  - Treatment Train
    - Physical adsorption, advanced oxidation, and reductive defluorination
    - AOP, Hydrated / aquated electron defluorination, membrane-based concentration
  - Electrochemical - numerous processes and electrode materials
    - Combined photo/electrochemical reduction
  - Thermal
    - Using calcium hydroxide amendments to lower the energy use
    - Thermal desorption coupled with Indirect Thermal Desorption/Thermal Oxidation
    - Smoldering combustion
  - Other oxidation / reduction processes (Plasma, AOP - ARP – see later case study)
  - Nanoscale Technologies

Treatability studies are needed

Chemical Oxidation / Reduction 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 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; high temperature and pressure ZVI
- Research ongoing using chemical oxidation to treat precursors to simplify overall treatment approach

Pretreatment of Precursors

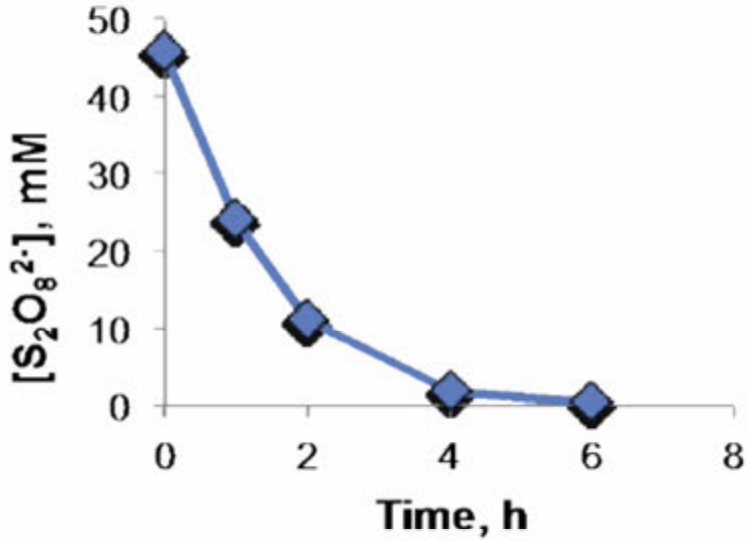
Fighting the Unbeatable Foe: Remediation of Groundwater Contaminated by PFASs with In Situ Chemical Oxidation

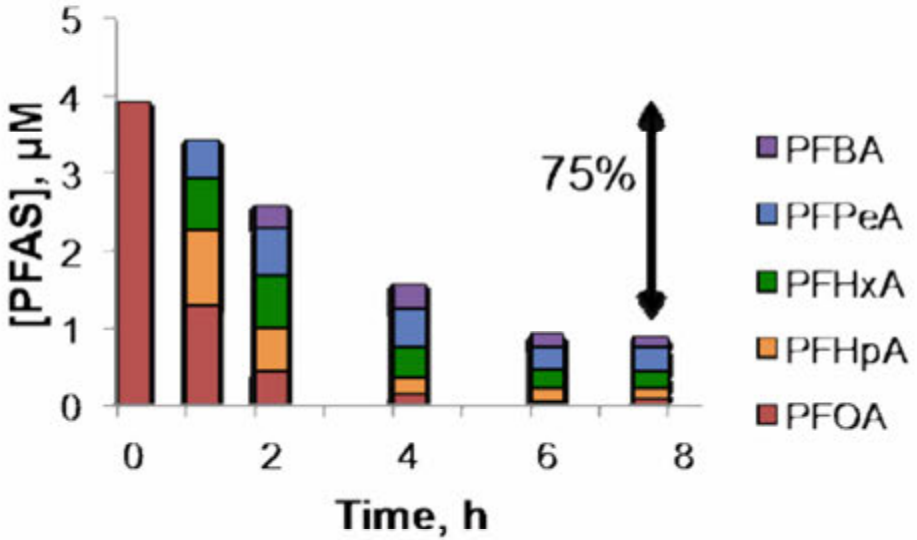
Dr. David Sedlak
University of California, Berkeley

SERDP DOD • EPA • DOE | ESTCP

XDD ENVIRONMENTAL
Do it right. Do it once.

PFOA in Deionized Water





Conditions:

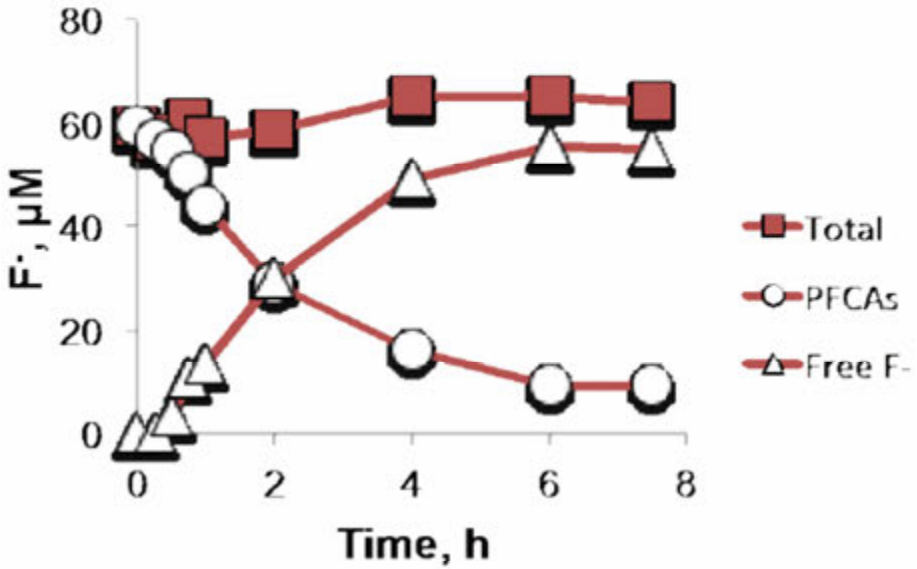
$[S_2O_8^{2-}]_0$ = 50 mM,

$[PFOA]_0$ = 4 µM

unbuffered (pH < 3) H_2O,

T = 85° C

Bruton and Sedlak, in review



XDD ENVIRONMENTAL
Do it right. Do it once.

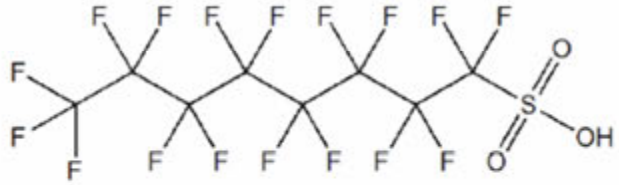
3M AFFF: Sulfonates

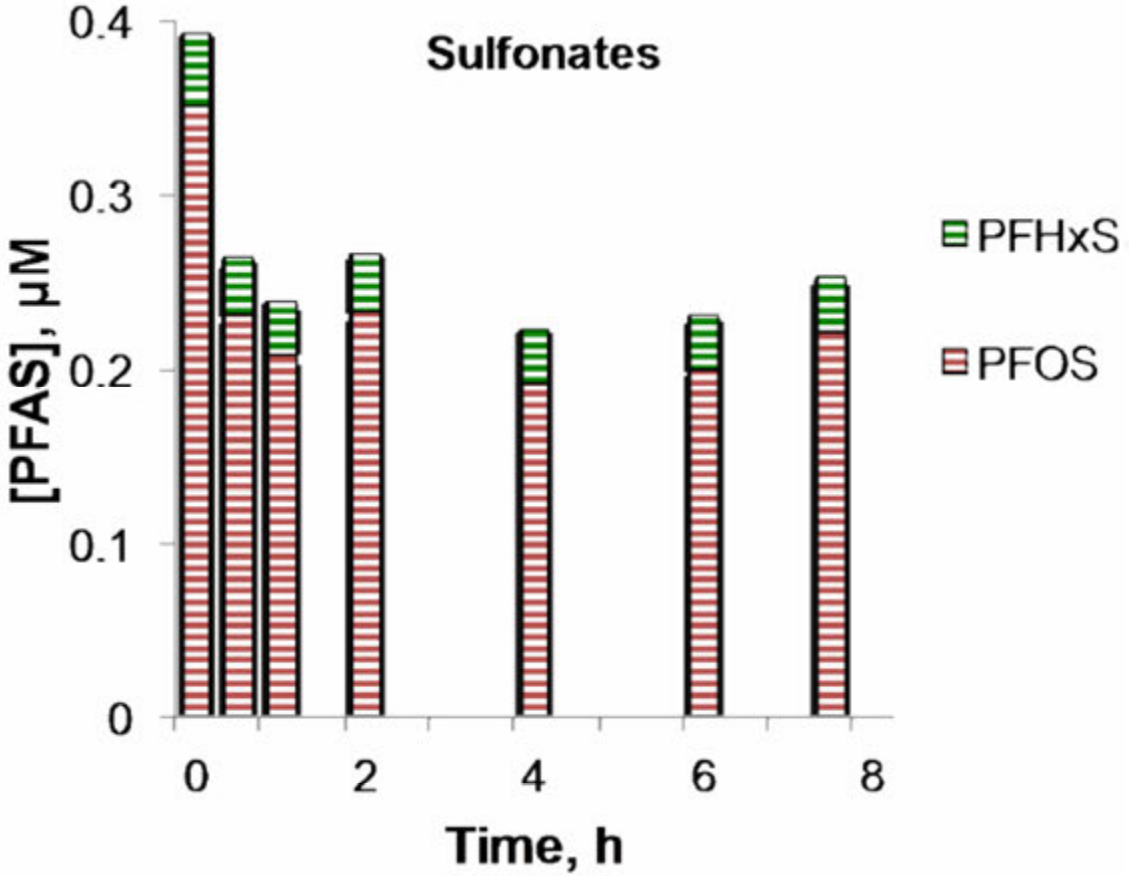
Conditions:

$[S_2O_8^{2-}]_0$ = 50 mM,

unbuffered (pH < 3) MQ H_2O

T = 85° C





Bruton and Sedlak, in review

XDD ENVIRONMENTAL
Do it right. Do it once.

Summary

- Persulfate or H_2O_2 ISCO can convert polyfluorinated compounds into PFCAs
  - Complex AFFF "precursors" converted to PFCAs
  - Benefit: simplifies remediation process
- Persulfate mineralizes PFCAs
  - Only under acidic conditions (pH<3)
  - Interference from chloride
  - Benefit: in situ remediation of PFCAs and Ansul AFFF
- Limitations
  - PFSAs, 3M AFFF, high alkalinity, Cl^-

Destructive Technologies

- Biodegradation
  - Evidence of transformations of Polys via natural and enhanced processes
    - Typical byproduct is Per's
    - Levels of available fluoride in many groundwaters up to low mg/L levels
  - Very limited research to date showing biodegradation of Pers
    - No accumulation of byproducts or Fluoride in studies raises questions
    - Observations of reductive pathways (thermodynamically favorable) with formation of lower C Pers
  - PFAS range of applicability may be limited
  - Question on whether can treat to the proposed standards
    - Polishing needed?
  - Mother nature may find a way to degrade Pers with time?
    - At one time chlorinated solvents were considered non-biodegradable

Destructive Technologies
(less sensitivity to PFAS range)

- Thermal destruction (higher temperatures ~1100°C)

- Sonolysis
  - Ultrasonic waves (can produce cavitation – bubble surface can reach several thousand oK and high pressures – hundreds of atmospheres)
  - Also can form free radicals (e.g. $OH\cdot$)

Treatability studies are needed

Question 4

To break apart the carbon-fluorine bond, we need:

- ❑ Low energy technologies
- ❑ High energy technologies
- ❑ Chuck Norris
- ❑ Biological processes

Integrating Key Data Collection into Characterization

Some of Issues / Options for Site Characterization

- Reminder on issues
  - Limitations of PFAS laboratory analyses
  - We don't understand the risk associated with every PFAS
  - We don't understand the physical – chemical properties of every PFAS
  - Focus on PFOA and PFOS may be forefront today, but…..
- General Parameters
  - Geology
  - Hydraulics
  - All contaminants of concern (source and plume)
  - Receptors
  - Remedial goals
  - Logistical issues (e.g. access)
  - Geochemistry – general (including DO, ORP, pH)
  - Geochemistry – technology specific (including alkalinity, metals, major anions and cations)?

Some of Issues / Options for Site Characterization

- To understand degree of PFAS impacts (i.e., not just PFOA and PFOS)
  - TOP analysis
  - Emerging analysis TOF
  - Free Fluoride – evidence of transformation?
- Source Treatment
  - Excavation
    - What is the cut-off concentration / limit for excavation?
  - Isolation / Stabilization
    - Compatibility with isolation materials
    - Treatability study on leachability of stabilized soils – TCLP?
  - In-situ chemical treatment
    - Treatability study on effectiveness, byproduct formation, chemical loading (includes non-target demand), remedial goal achievable?
  - In-situ adsorption
    - Treatability study on amendment loading, effectiveness for all PFAS, leachability of sorbents and competitive adsorption species (e.g. TOC)

Some of Issues / Options for Site Characterization

Plume Treatment:

- ❑ Containment
  - Pump and Treat
    - Sorbents - treatability study on effectiveness all PFAS of concern, EBCT, breakthrough, remedial goal achievable
    - Filtration - treatability study on effectiveness all PFAS of concern, system sizing, remedial goal achievable
    - Chemical treatment - treatability study on effectiveness all PFAS of concern, byproduct formation, chemical loading, EBCT, remedial goal achievable
  - Barrier systems
    - Sorbents - treatability study on effectiveness all PFAS of concern, loading, breakthrough, remedial goal achievable
    - Chemical treatment - treatability study on effectiveness all PFAS of concern, byproduct formation, chemical loading, breakthrough, remedial goal achievable

Some of Issues / Options for Site Characterization

- Plume Treatment
  - In-situ chemical treatment
    - Treatability study on effectiveness for all PFAS, byproduct formation, chemical loading, remedial goal achievable, aquifer clogging potential (e.g., mineral precipitation)
  - In-situ adsorption
    - Treatability study on material loading, effectiveness for all PFAS, leachability of sorbents and competitive adsorption species (e.g. DOM), aquifer clogging potential (e.g., mineral precipitation)

Non-Destructive Case Studies

Adsorptive 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 EBCT – 10 minutes

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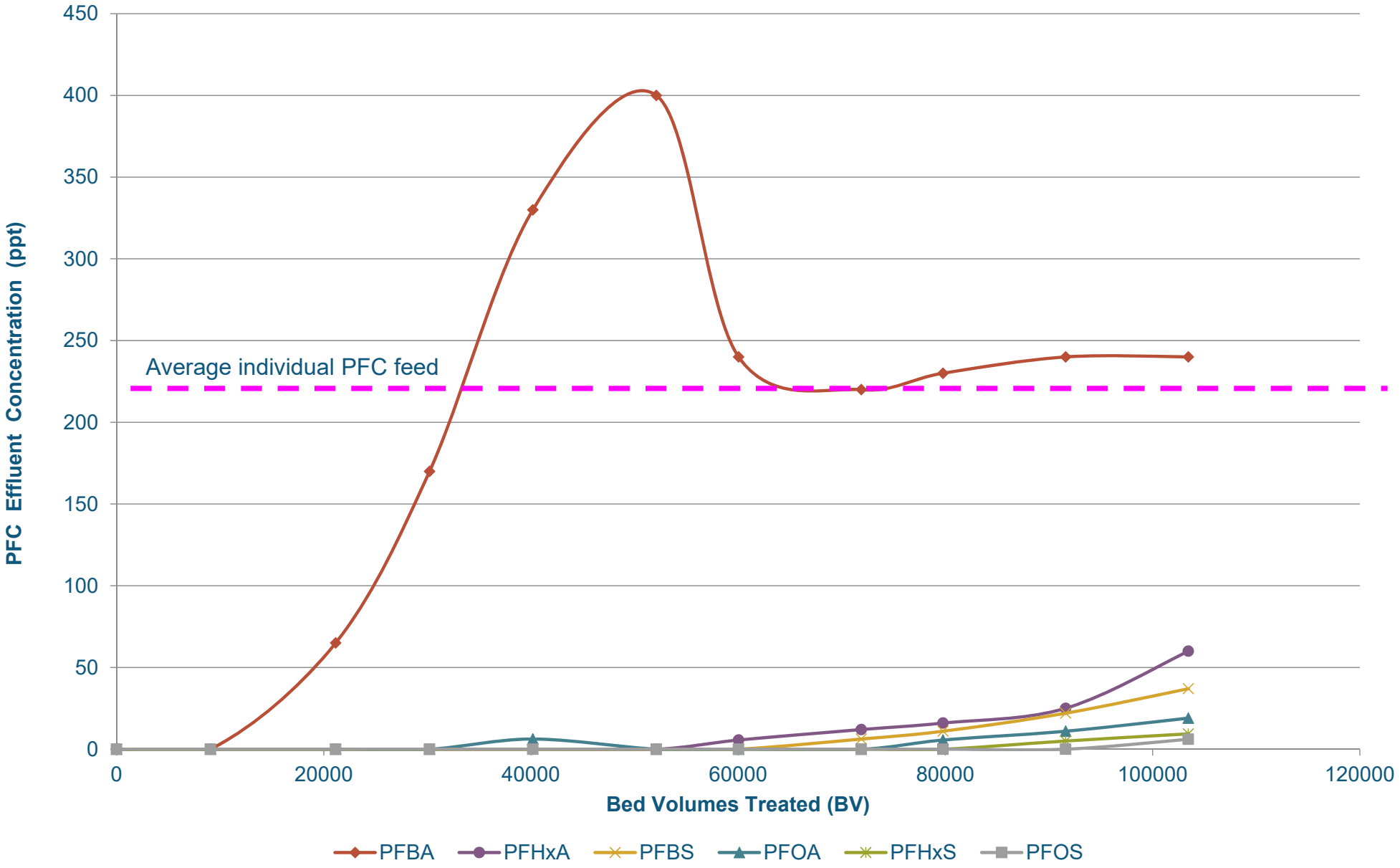
Removal of Various PFAS using Virgin Filtrasorb



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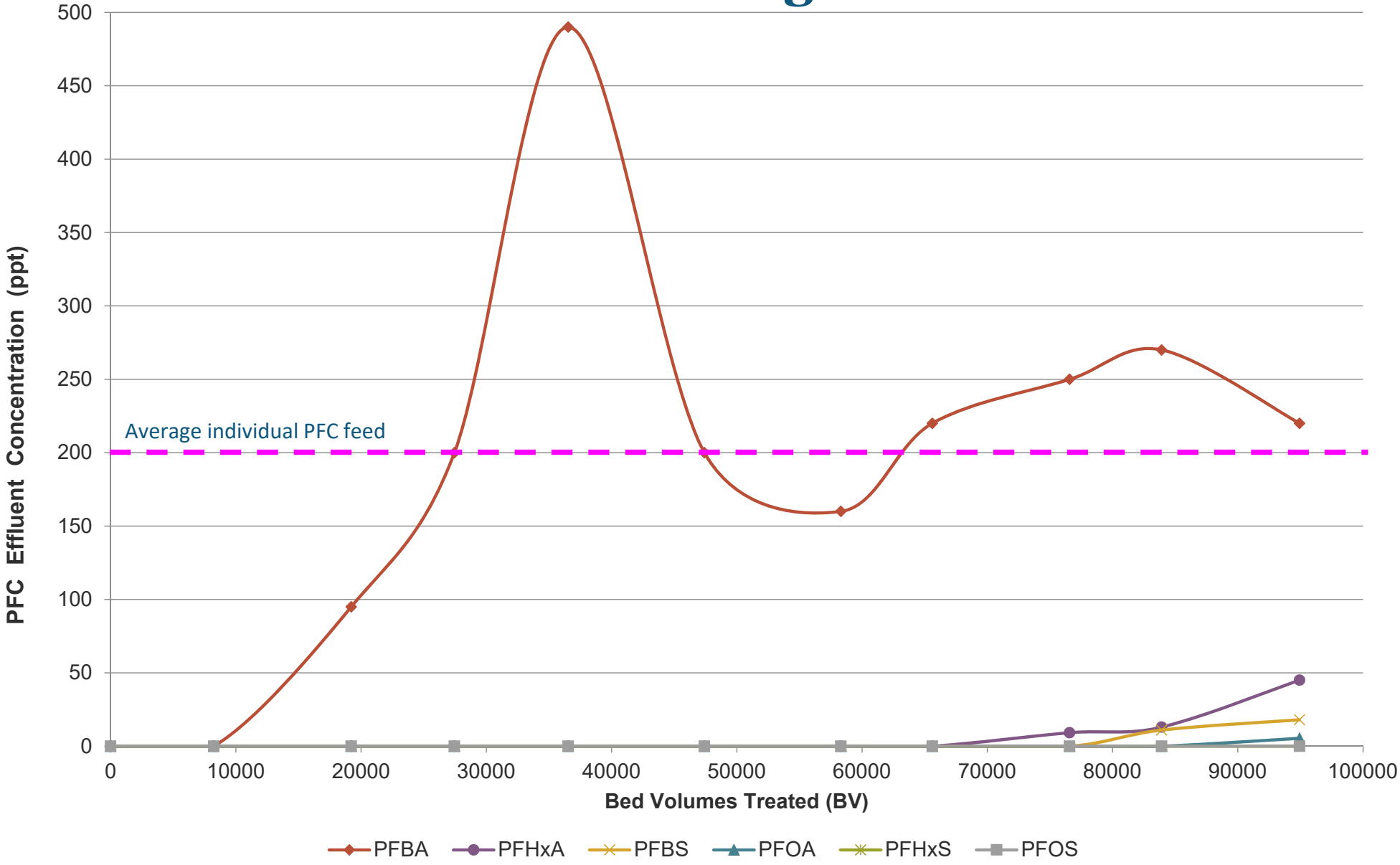
Removal of Various PFAS using Reactivated Filtrasorb



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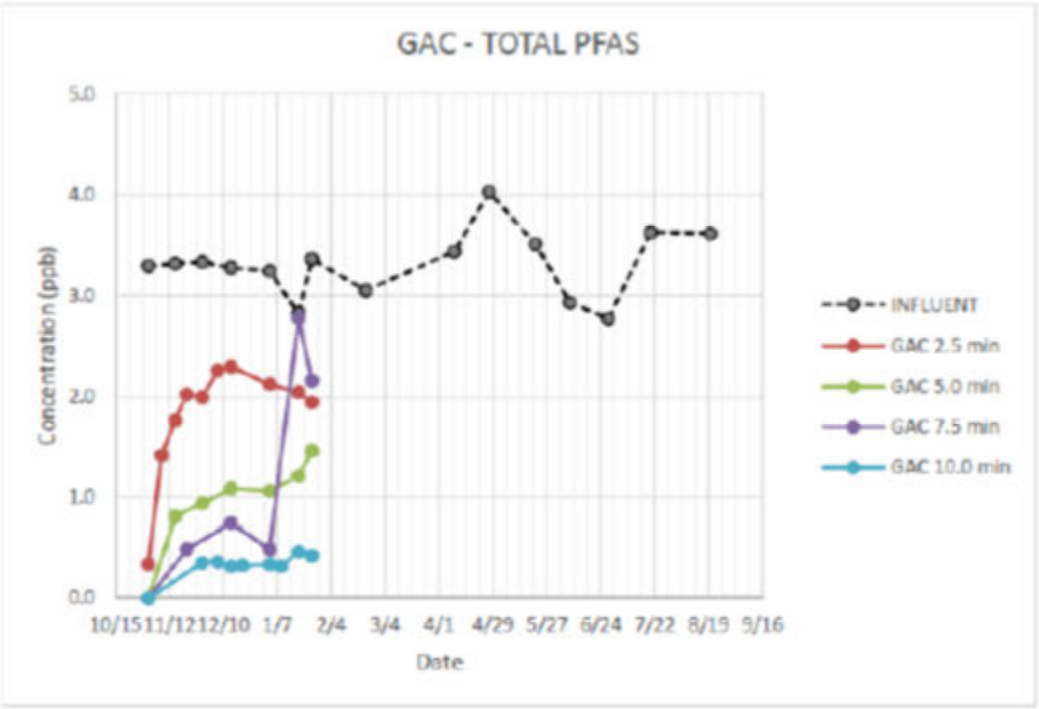
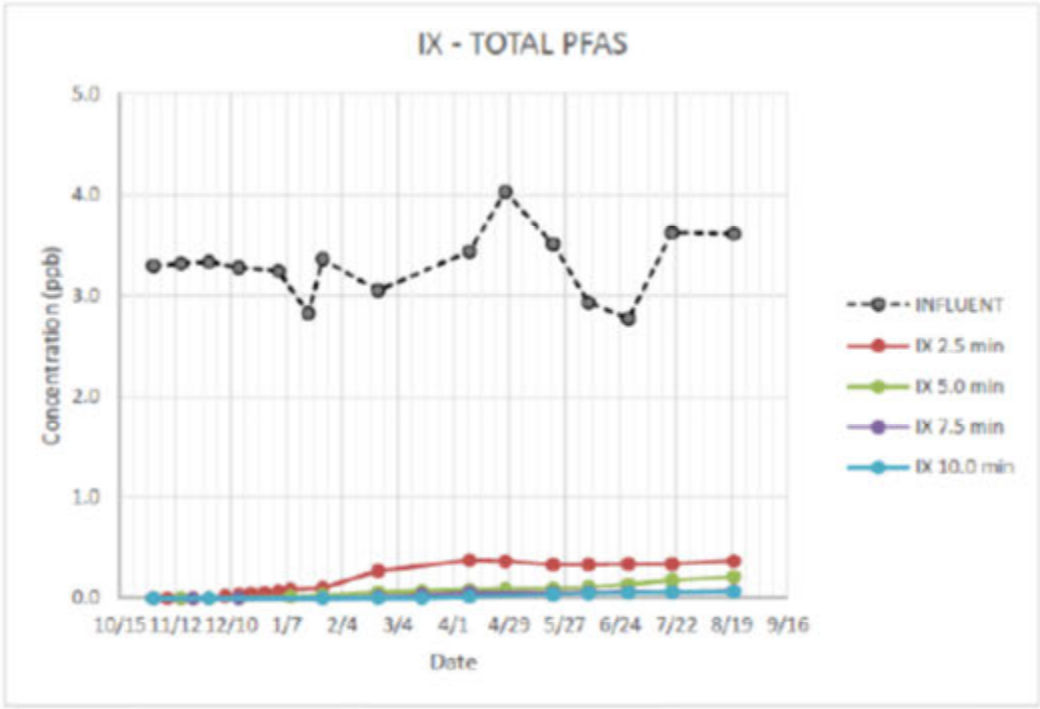
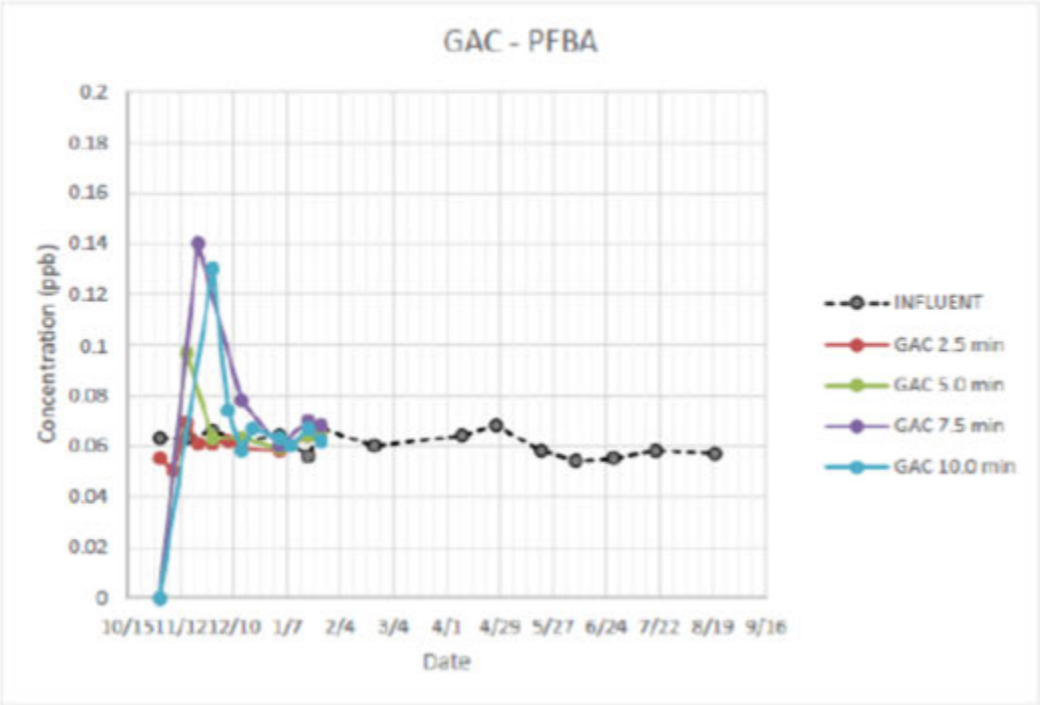
Public water supply well (in NH) side-by-side pilot: Sorbix LC1 resin vs. Calgon F400 GAC

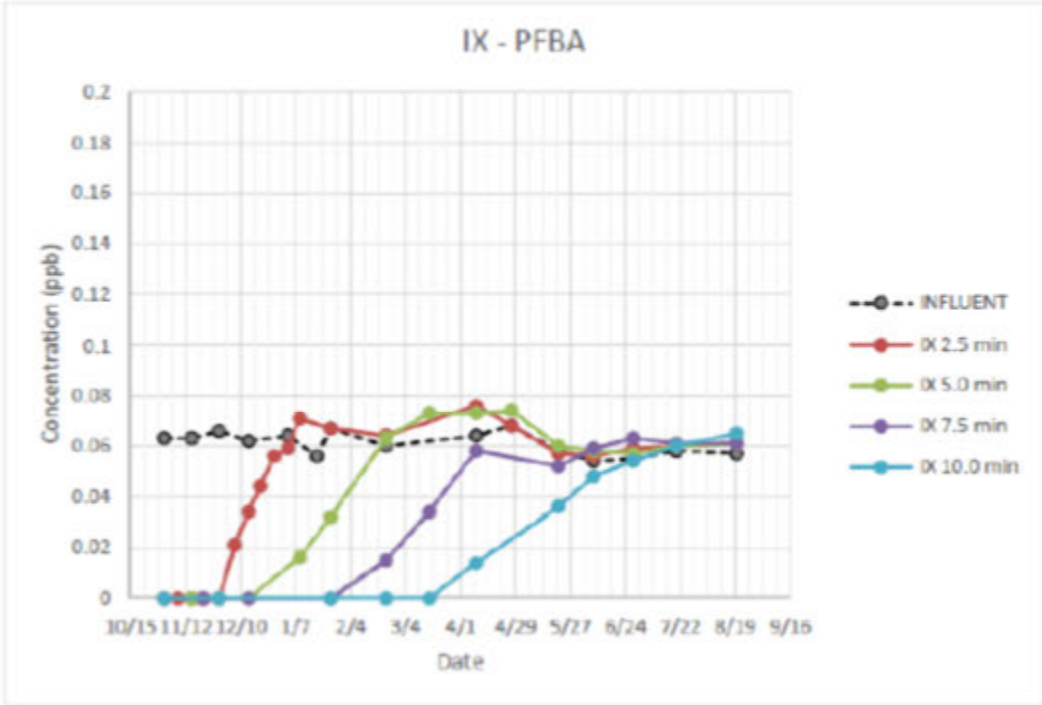
Removal comparison – Total PFAS



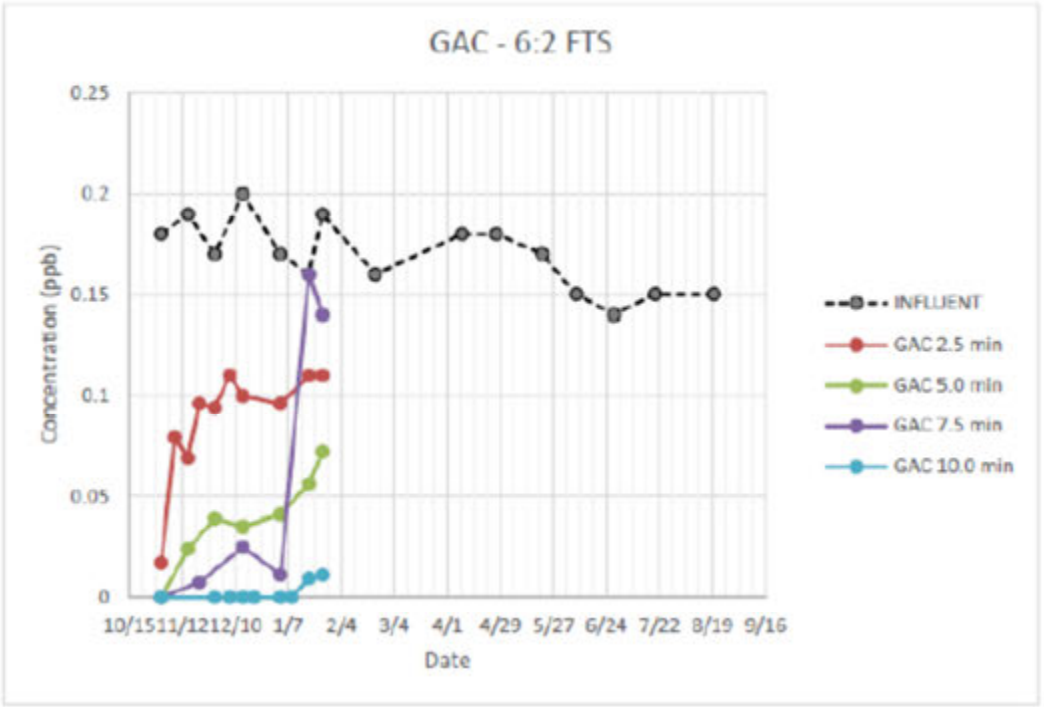


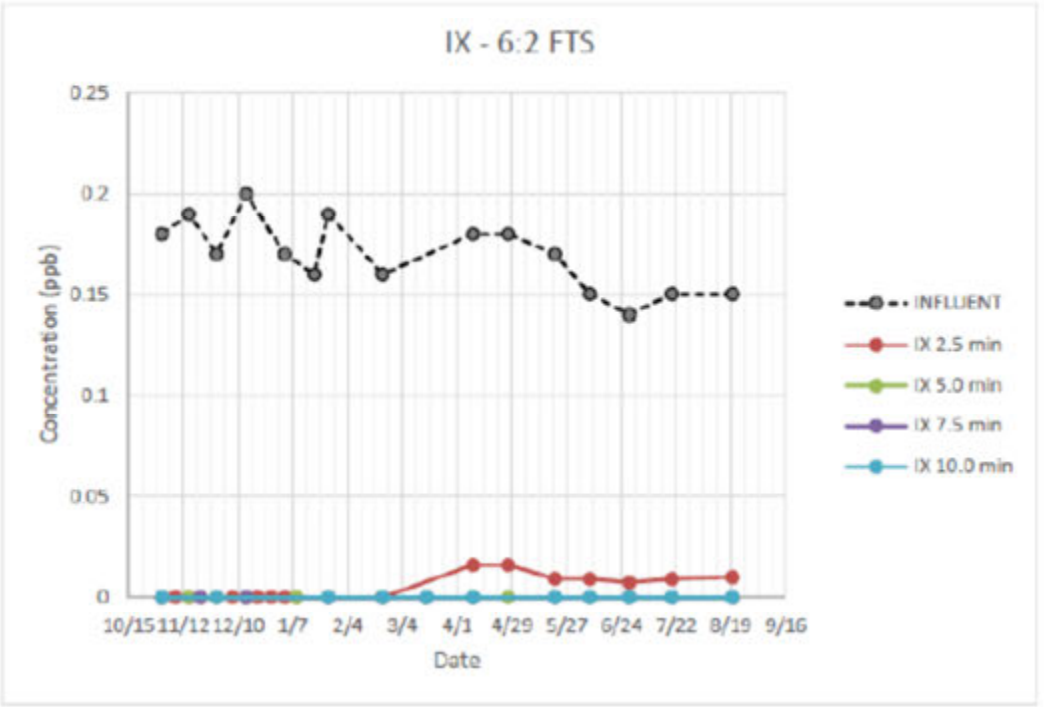
Short chain removal comparison - PFBA





Precursor removal comparison – 6:2 FTS





CASE STUDY
PFAS – FORMER FURNITURE FACILITY

ONTARIO, CANADA

BACKGROUND

Initial Driver: Hydrocarbons

- Mixed chain lengths, 100 – 5,000 µg/L

Formation

- Silty sand – till based with sand seams
- Water at 3 – 5’ below grade

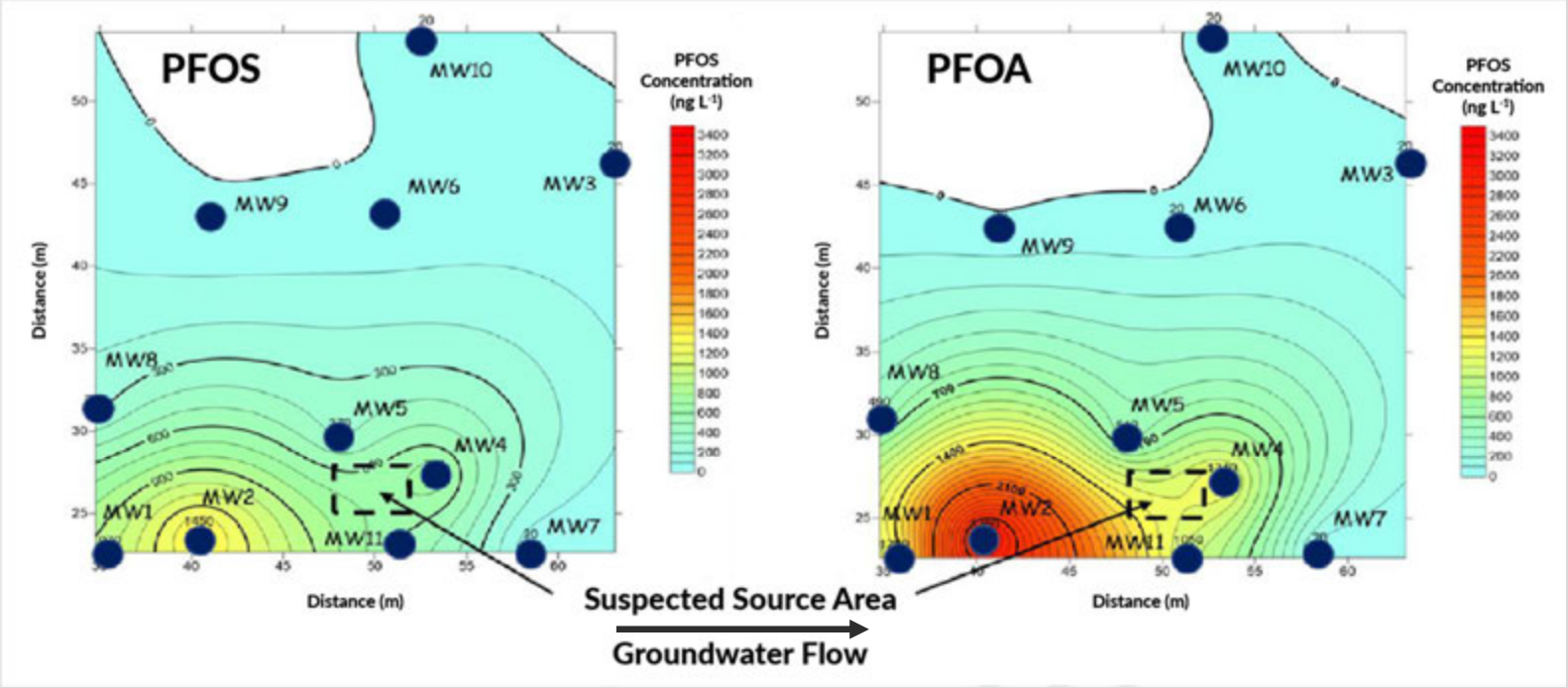
Former Fire Training Area

- History of furniture manufacturing
- PFAS tested for just in case and found!

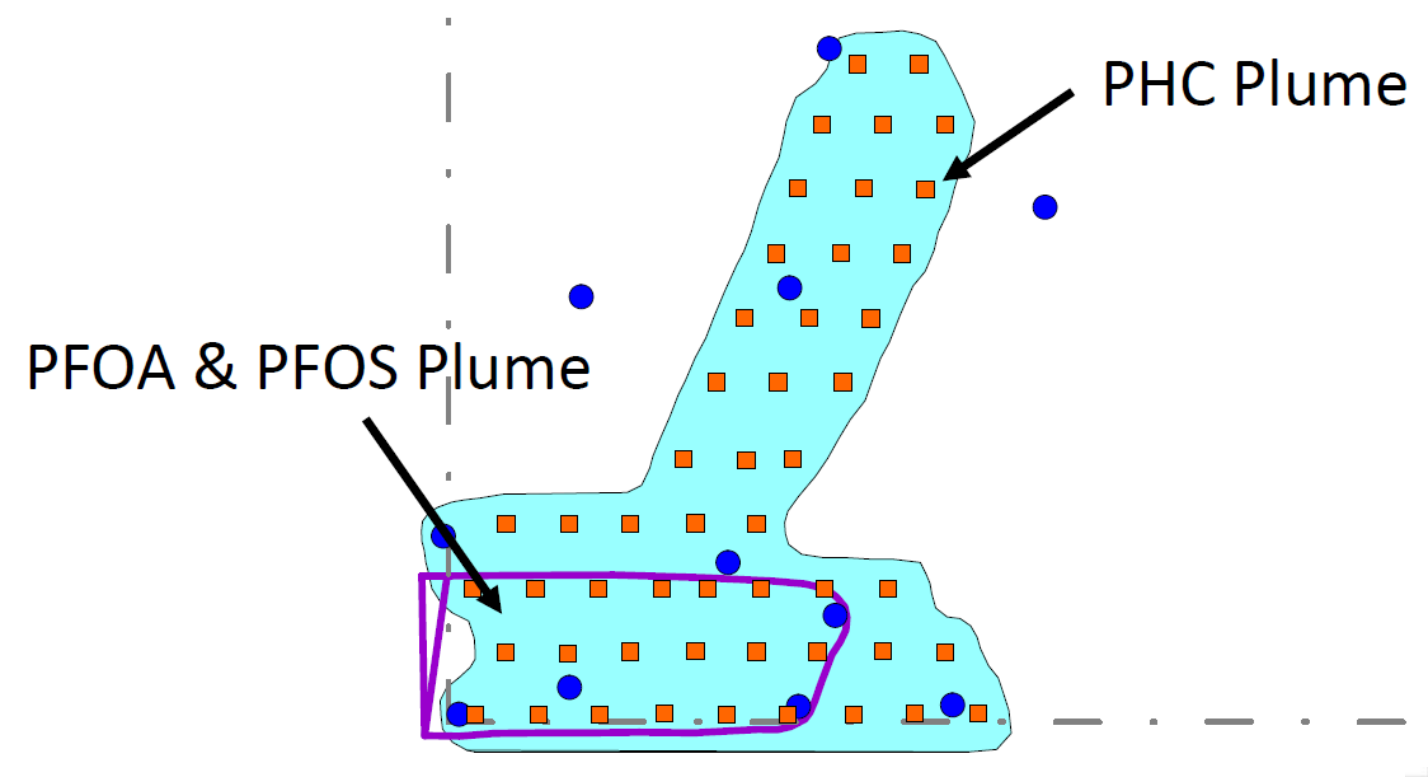
Rick McGregor

INSITU

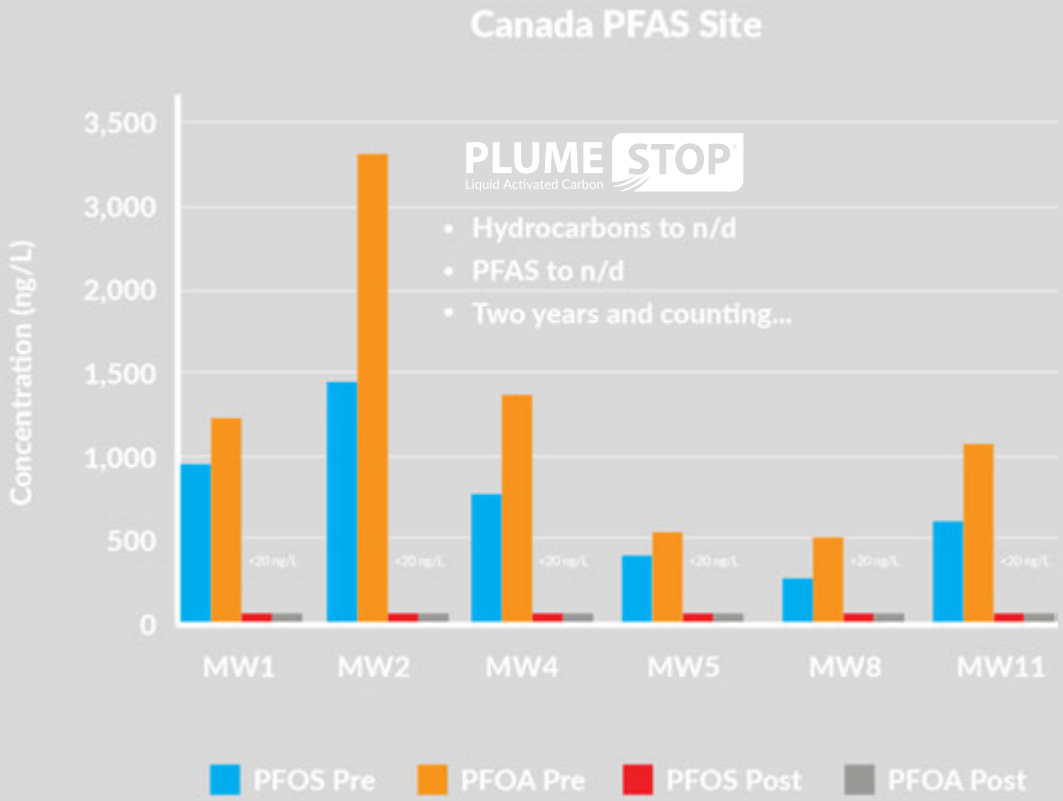
EXTENT OF PFAS AND PFOA CONTAMINATION PRE-TREATMENT



PLUME AREA DIAGRAM



PFAS FORMER FURNITURE SITE



Site Location:
Ontario, Canada

Chemical Oxidation Case Study

Remediation of Mixed Organics and PFAS Compounds with OxyZone®, a Multi-Oxidant Blend

AEHS Conference Workshop

October 16, 2018

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

www.en-chem.com

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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
- Previously proven effective for in-situ treatment of conventional contaminants

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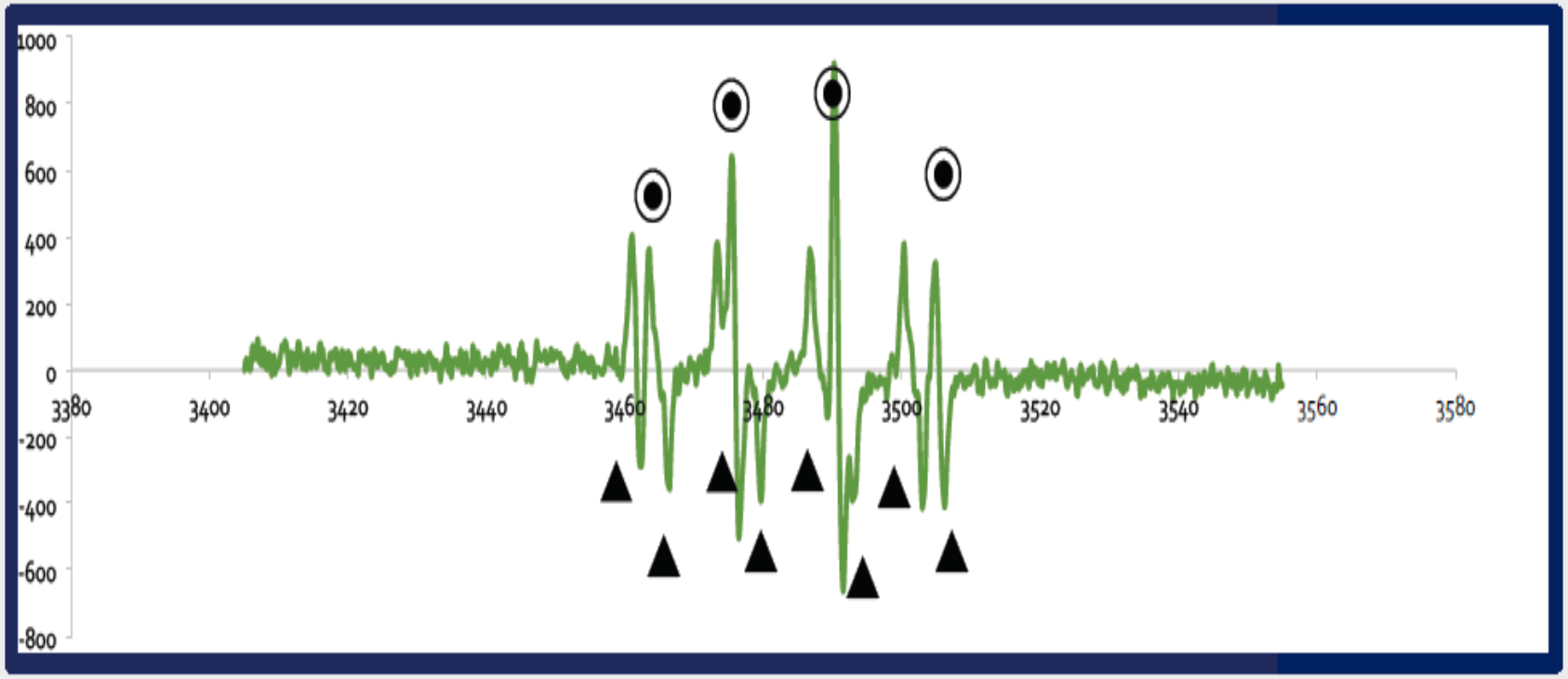

Figure 5. EPR spectra of OxyZone®- Presence of (•OH) and (•SO_4-) radicals detected. (•OH) radicals are depicted with the symbol, "◉" and (•SO_4-) radicals are depicted with the symbol, "▲".

Cashman et al, 2016

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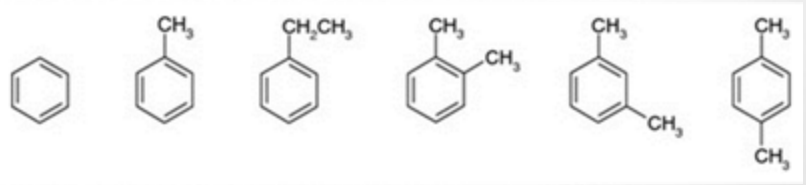
OxyZone®: Contaminants Previously Treated

- Gasoline & diesel fuel oil spills:
  - Petroleum hydrocarbons (e.g., gasoline, fuel oil – including achieving GW-1 drinking water standards)
  - BTEX, MTBE
  - Polynuclear aromatic hydrocarbons (PAH)



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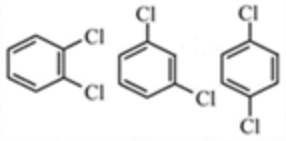
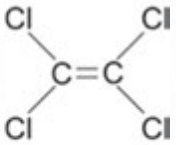
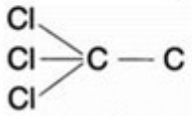
OxyZone®: Contaminants Previously Treated

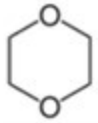
- Dry Cleaners and other chlorinated VOCs
  - Dichlorobenzenes
  - Tetrachloroethylene (PCE)
  - 1,1,1-Trichloroethane (TCA)

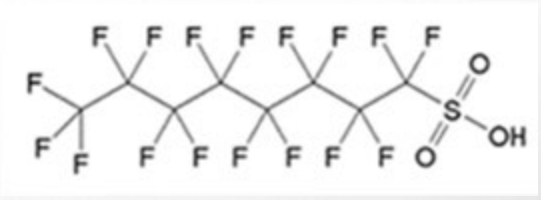






- Emerging Contaminants
  - 1,4-Dioxane
  - PFOS, PFOA and other PFAS





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Field Demonstration Test of Mixed Organics (PFAS) Remediation

Summary of 9-month Field Demonstration

- Fire Training Area (FTA) at Joint Base Langley-Eustis, Hampton, VA
- Mixed organic wastes & AFFF released to soil and GW
- OxyZone® Injection test cell of 20 feet by 30 feet
- Successful treatment of aromatic and chlorinated VOCs
- Groundwater PFAS results showed statistically significant reduction
- PFAS destruction confirmed by lab bench scale testing

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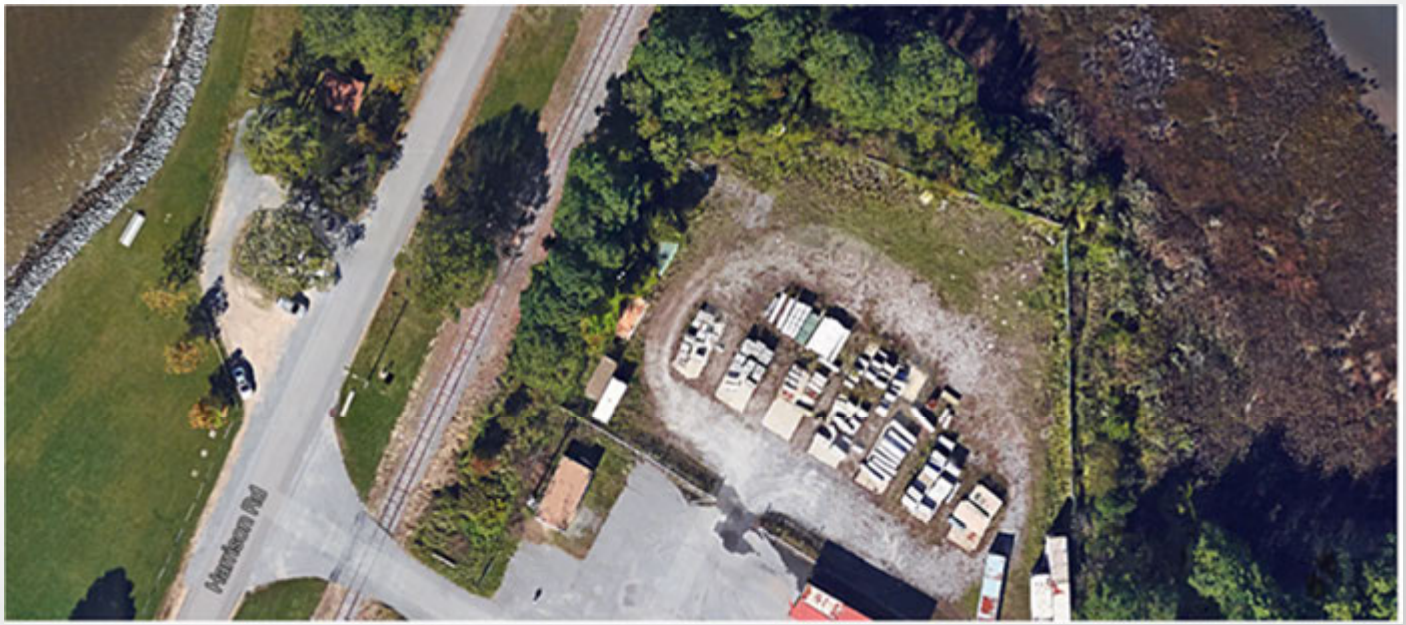
Field Demonstration – Hydrogeological conditions

- 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)



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Field Demonstration – Contamination Conditions

- 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

    * CoCs with highest concentrations

  - Total of 9 detected PFAS: 28 – 280 ug/l
  - PFOS (the dominant PFAS): 7 – 200 ug/l
  - PFOS also the dominant PFAS in soil: 1 - 150 ug/kg

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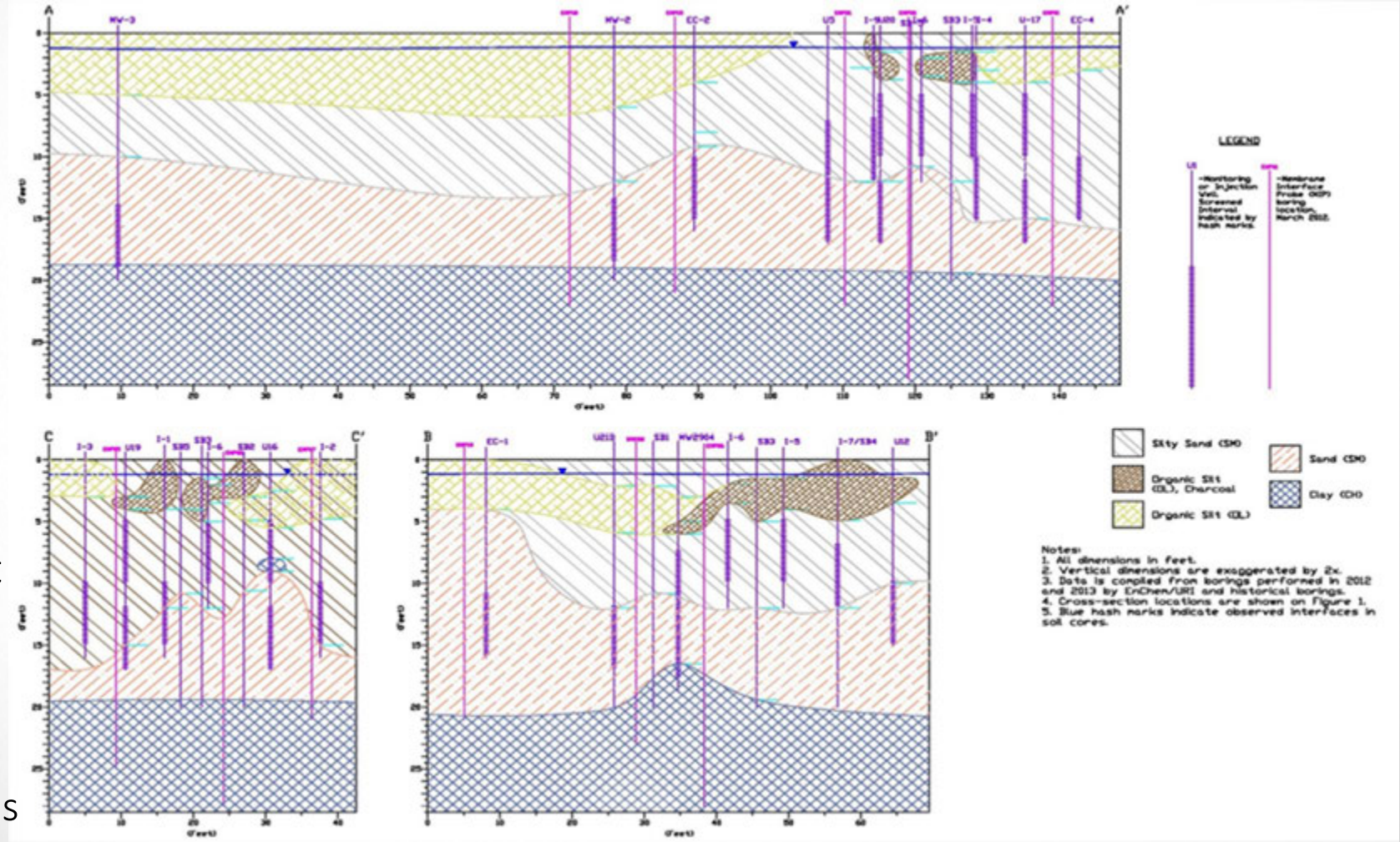
Field Demonstration

Geologic Cross-Sections

- Shallow (2-10’ bg) – silty sands and organic silt
- Intermediate (10-20’ bg) - Highly permeable poorly sorted sands



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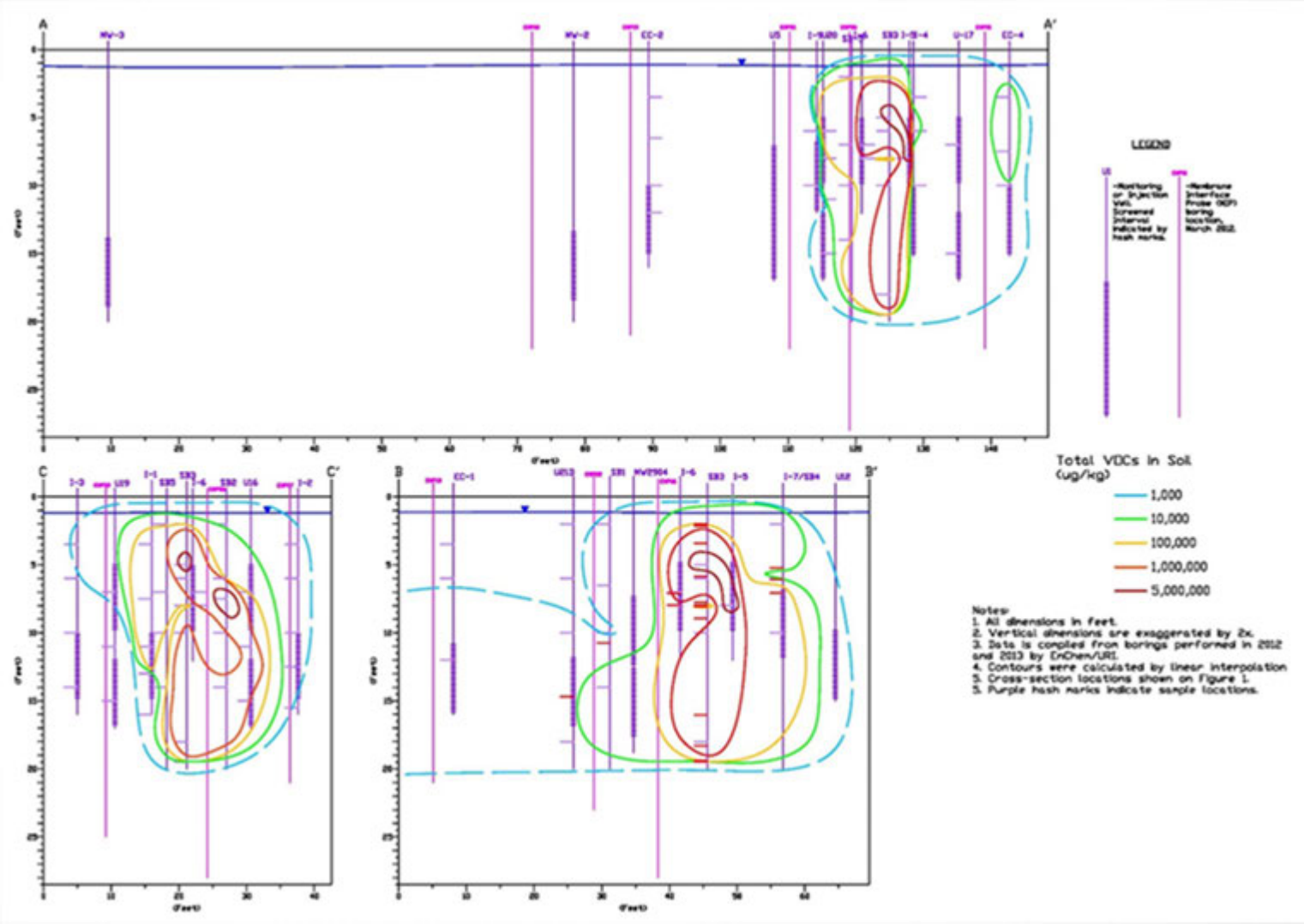
Field Demonstration – Cross Sections

Contamination Cross-Sections



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Field Demonstration

Study Approach

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

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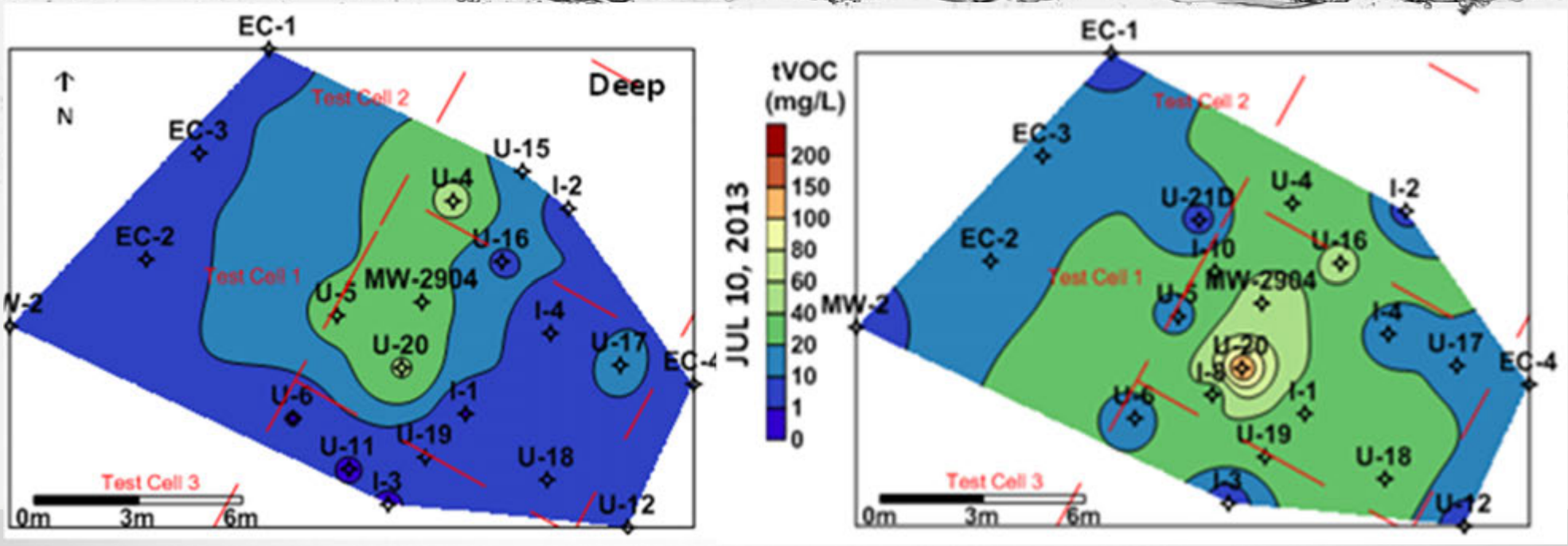
Impact of XCT® on Total VOC Concentration in Groundwater

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)

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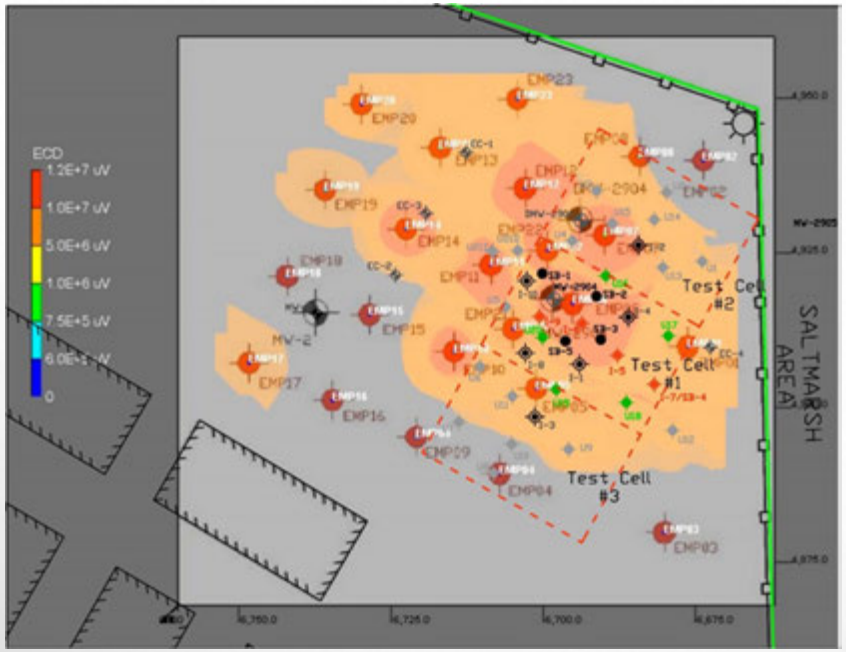
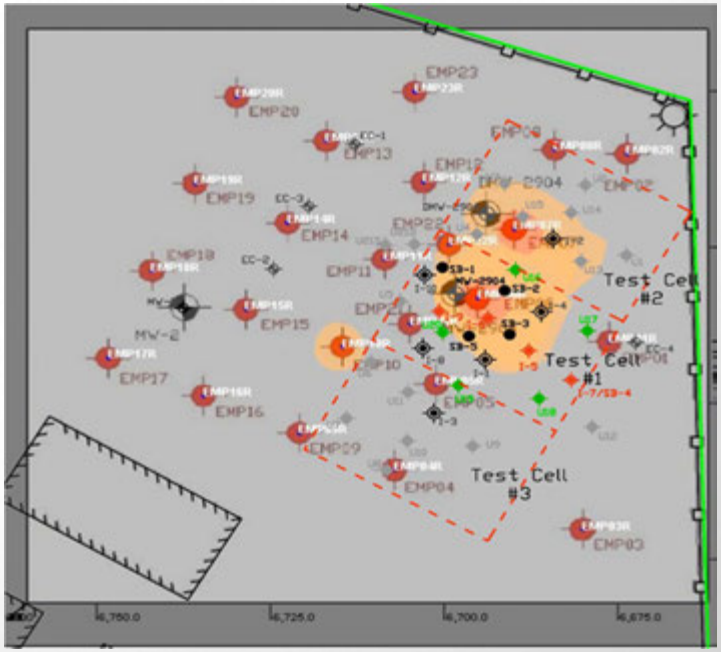
Field Demonstration Results for Chlorinated VOCs using MIPs:

- Significant overall reduction in Chlorinated VOCs
- NOTE: PFAS concentrations too low to be detected by MIPS

Pre-injection



Post-injection



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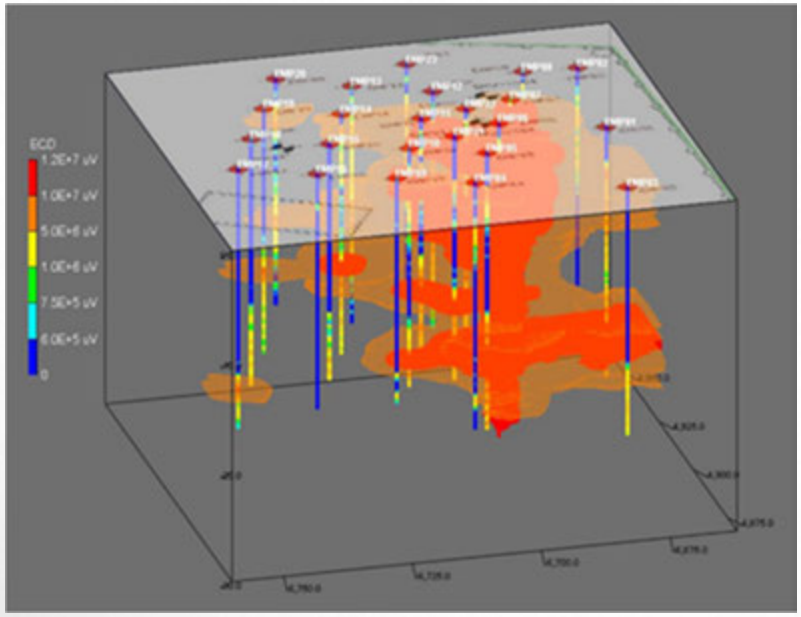
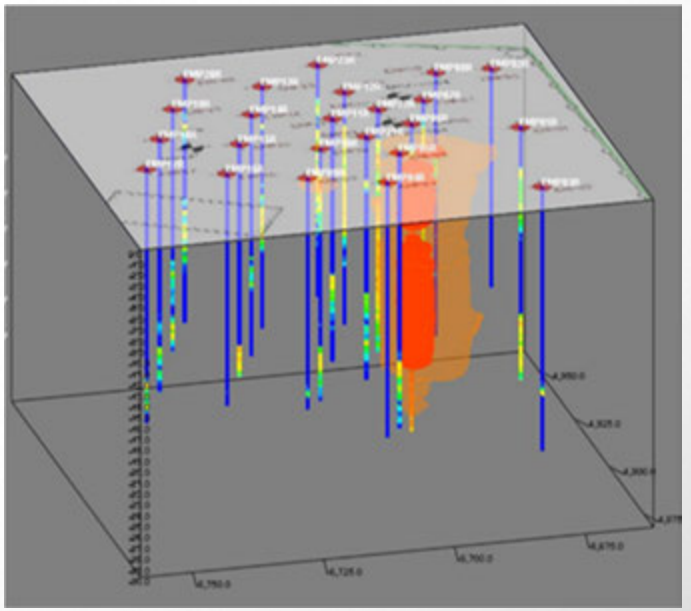
Pre-injection



Post-injection



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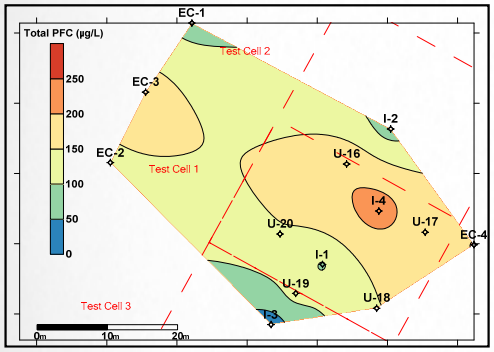
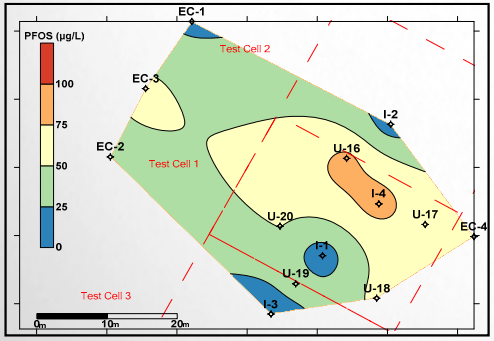
Field Demonstration Groundwater Results for PFAS

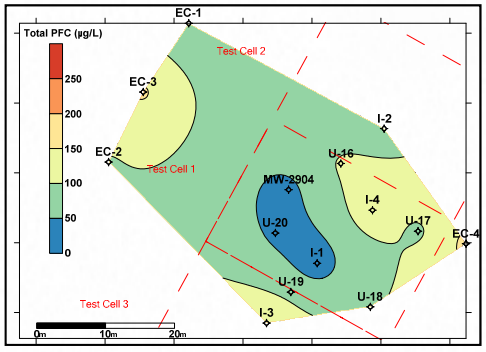
April 2013 - BEFORE

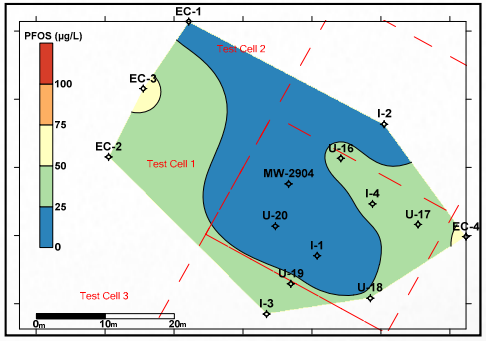




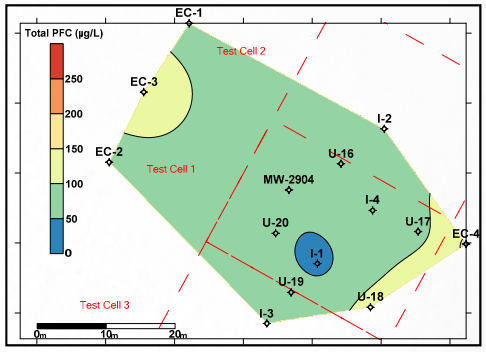
OxyZone® Injections: May & July-August 2013

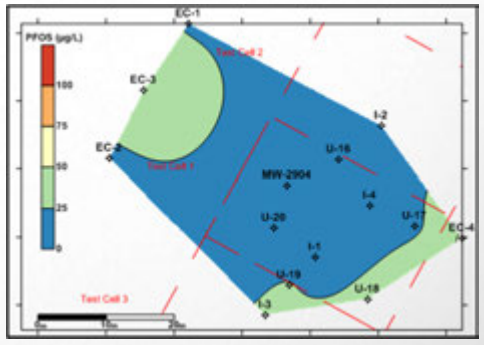
October 2013





February 2014





Total PFAS

PFOS only

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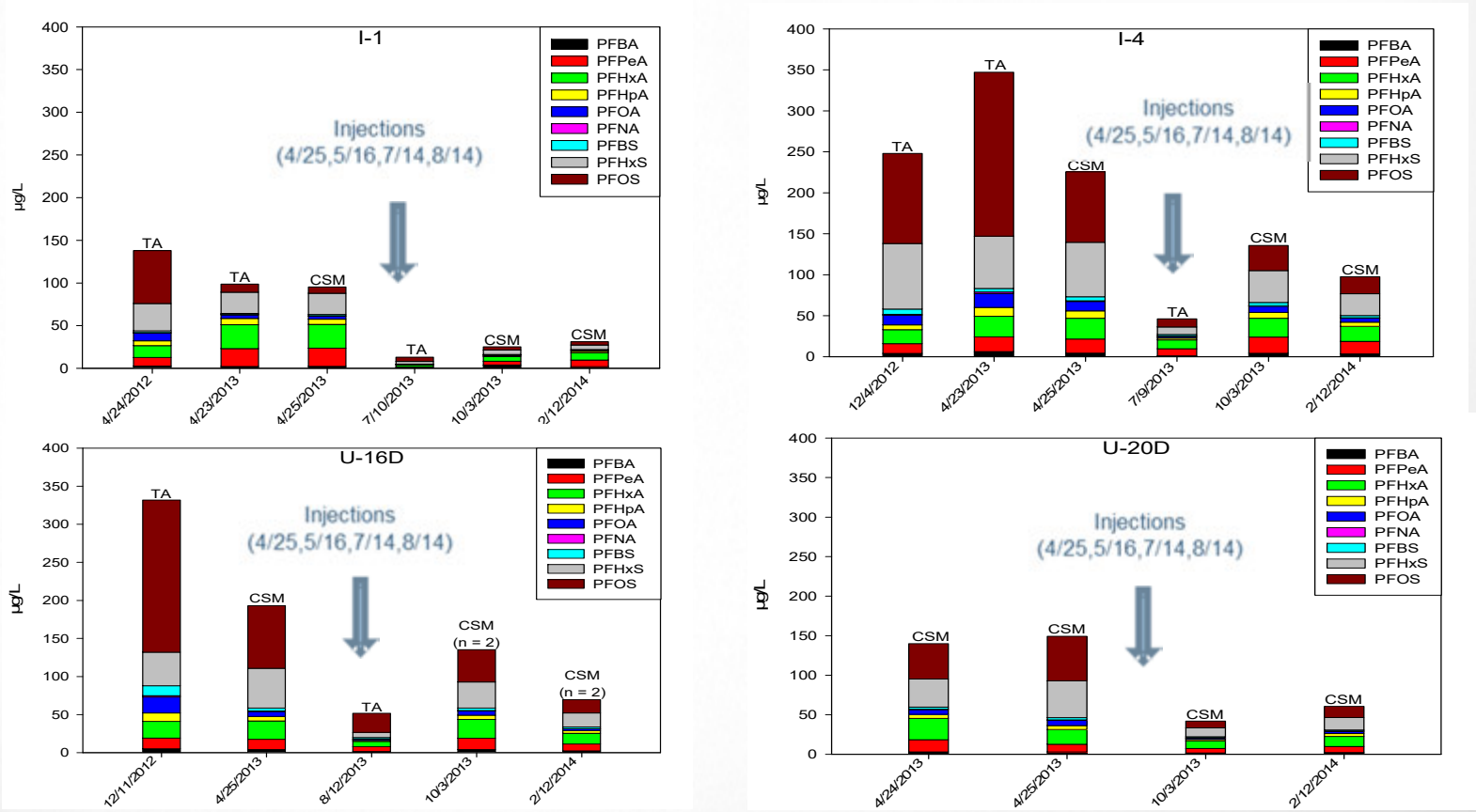
Field Demonstration Results for PFAS

Four deep groundwater wells **within** injection test cell

Showed a statistically significant (p=0.005) decrease in PFAS concentration after injections



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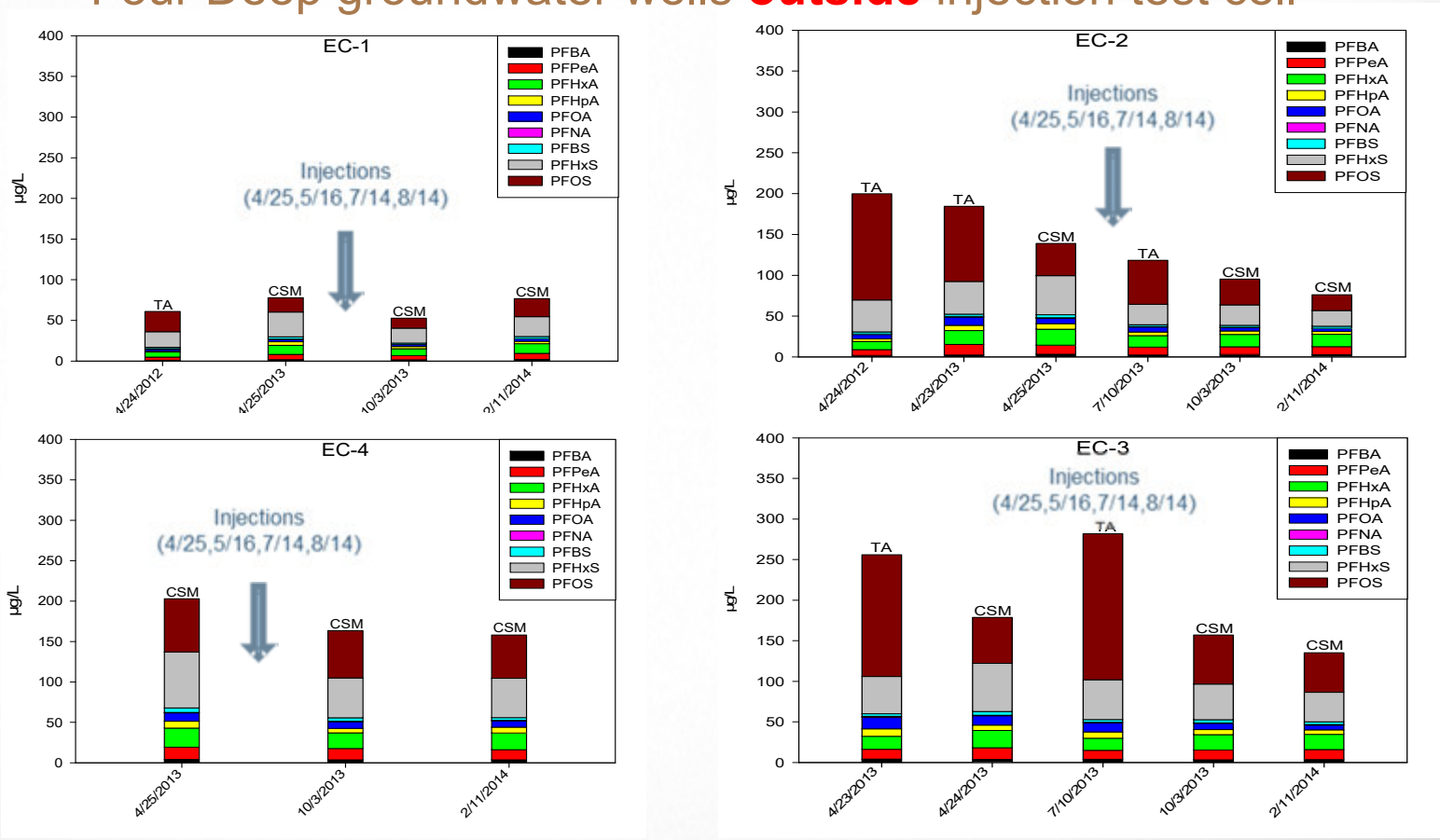
Field Demonstration Results for PFAS

Four Deep groundwater wells **outside** injection test cell

Did **not** show a statistically significant (p=0.005) decrease in PFAS concentration after injections



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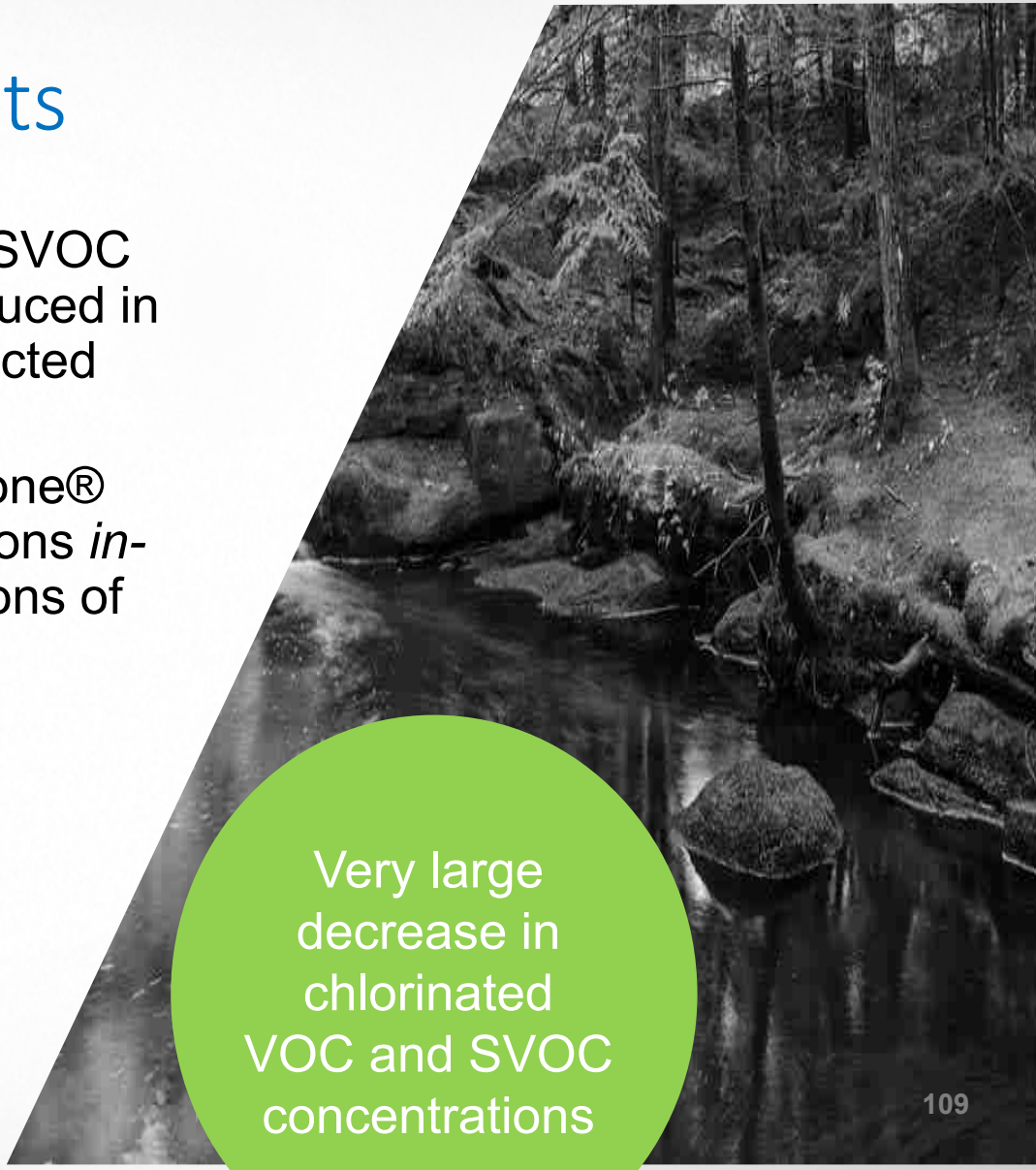
Field Demonstration Results

- Based on MIPs data, overall VOC and SVOC contaminant mass was significantly reduced in the Test Cell where OxyZone® was injected
- Statistical analysis indicated that OxyZone® successfully reduced PFAS concentrations *in-situ* in the presence of high concentrations of other organic contaminants
- Groundwater concentrations of the conservative tracer chloride showed no (dilution) impact from fluid injections



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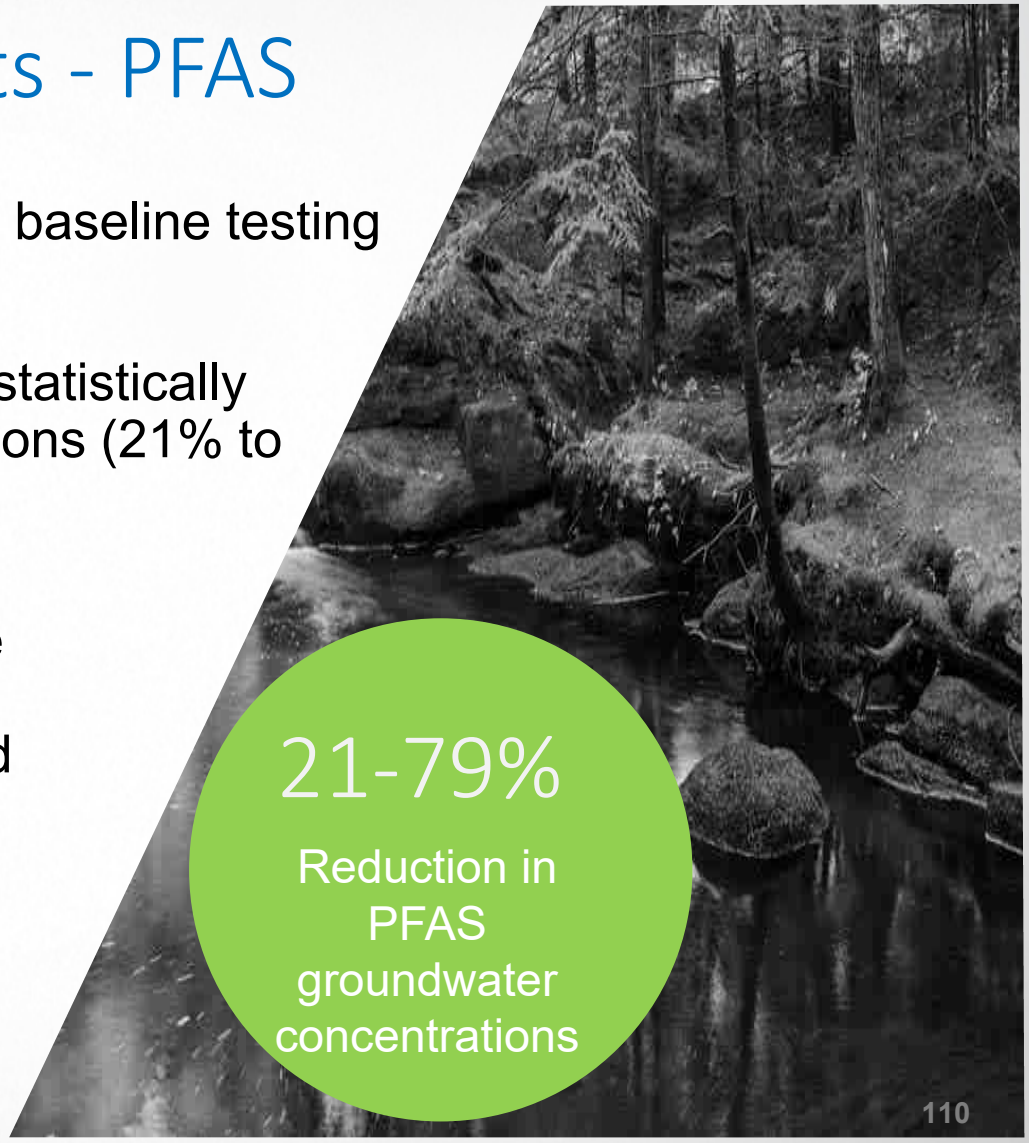
Field Demonstration Results - PFAS

- 9 different PFAS were discovered during baseline testing
- Groundwater data analysis supported a statistically significant reduction in PFAS concentrations (21% to 79%) in groundwater
- Statistical comparison of wells within the Test Cell to those outside the Test Cell showed PFAS concentrations decreased within the Test Cell and not outside



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In-House Bench Scale Treatability Testing on Spiked Deionized water

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

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In-House Bench Scale Treatability Testing on Groundwater (from Virginia FTA site)

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

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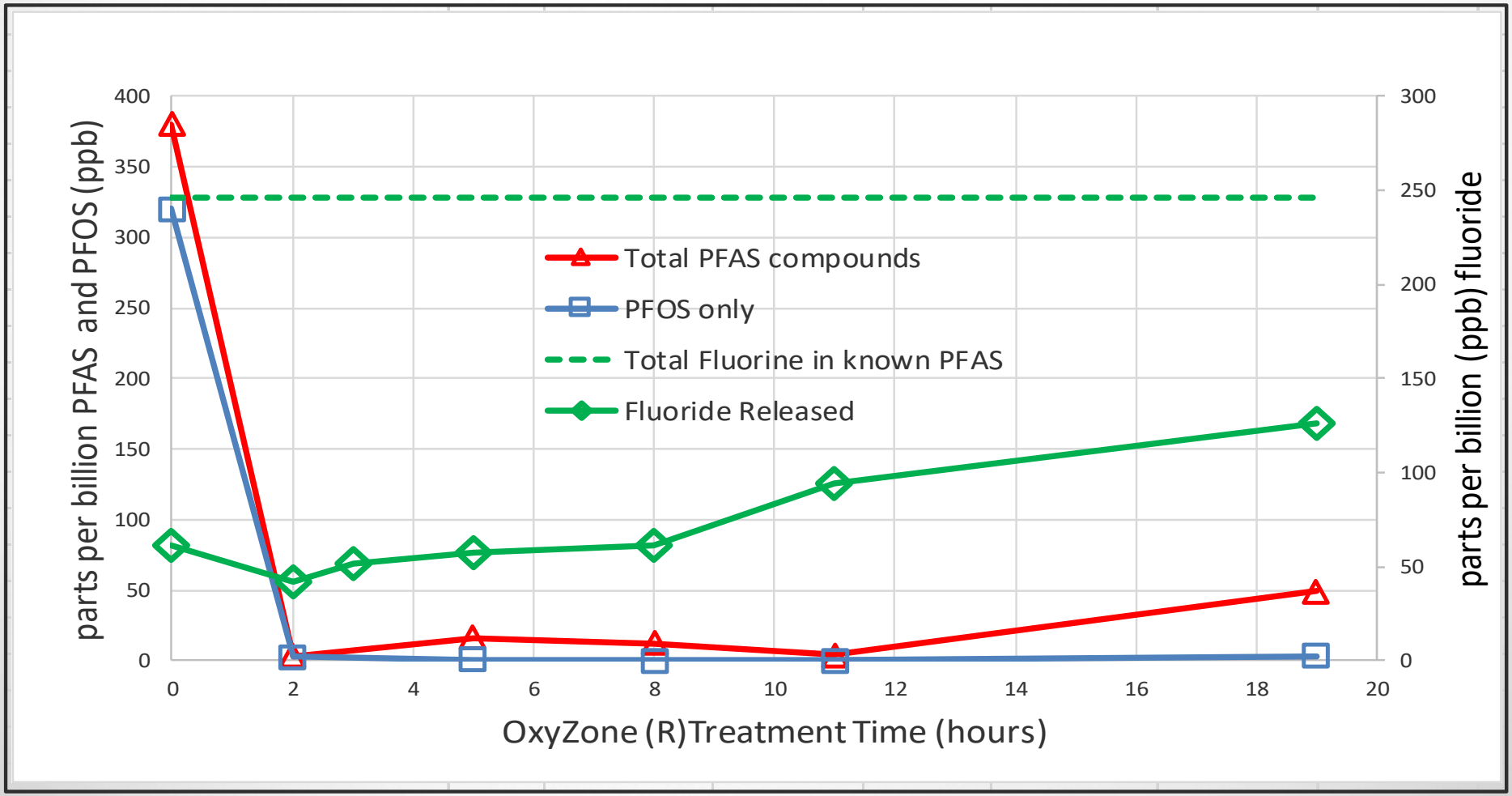
In-House Bench Scale Lab Results

Actual AFFF Site Contaminated Groundwater - 39% of known organofluorine released as fluoride



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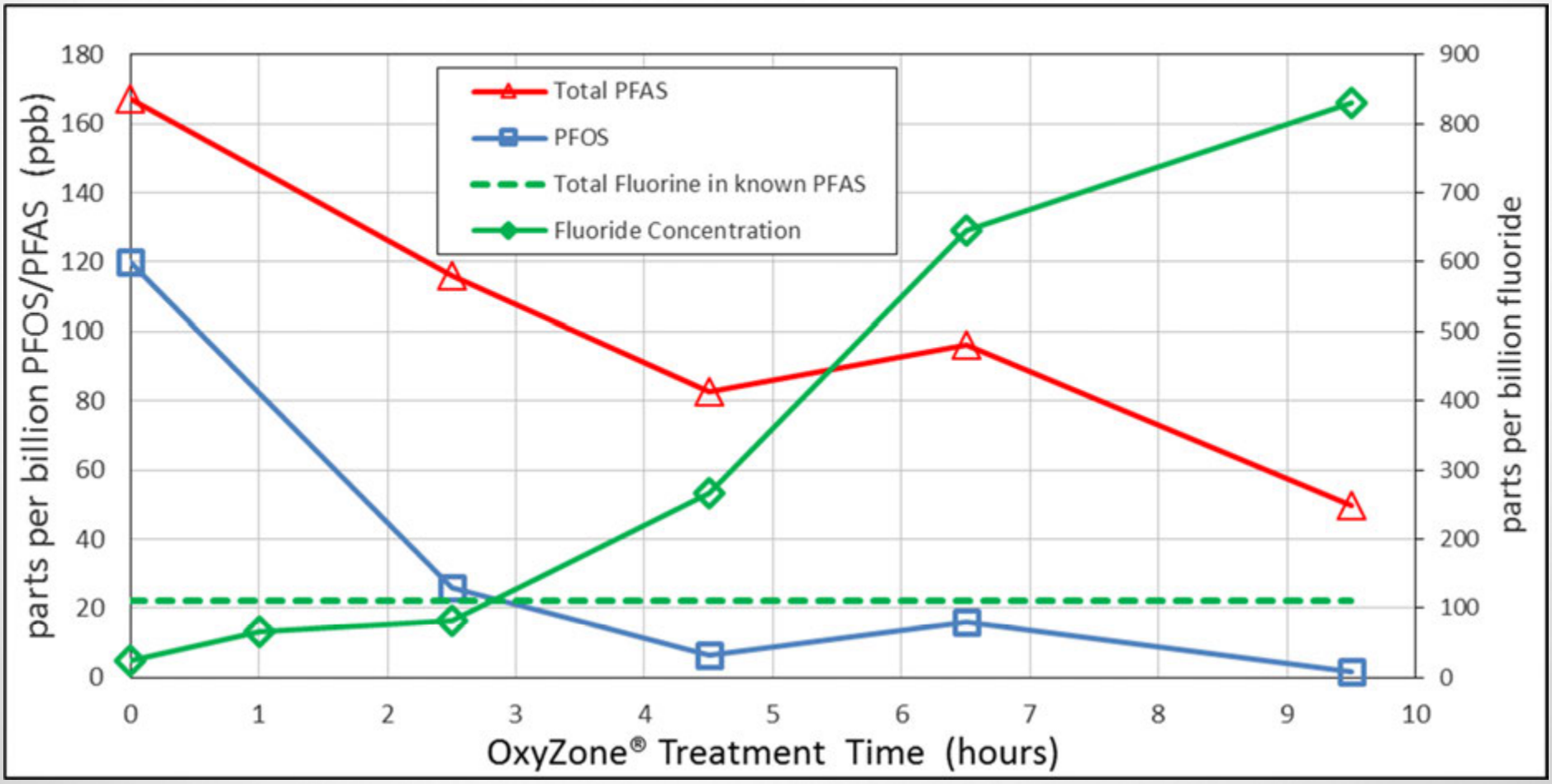
In-House Bench Scale Lab Results

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



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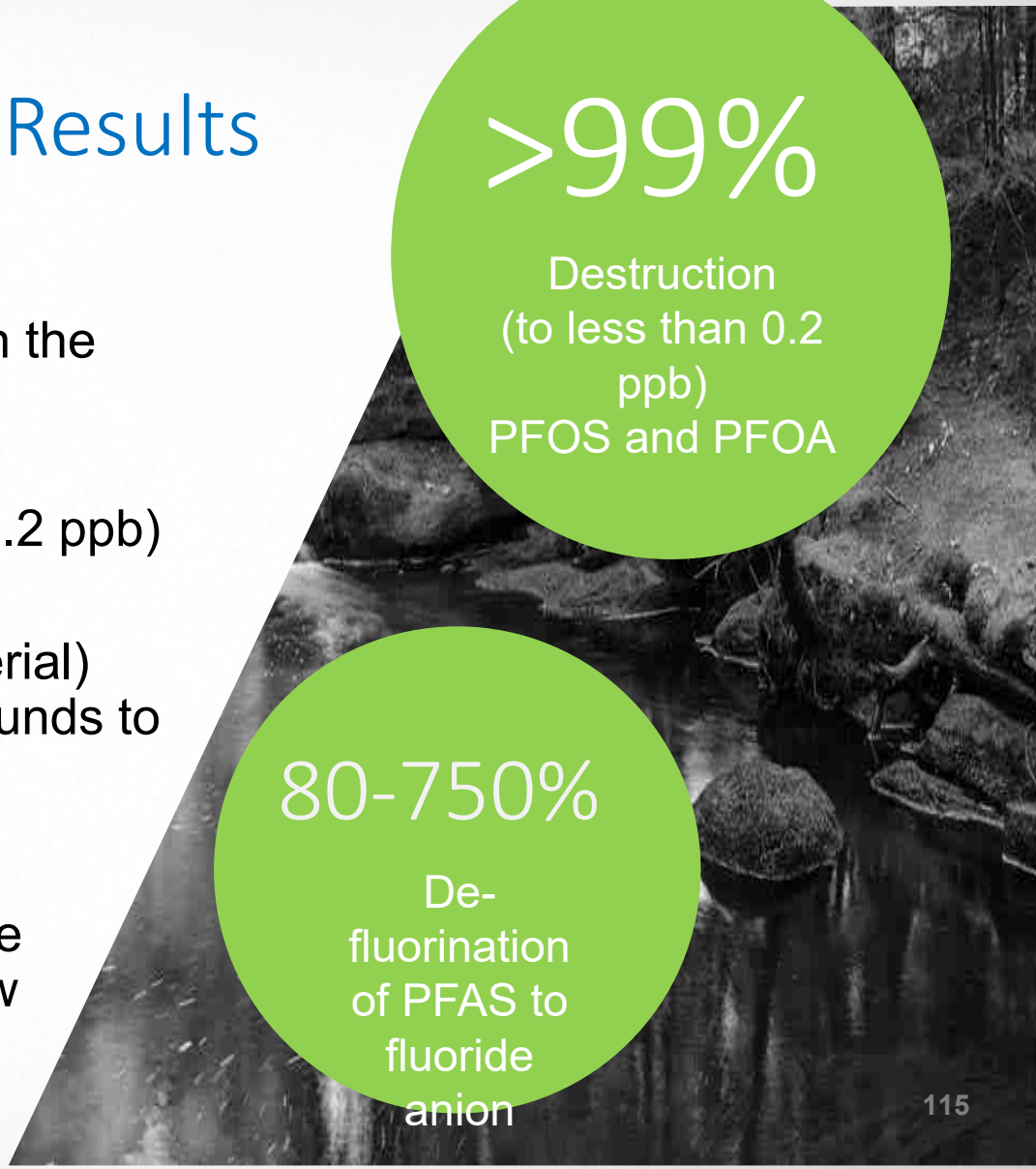
Case Study – Summary of Results

In-House 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% (depending on starting material) defluorination of organofluorine compounds to fluoride anion

Conclusion

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



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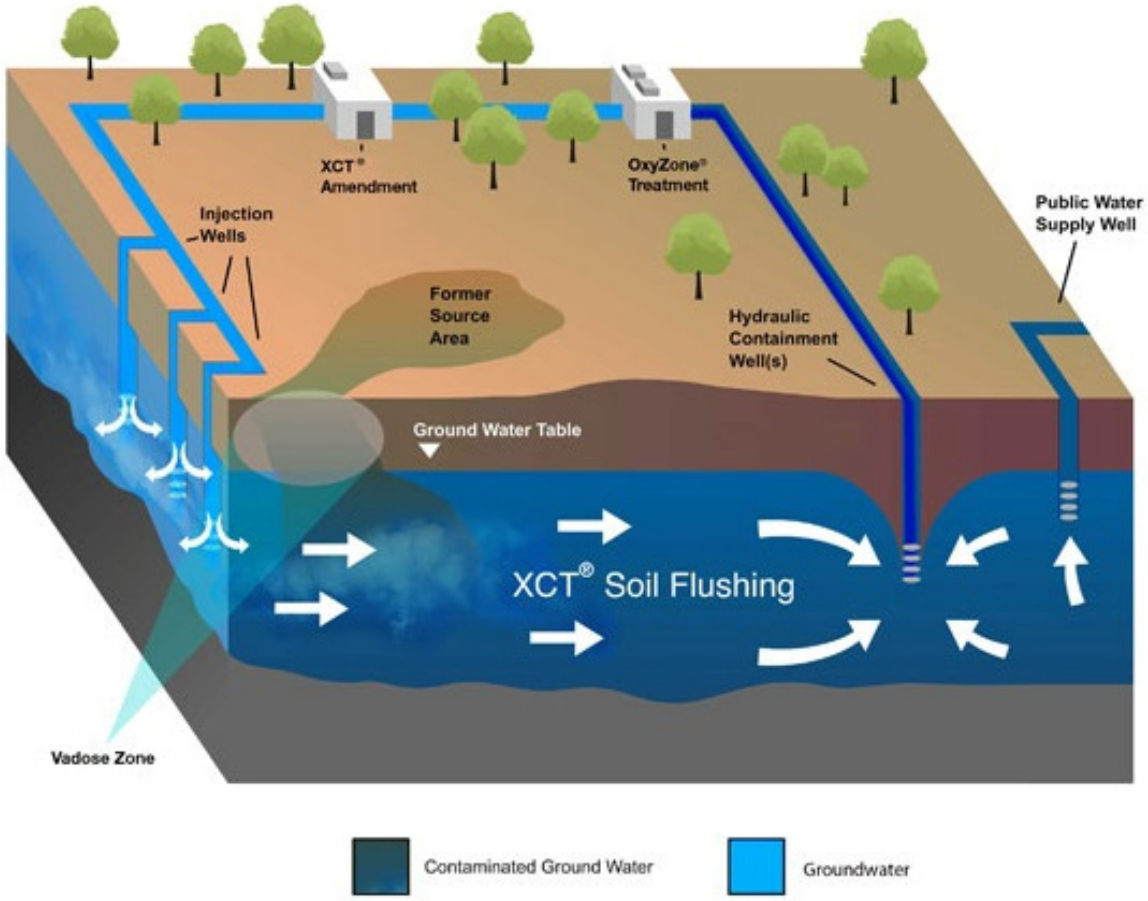
XCT® and OxyZone® Process Combined Remedy

- In-Situ Source Treatment & Contaminant Mass Removal
- In-Situ Reactive Zones
- Migration Control at a Property Boundary
- Above-ground Treatment & Reinjection
- Drinking Water Well Protection



XCT® Combined In-Situ & Ex-Situ Treatment

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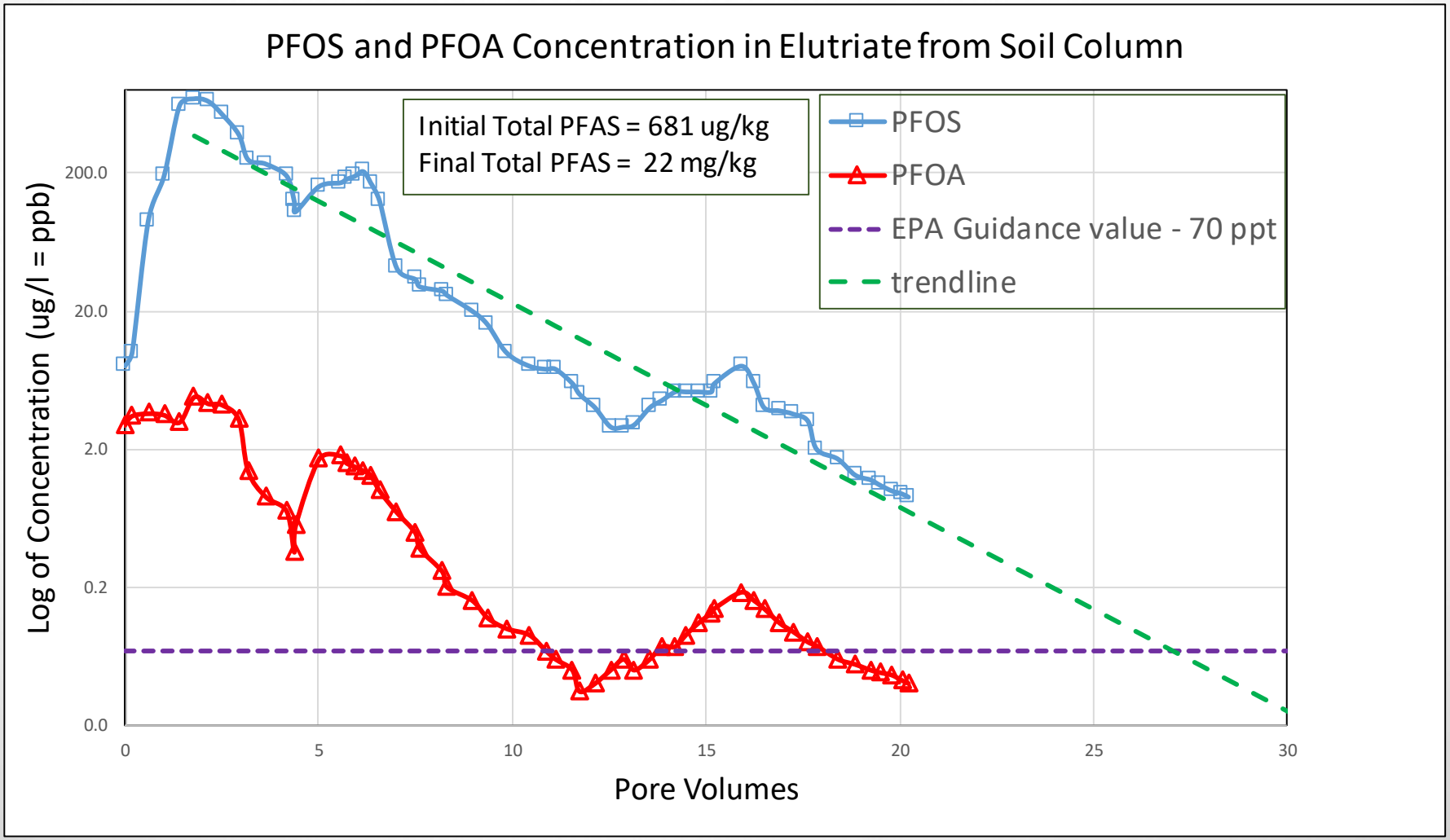
In-House Bench Scale Lab Results

XCT® Soil Flushing of PFAS



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Summary

- **XCT® and OxyZone® Extend the Capture, Removal and Destruction of PFAS Beyond What is Currently Possible with Other Existing Technologies**

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Question 5

What can be answered from treatability testing?

- ❑ Material loading
- ❑ Failure mechanisms
- ❑ Ability to meet remedial goals
- ❑ Unintended consequences (metals mobilization)
- ❑ Regulatory acceptance
- ❑ The question that has plagued philosophers since the dawn of time: Is a hot dog a sandwich?

ONGOING RESEARCH: PFAS

ALPHA ANALYTICAL, INC

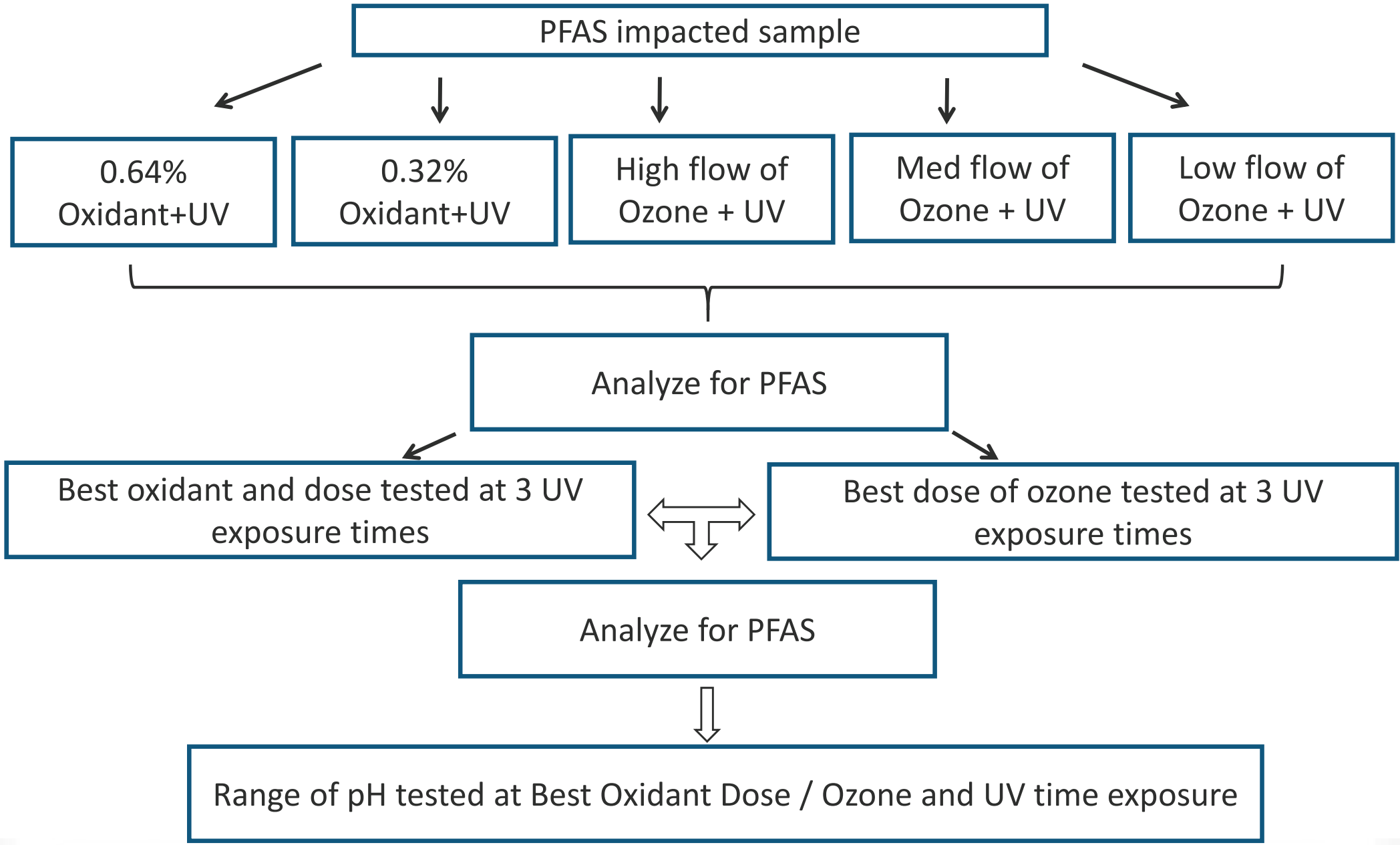
GHD

TestAmerica

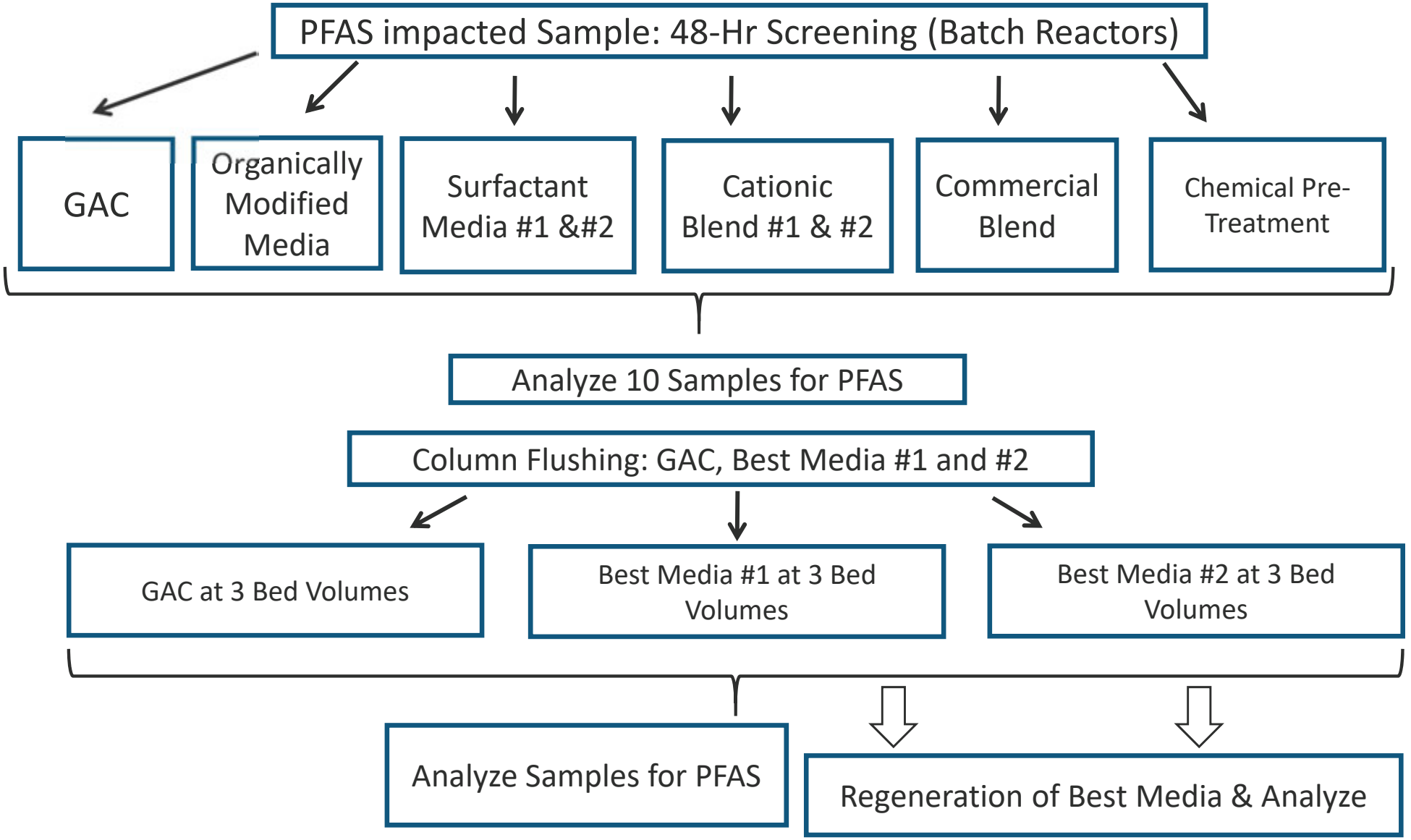
THE LEADER IN ENVIRONMENTAL TESTING

XDD ENVIRONMENTAL

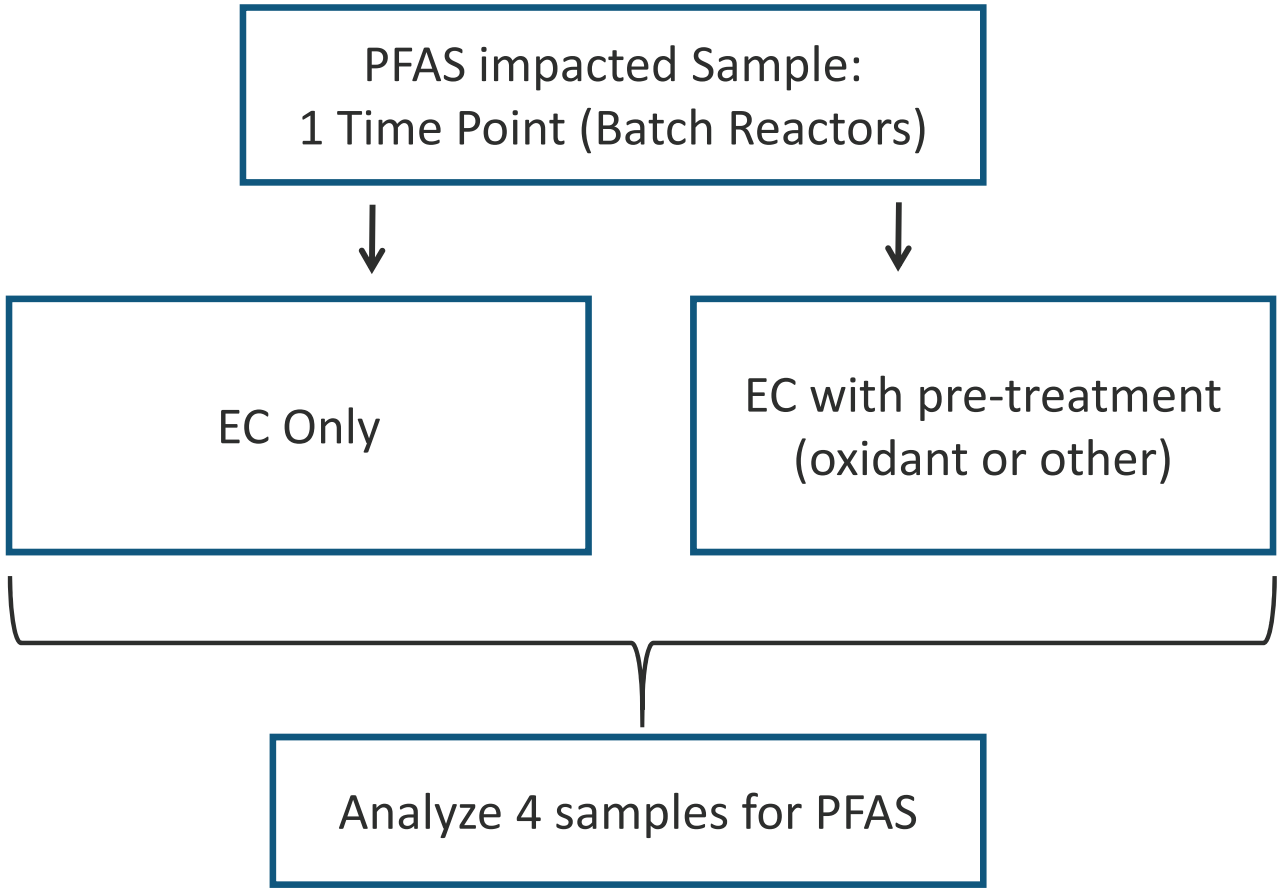
UV/Oxidant Studies



Adsorption / Ion Exchange Studies



Destruction (Electrochemical [EC]) Studies



Last Thoughts

- PFAS on most people's radar screen 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
  - 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 for PFAS
  - Filtration (Nano-filtration, reverse osmosis)
  - Separation / pretreatment
  - Adsorbents
  - Ion exchange / adsorption resins
  - Redox manipulation

- Treatability studies should be considered:
  - Select the best technology(s)
    - Function of PFAS concentrations
  - Optimize remediation design
  - Minimize the risk of unintended consequences

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)