

Colloidal Activated Carbon for In Situ Remediation of PFAS: A Review of Multiple Case Studies

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AND GROUNDWATER REMEDIATION

NEWMOA
May 18, 2021

Maureen Dooley, Director of Strategic Projects

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OVERVIEW

- The PFAS Challenge
- Description In Situ Treatment Using Colloidal Carbon
- Case Studies
- Questions and Answers



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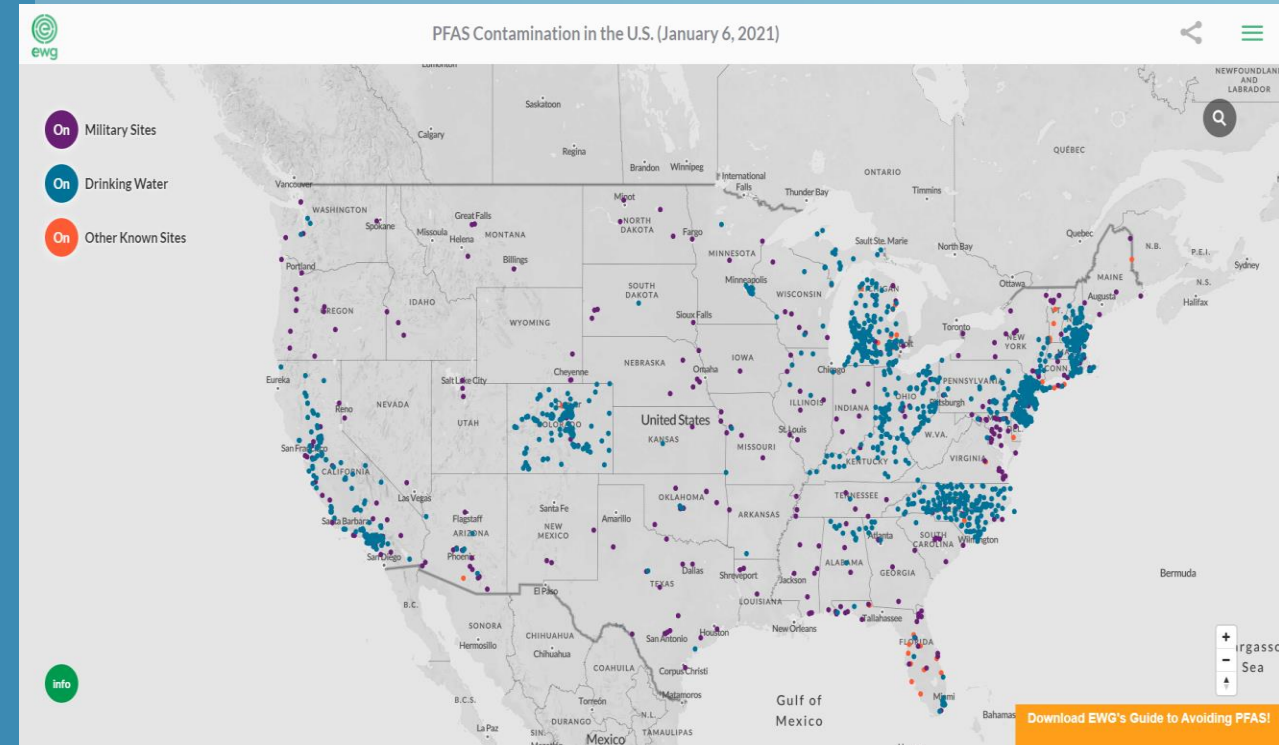
PFAS: The Challenge



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- Regulatory Pressure
 - PFAS Action Act H.R. 535 (2020)
 - Designates PFAS as a hazardous substance under CERCLA
 - Calls to eliminate the unsafe incineration of PFAS-Laden waste
 - Many states have adopted or are in the process of adopting PFAS standards





PFAS Treatment Obstacles

- **Non-Technical:**
 - Prioritization – where do we start?
 - Public awareness & sensitivity
 - Are closed sites closed?
- **Technical:**
 - 5,000+ compounds!
 - Toxicological understanding
 - Commingled plumes/co-contaminants
 - Resistance to conventional treatment
 - Parts per trillion criteria

PFAS: The Challenge

- Pump and Treat
 - Mass Reduction Technology
 - Large Infrastructure Required
 - Continued O&M
 - Decades of Operation
 - Waste Stream
 - Concerns over disposal of PFAS laden carbon\resins from P&T systems



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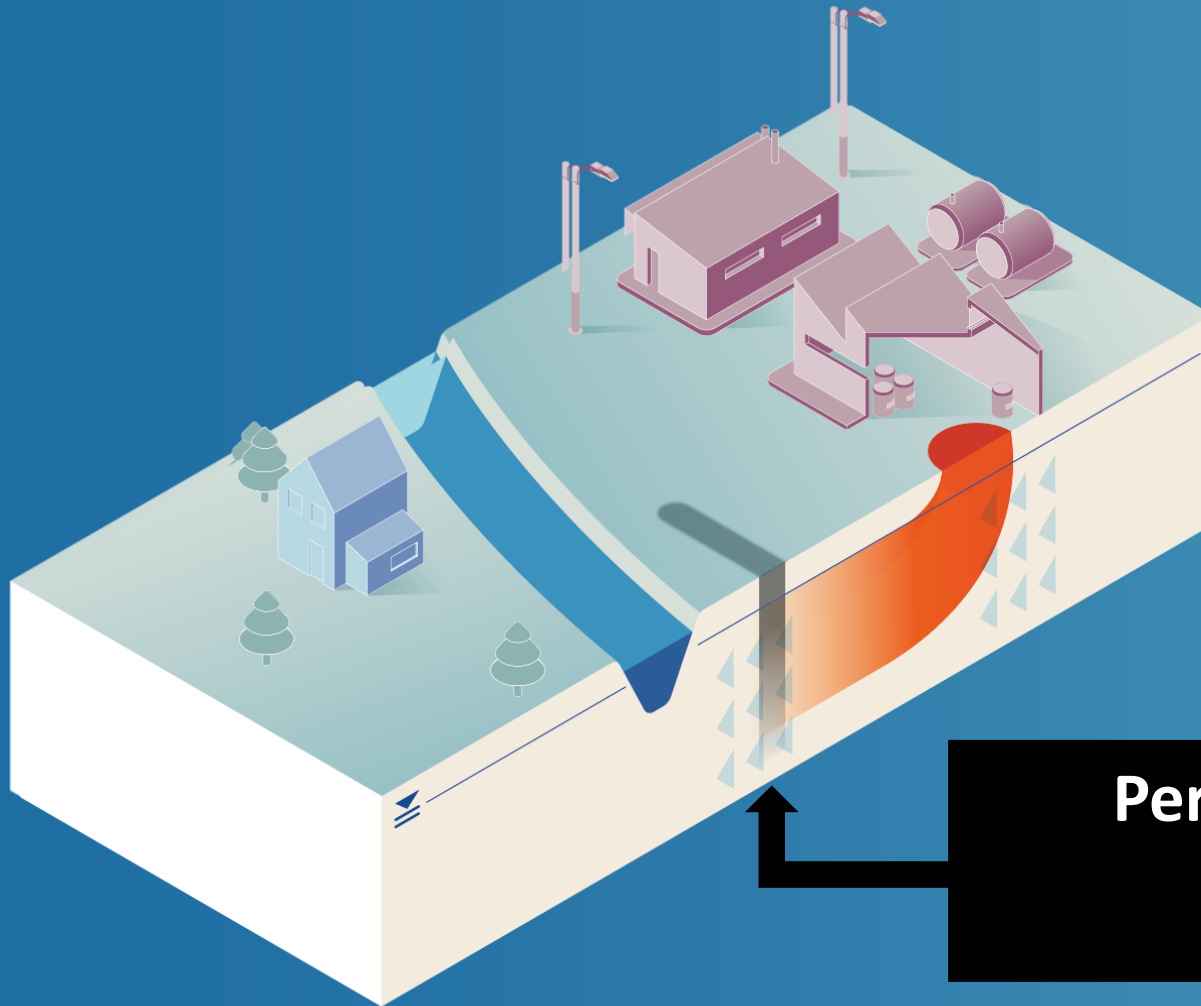


PFAS-In Situ Remediation

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- No infrastructure required
- No equipment O&M
- Passive management
- Zero waste stream
- Achieves low standards (ppt)
- Decades of treatment
- Cost Effective
- Compatibility Future Technologies



Permeable Reactive Barrier

PlumeStop: Colloidal Activated Carbon (CAC)

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- Size: 1 – 2 μm
 - 2-3 OOM smaller than GAC (500-1,000 μm)
 - Size of a red blood cell
 - Suspended as a colloid in water/polymer
 - Distributes widely at low pressure
 - Extremely fast sorption
 - Converts polluted aquifer into purifying filter

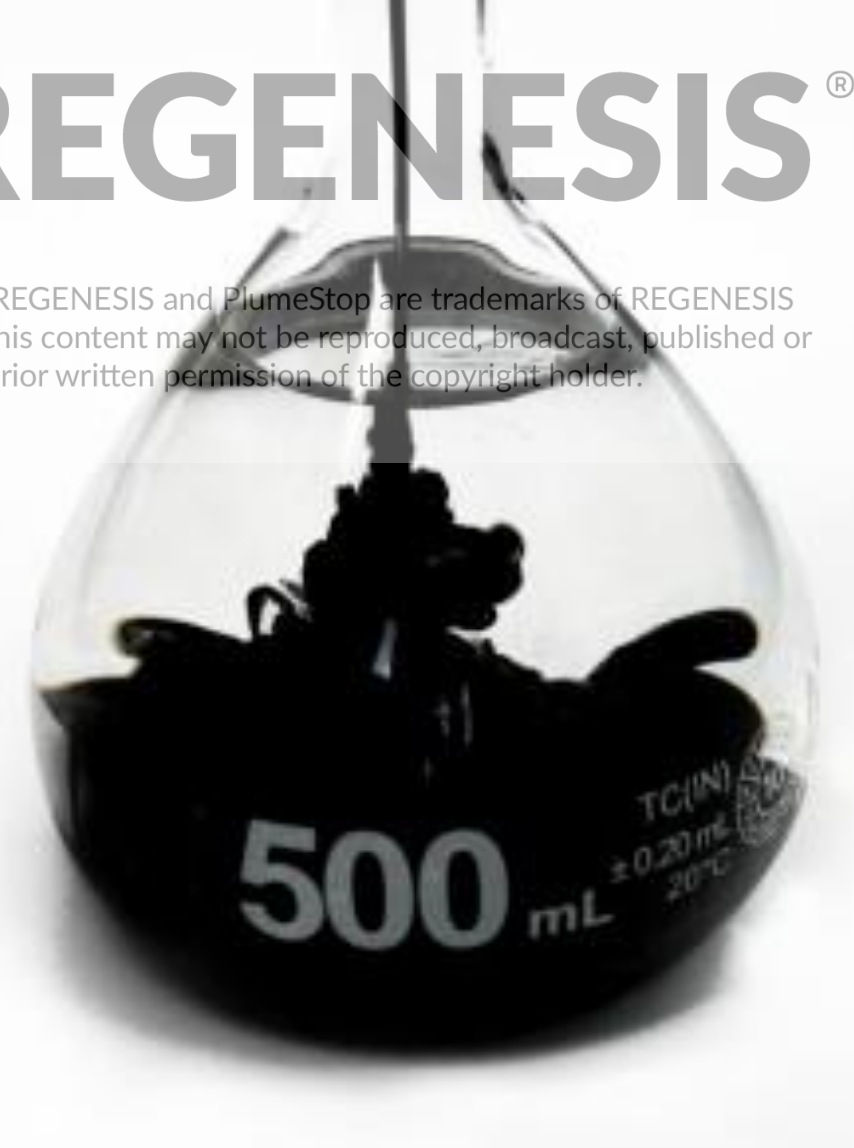


PlumeStop: How it Works

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- Activated carbon coats aquifer matrix
- Provides extremely fast sorption sites
- Converts underlying geology into purifying filter
 - As the plume migrates, contaminants are sorbed and groundwater passes through



PLUME STOP[™]
Liquid Activated Carbon



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SEM Image of Sand Particles Pre-PlumeStop Application

Acc V Spot Magn Det WD |-----| 50 µm
10.0 kV 3.0 500x GSE 10.0 3.7 Torr KT5-1051 - SAND



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SEM Image of Sand Particles Post-PlumeStop Application

Acc.V Spot Magn
12.0 kV 3.0 1500x

Det WD
GSE 7.8

3.7 Torr KT5-105B

20 µm



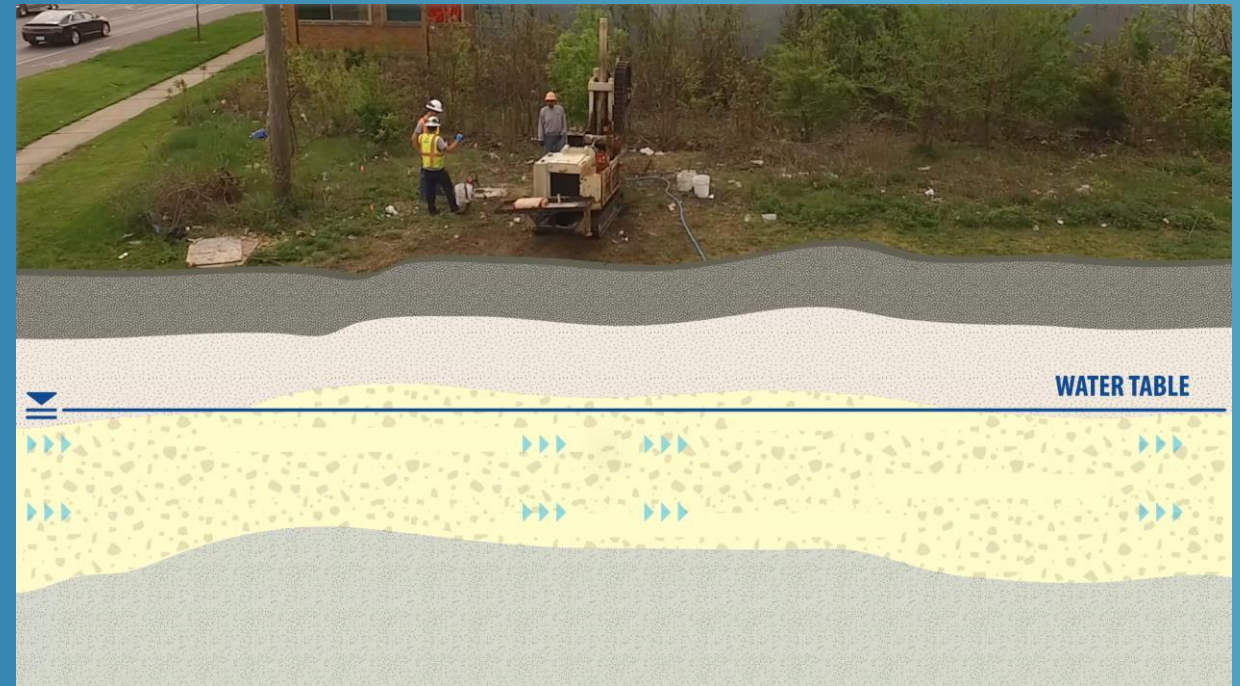
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Colloidal Carbon Converts Aquifer into Purifying Filter

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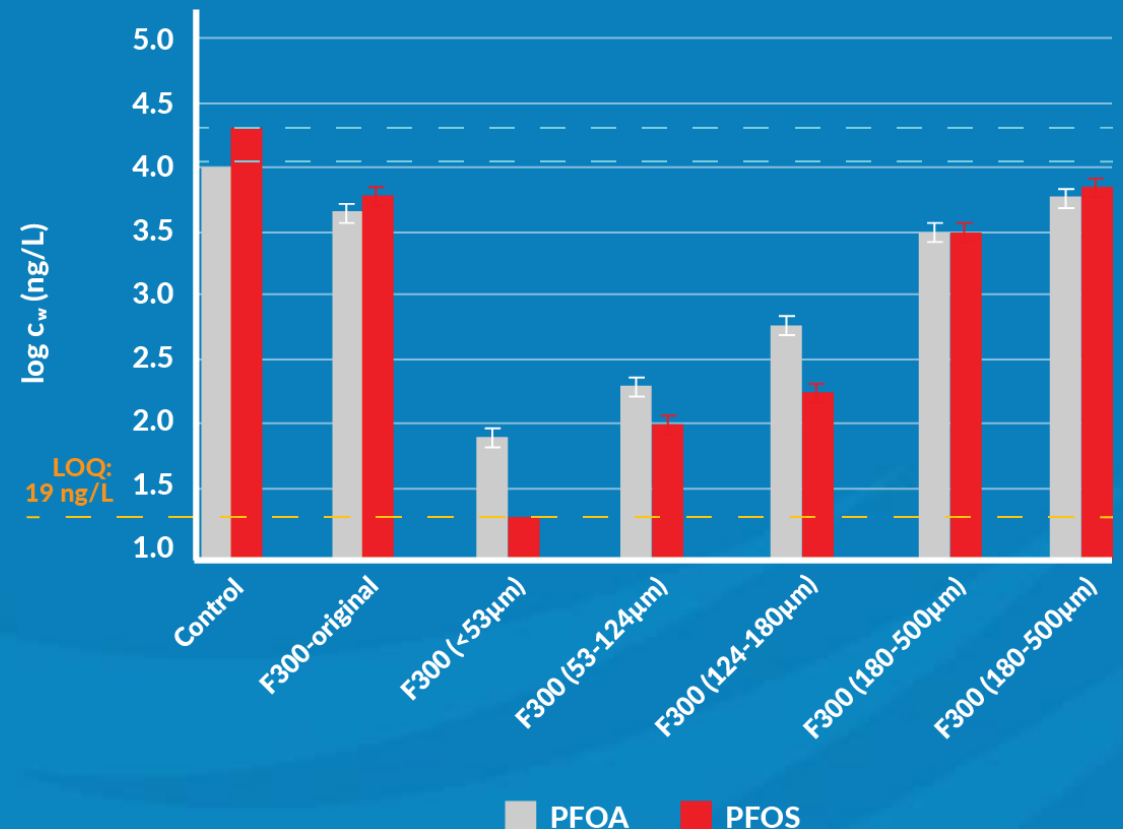
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ACTIVATED CARBON PARTICLE SIZE AND ADSORPTION EFFICACY

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- Recent study demonstrated 2 OoM improved removal with smaller activated carbon particles
 - 180–500 μm AC removed 90% PFOS
 - <53 μm AC removed 99.9+% PFOS
- *GAC particles are less efficient at adsorbing PFAS than PlumeStop because of their size



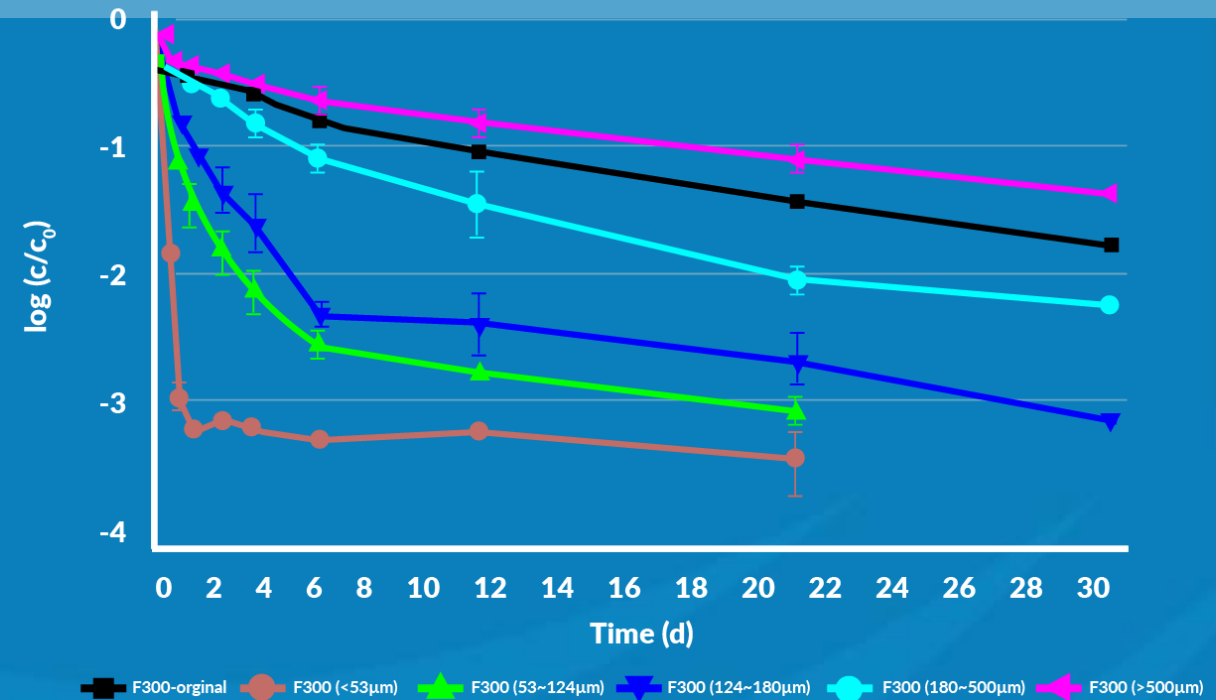
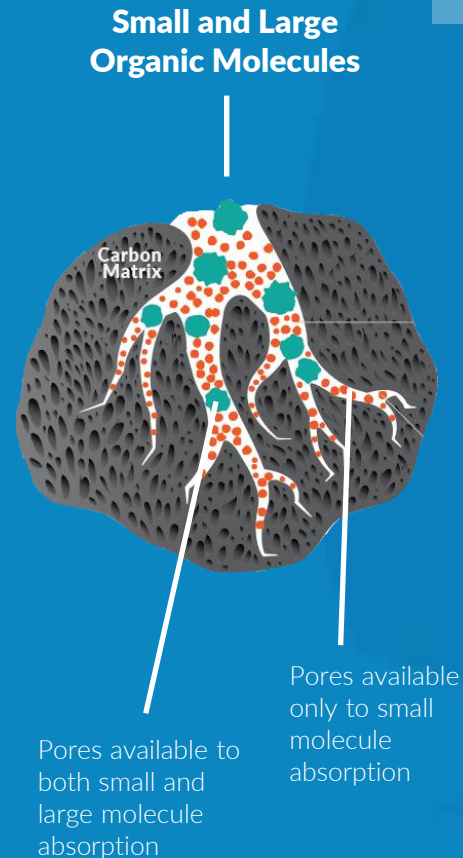
^aXiao, Ulrich, Chen & Higgins. Environ. Sci. Technol. 2017, 51, 6342.

PFAS ADSORPTION KINETICS & PARTICLE SIZE

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PFOS

- The reason can be attributed to kinetics: intraparticle diffusion
- Smaller particles provide better access to all the sorption sites that activated carbon provides.



PFAS ADSORPTION KINETICS & PARTICLE SIZE

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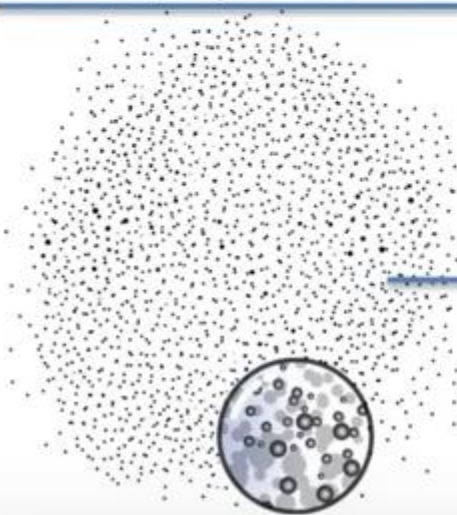


+ PFAS

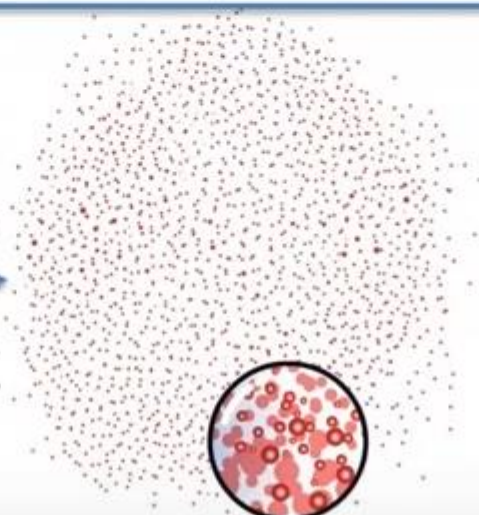


Granular Activated Carbon (>500µm):

Slow sorption due to limited surface area exposed to solute



+ PFAS



Colloidal Activated Carbon (1-2 µm):

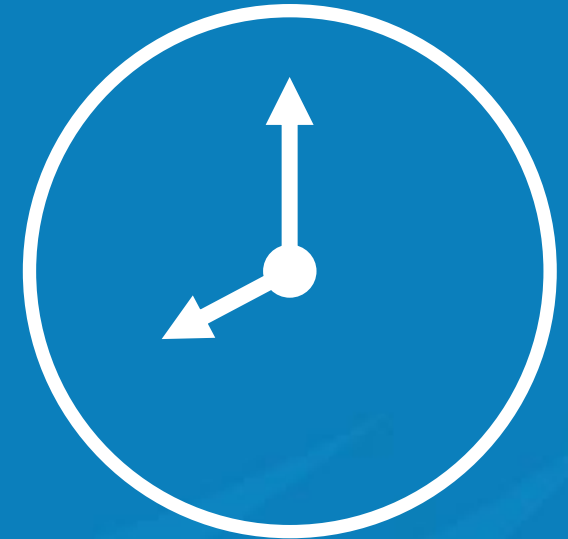
Rapid sorption and more complete use of sorption sites

PLUMESTOP + PFOA/PFOS: CAPTURE EFFICIENCY

So what happens over time?

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- Won't the barrier eventually fill up and breakthrough?
- As PFAS do not degrade, the answer is **yes**
- What's important is **how long this will take**

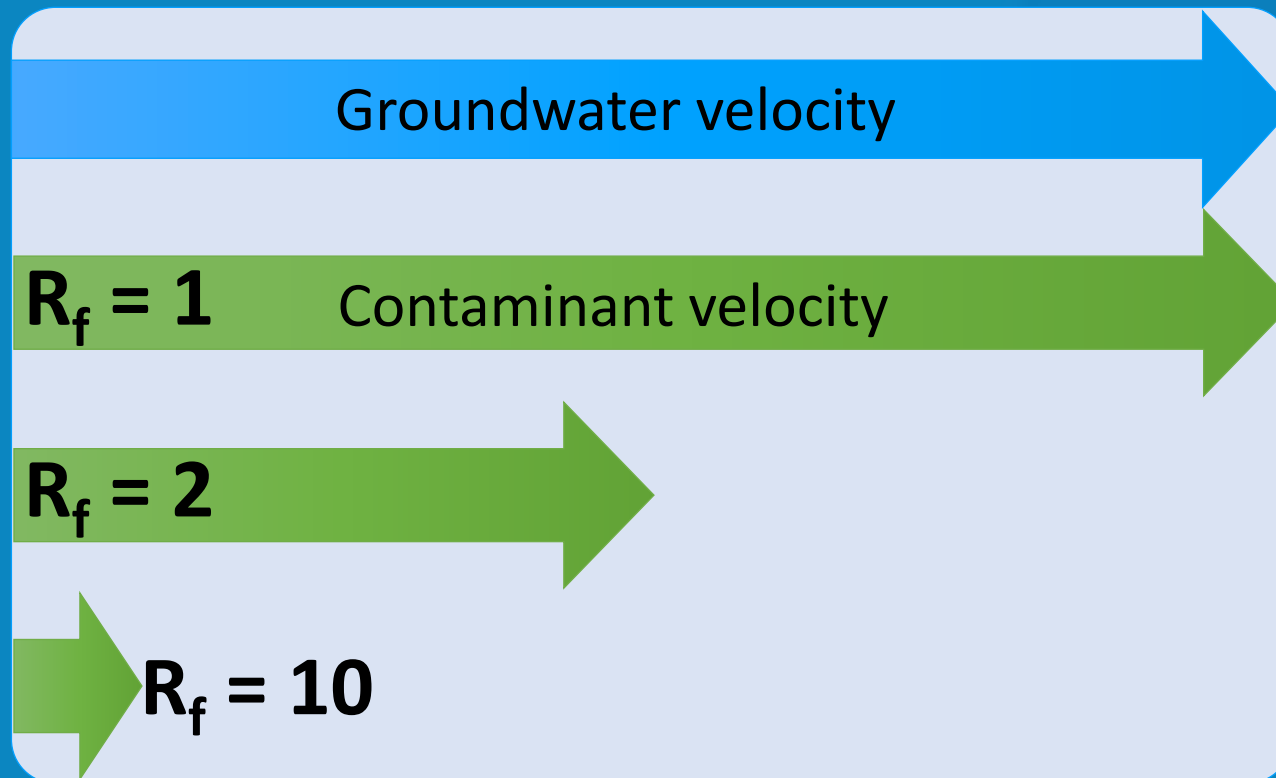


Engineering the Retardation factor

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The Retardation Factor (R_f) determines how fast a contaminant moves relative to the groundwater.

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Natural R_f :

PFOA = 3^a

PFOS = 19^a

**R_f with PlumeStop for PFOA
and PFOS:**

500 – 5,000

PLUMESTOP + PFAS: RETARDATION FACTOR

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For a PlumeStop Barrier at a Mid-Range Dose:

PFOA

- The R of a 1,000 µg/L plume is 80
- The R of a 100 µg/L plume is 570
- The R of a 10 µg/L plume is 4,000

PFOS

- The R of a 1,000 µg/L plume is 375
- The R of a 100 µg/L plume is 2,000
- The R of a 10 µg/L plume is 10,000

**based on individual components*



PLUMESTOP + PFAS: RETARDATION FACTOR

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Example:

- PlumeStop barrier width 16' (single application at mid-range dose)
 - 160' per year seepage velocity
 - 100 µg/L influent concentration
-
- Groundwater transit time 36.5 days
 - PFOA transit time* = 20,800 days (57 years)
 - PFOS transit time* = 73,000 days (200 years)

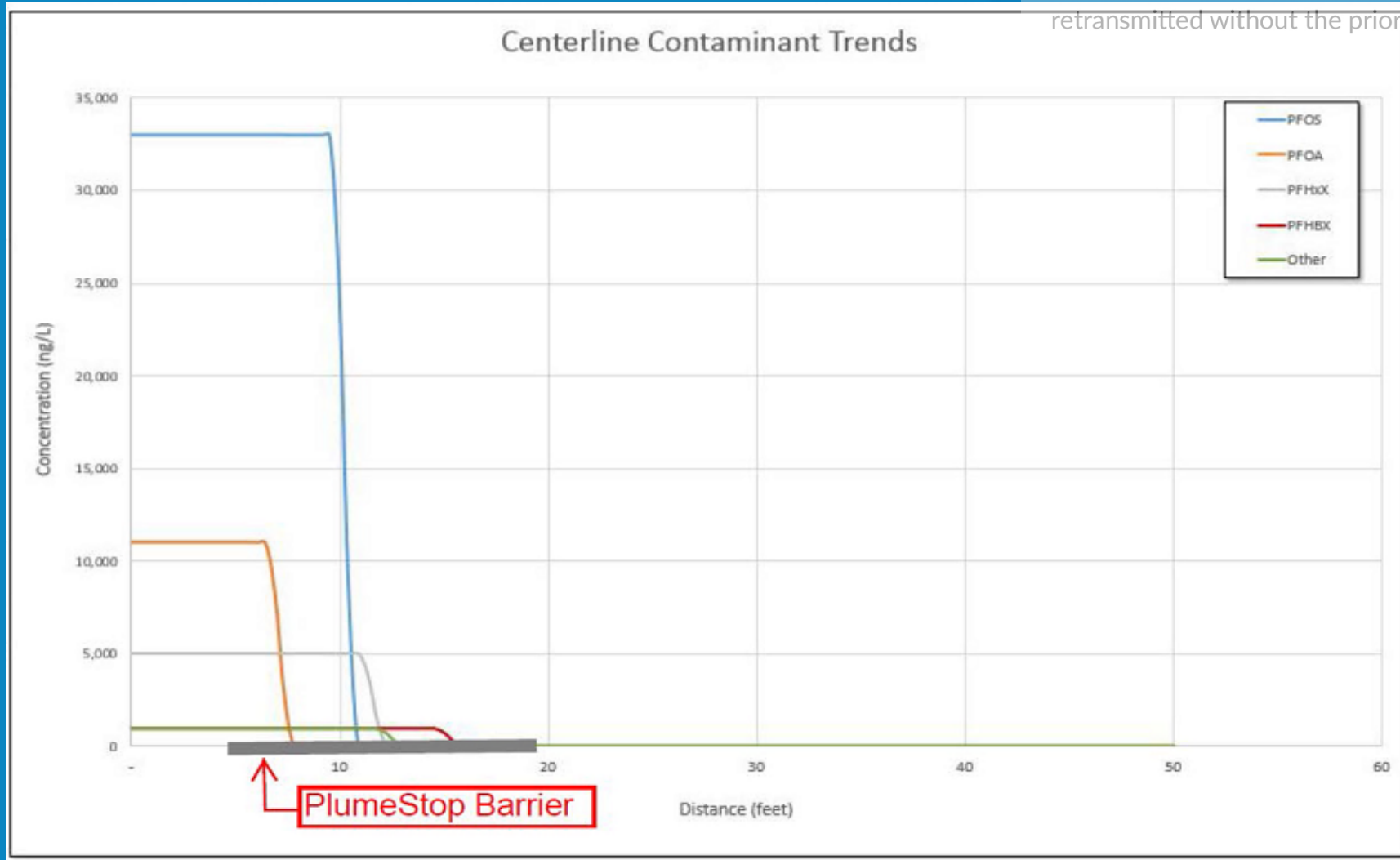
This is at 100 µg/L

At lower influent concentrations, the retardation quickly becomes **much** greater.

* transit time peak based on individual components

PlumeStop® Integration with Fate & Transport Models

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Incorporate PlumeStop
isotherm parameters
into models



Predict longevity of
PlumeStop dose



Optimize the dose to
meet desired longevity

Eliminates Risk of PFAS

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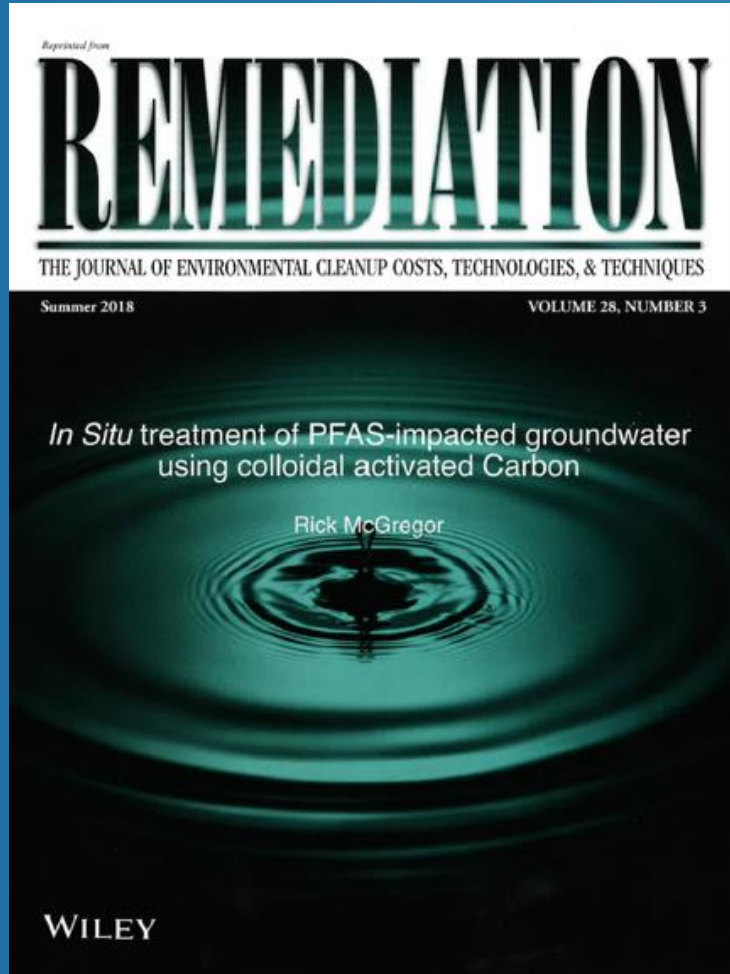
- ~~Risk~~ = Hazard x ~~Exposure~~
- PlumeStop binds up PFAS *in situ*
- Eliminates potential for down gradient exposure
- Eliminates the Risk



Longevity-Third Party Review

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- University of Waterloo, Waterloo, Ontario, Canada
- University of Toronto, Toronto, Ontario, Canada
- Porewater Solutions, Ottawa, Ontario Canada
- In Situ Remediation Services Ltd., St. George, Ontario, Canada

Longevity-Conclusions:

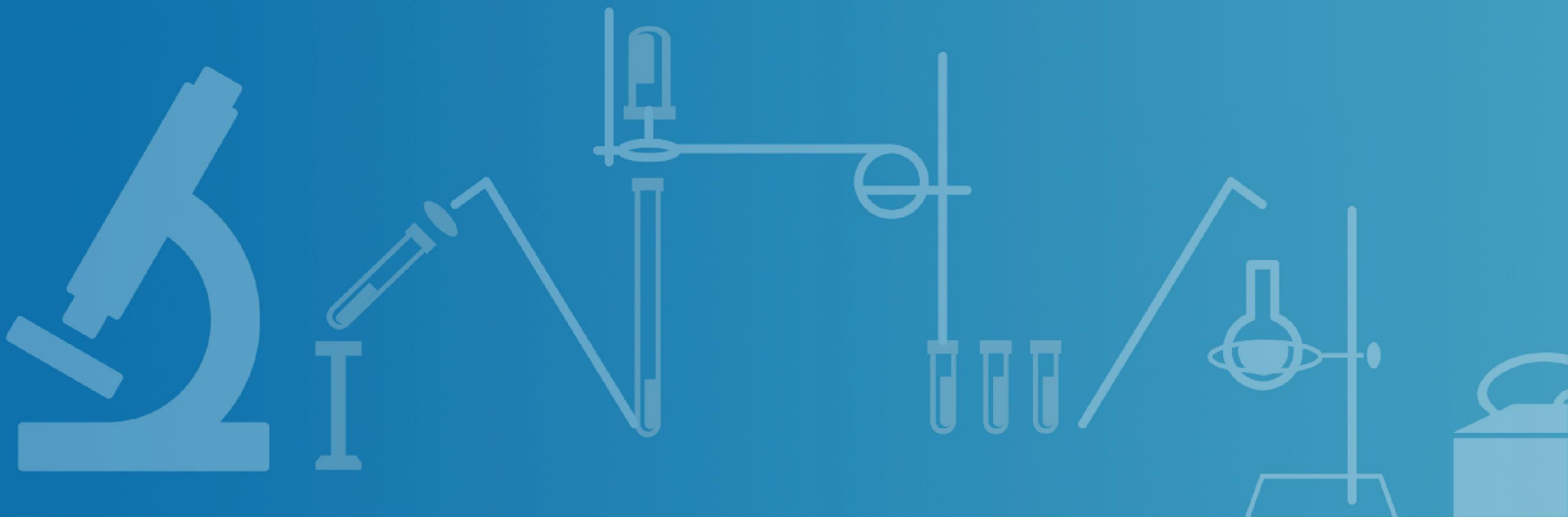
- Increased by CAC concentration injected
- Length of treatment area



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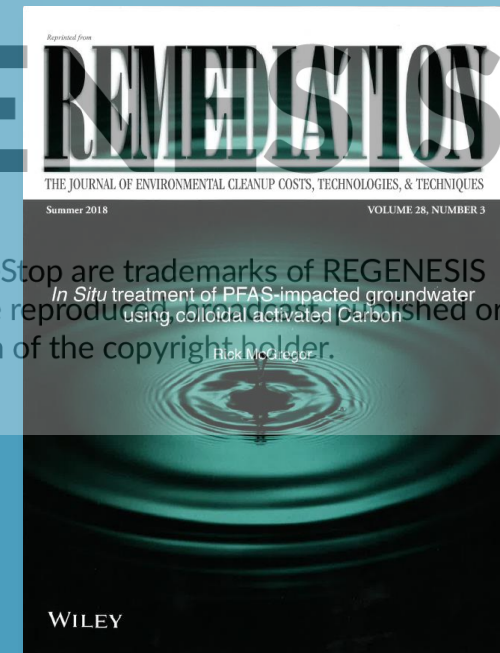
CASE STUDIES





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FORMER FURNITURE FACILITY

ONTARIO, CANADA



McGregor, R. In Situ Treatment of PFAS-impacted groundwater using colloidal activated carbon. *Remediation*. 2018;28:33-41.

Case Study #1 Background

Initial Driver: Hydrocarbons

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

Formation

- GW Velocity: .8m/day
- Silty sand – till based with sand seams
- Water at 3 – 5' below grade

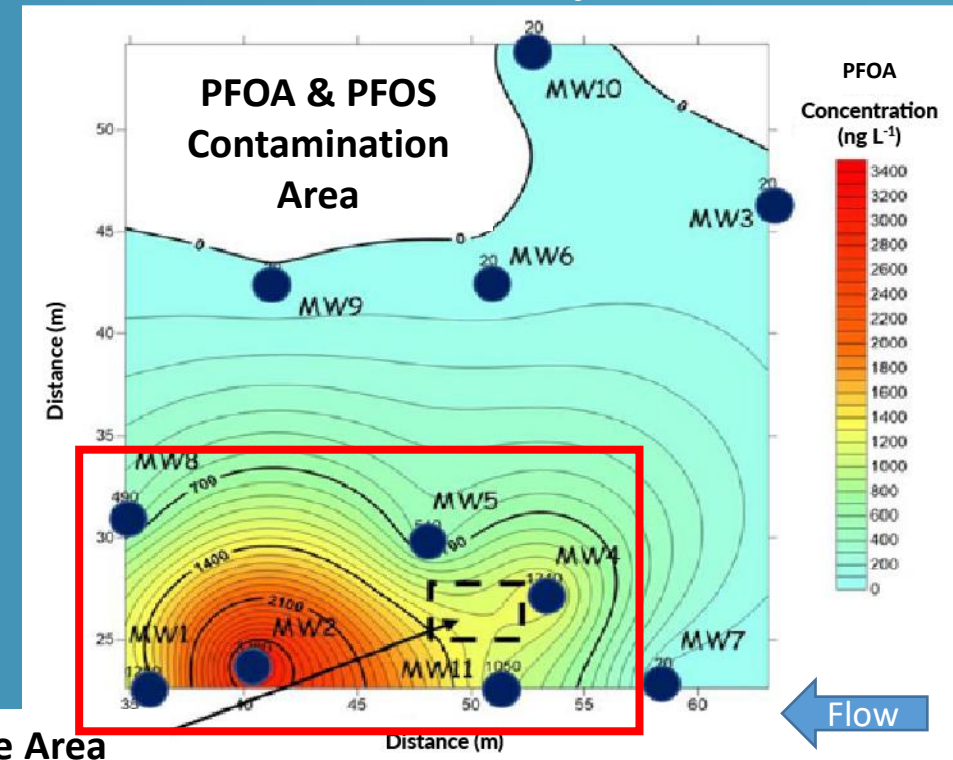
Former Fire Training Area

- History of furniture manufacturing
- PFAS tested for just in case and found!
 - 6 wells impacted by PFOS (300 to 1,400 ng/L) & PFOA (400 to 3,400 ng/L)

Remedial Approach

- Aerobically degrade hydrocarbons
- PlumeStop to prevent off-site plume migration

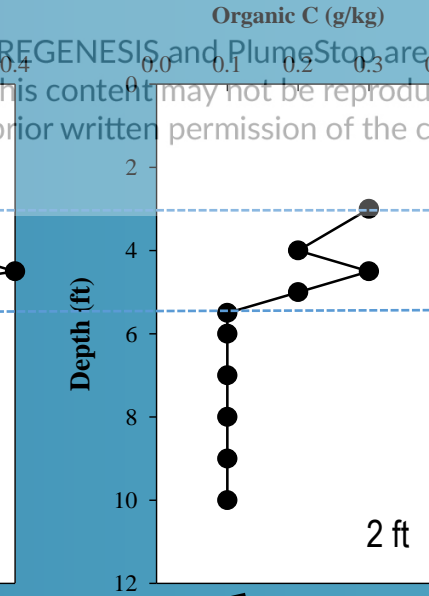
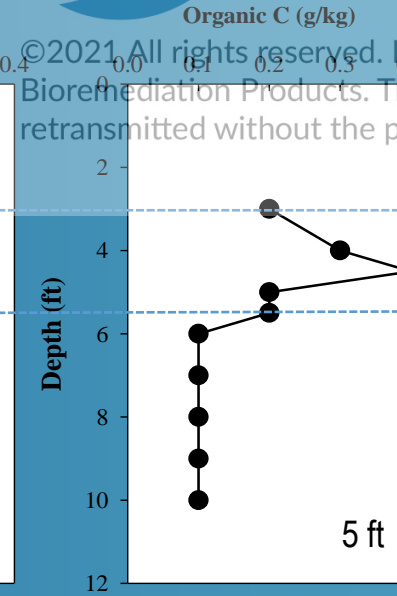
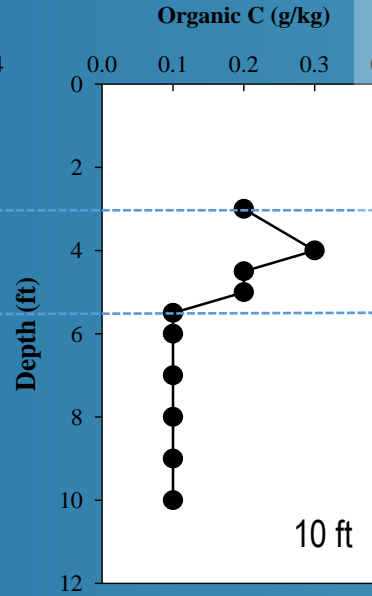
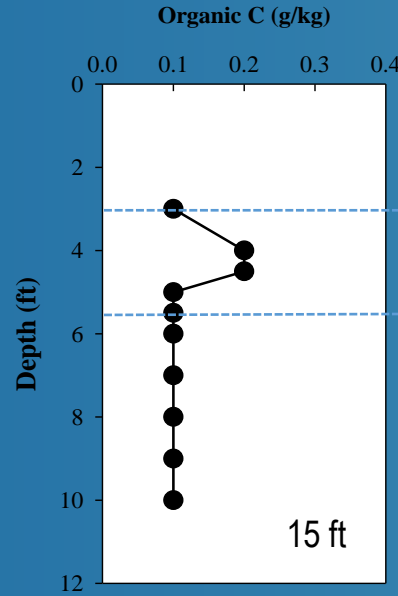
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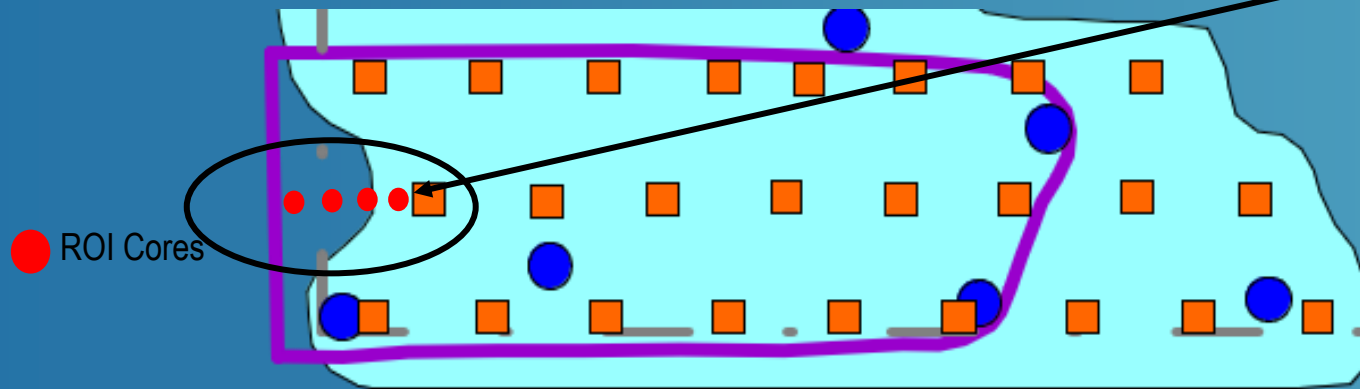
“Accidental” Site



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Injection Pt



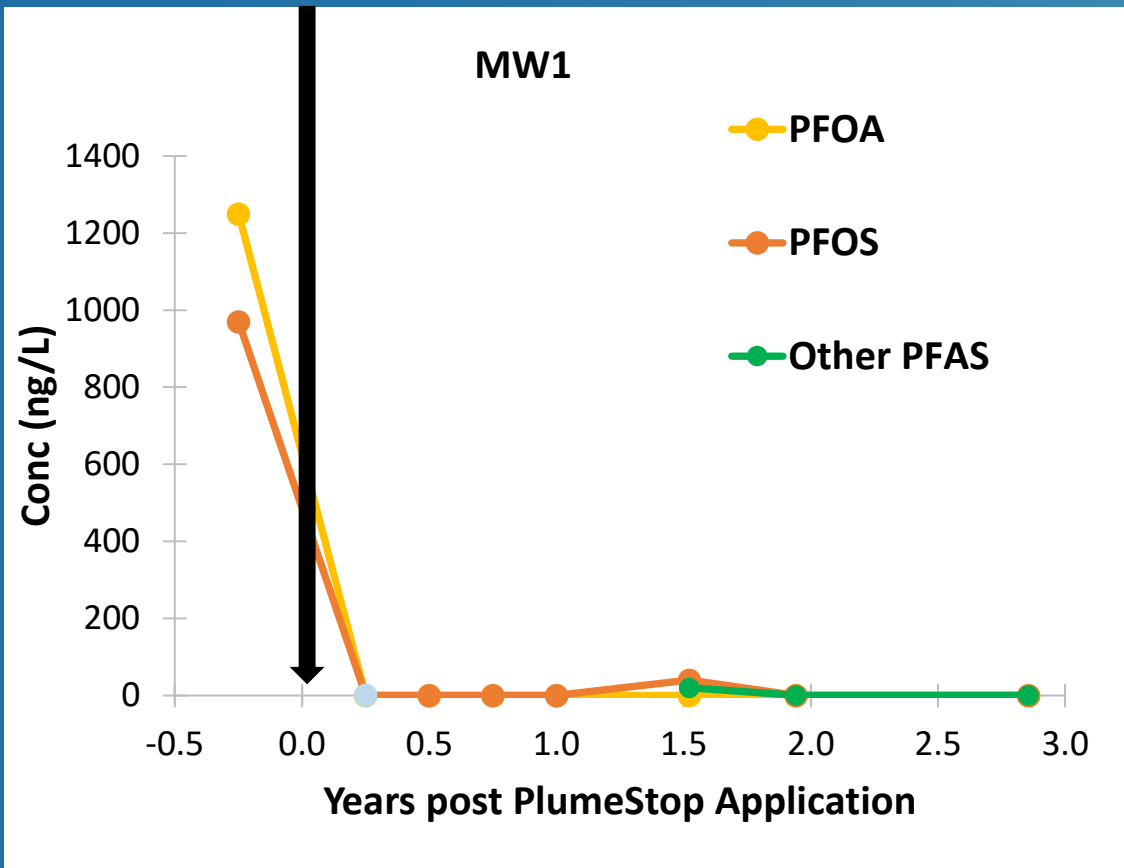
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Case Study #1 Monitoring & Results



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PLUME STOP
Liquid Activated Carbon



Monitoring events:

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

Results for MW1 are shown

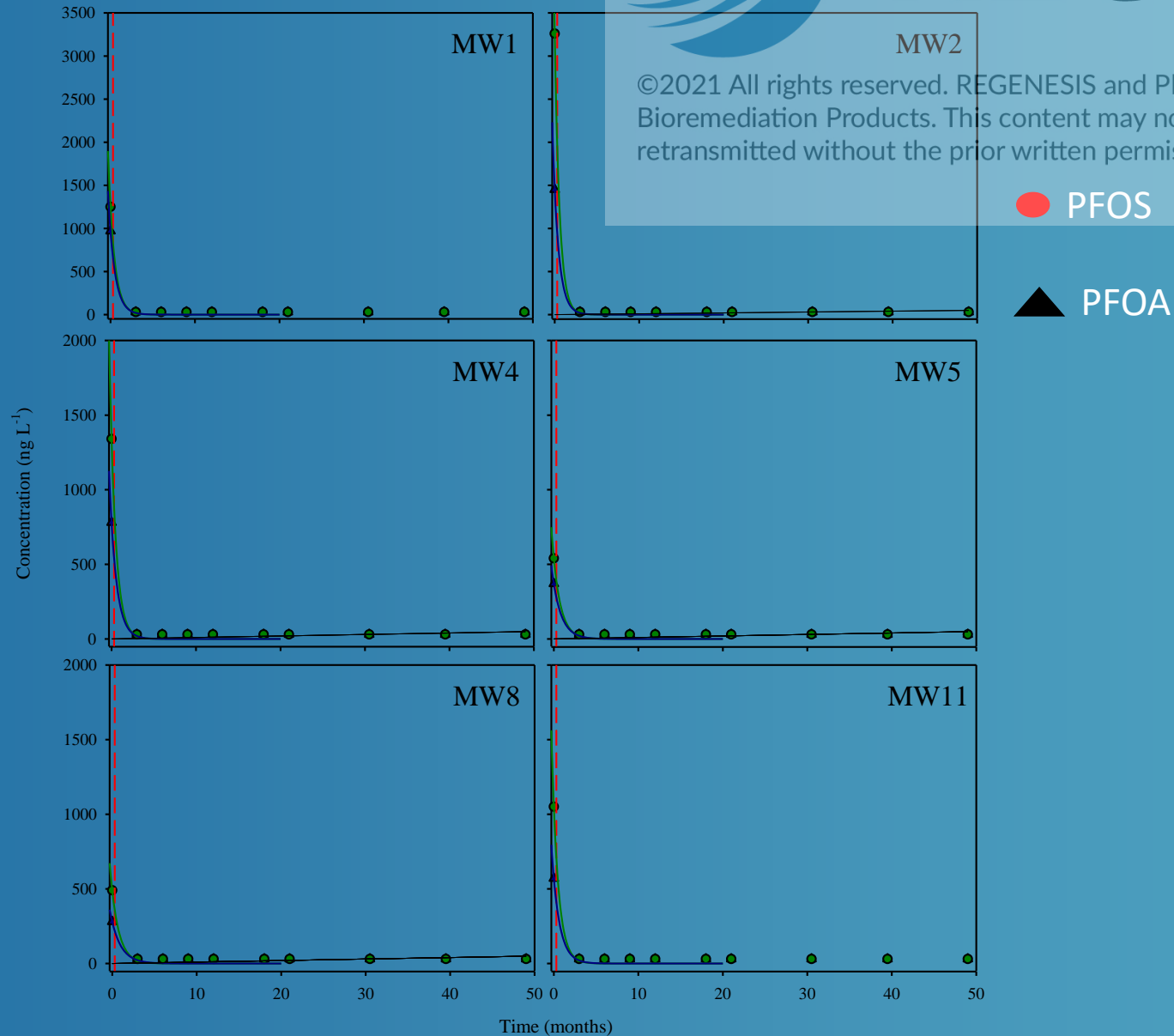
- **Non-detect (typical RL = 20 ng/L)**
- **Only one hit of PFOS at 18 months, just above RL**
- **Data are representative of all 6 wells**

“Accidental” Site



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“Accidental” Site

Preliminary Observations

- Distribution of CAC
 - > 96% of CAC injected into Targeted Injection Zone
 - Uniform distribution with TIZ
 - Up to 5 m ROI
- Chemistry
 - PFOS & PFOA ND after 4 years
 - Other PFAS ND after 4 years
 - BTEX, GRO and DRO remain below regulatory limits after 4 years
 - Modelling by Dr. Grant Carey suggest long-term performance is achievable



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"Accidental" Site



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WILEY

DOI: 10.1002/rem.21558

RESEARCH ARTICLE

In Situ treatment of PFAS-impacted groundwater using colloidal activated Carbon

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WILEY

Abstract

Poly- and perfluoroalkyl substances (PFASs) have been identified by many regulatory agencies as contaminants of concern within the environment. In recent years, regulatory authorities have established a number of health based regulatory and evaluation criteria with ground water PFAS concentrations typically being less than 50 nanograms per liter (ng/L). Subsurface studies suggest that PFAS compounds are recalcitrant and widespread in the environment. Traditionally, impacted groundwater is extracted and treated on the surface using media such as activated carbon and exchange resins. These treatment technologies are generally expensive, inefficient, and can take decades to reach treatment objectives. The application of in situ remedial technologies is common for a wide variety of contaminants of concern such as petroleum hydrocarbons and volatile organic compounds; however, for PFASs, the technology is currently emerging. This study involved the application of colloidal activated carbon at a site in Canada where the PFASs perfluorooctanoate (PFOA) and perfluorooctane sulfonic acid (PFOS) were detected in groundwater at concentrations up to 3,260 ng/L and 1,450 ng/L, respectively. The shallow silty-sand aquifer was anaerobic with an average linear groundwater velocity of approximately 2.6 meters per day. The colloidal activated carbon was applied using direct-push technology and PFOA and PFOS concentrations below 30 ng/L were subsequently measured in groundwater samples over an 18-month period. With the exception of perfluoroundecanoic acid, which was detected at 20 ng/L and perfluorooctanesulfonic acid which was detected at 40 ng/L after 18 months, all PFASs were below their respective method detection limits in all post-injection samples. Colloidal activated carbon was successfully distributed within the target zone of the impacted aquifer with the activated carbon being measured in cores up to 5 meters from the injection point. This case study suggests that colloidal activated carbon can be successfully applied to address low to moderate concentrations of PFASs within similar shallow anaerobic aquifers.

1 | INTRODUCTION

Poly- and perfluoroalkyl substances (PFASs) have been identified as emerging contaminants and have attracted concern from regulatory bodies over the past 20 years because they are widespread and persistent in the environment, have potential for bioaccumulation, and may have adverse effects on the immune system, liver, and development of children/fetuses (U.S. Environmental Protection Agency [EPA], 2009; Environment and Climate Change Canada [ECCC], 2017a). These compounds are used in metal plating, firefighting, photography, and aviation industries for applications including flame suppressants, foaming agents, and hydraulic fluid additives (Hunter-Anderson, Long, Purton, & Anderson, 2016; Government of Canada, 2008). PFASs are no longer produced in Canada (ECCC, 2016) or the United States

(ECCC, 2017b), but can be imported from China as of 2003 (Butt, Berger, Bossi, & Tomy, 2010). Canada has no current drinking water or groundwater regulations for any PFAS; however, the Federal Soil Quality Guidelines and Groundwater Quality Guidelines for PFOS indicate 0.21 milligrams per kilogram (mg/kg) for fine soil, 0.14 mg/kg for coarse soil, and 68 micrograms per liter ($\mu\text{g/L}$) for groundwater for the protection of freshwater life (ECCC, 2017b). The EPA drinking water health advisory level for the sum of perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) concentrations is 70 nanograms per liter (ng/L), while other jurisdictions pose stricter regulations (NGWA, 2017).

The remediation of PFASs is challenging for many reasons, including the highly recalcitrant nature of these compounds which is likely due to multiple stable fluoride-carbon bonds (National Ground Water

Remediation, 2018, 28:33–41.

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doi.org/10.1002/rem.21593

RESEARCH ARTICLE

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

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Abstract

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

1 | INTRODUCTION

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

There are two classes of PFAAs: perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs). The most commonly regulated PFAS in the environment are perfluorooctanoate (PFOA), which is a PFCA, and perfluorooctane sulfonate (PFOS), which is a PFSA. Regulatory cleanup criteria for these and other PFAS are

undergoing development; at present, the U.S. Environmental Protection Agency (USEPA) has imposed a Lifetime Health Advisory for PFOS and PFOA individually or in combination, of 0.07 microgram per liter ($\mu\text{g/L}$; USEPA, 2016a, 2016b). Health Canada drinking water screening values for PFOS and PFOA are 0.6 and 0.2 $\mu\text{g/L}$, respectively (Health Canada, 2018). These low cleanup levels and the persistent nature of PFAAs pose a significant challenge in remediating PFAS sites.

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

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COST COMPARISON



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Actual Cost of PlumeStop Treatment

• Design, product and application (total)	\$73,000
• Ongoing system O & M (ex. monitoring)	\$0
	<hr/>
	\$73,000

Estimated Cost of Pumping & Treating (Most Efficient GAC)

• Design, permitting, construction, startup	\$150,000
• Ongoing system O&M	\$1,200,000
• (ex. monitoring @ \$60k/yr X 20 yrs)	
	<hr/>
	\$1,350,000



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CASE STUDY

PFAS – SOLVENT RECOVERY FACILITY

CONNECTICUT



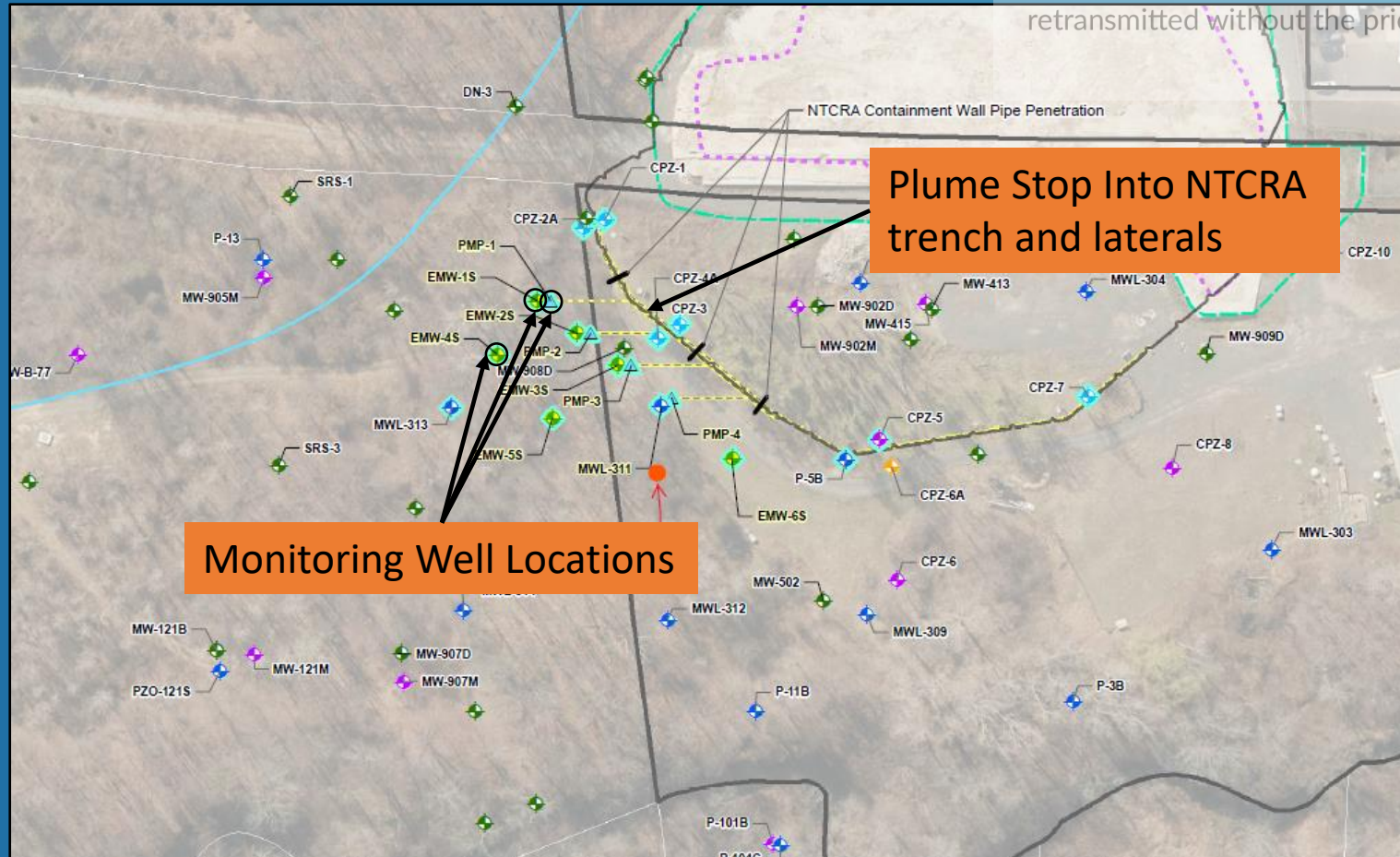
Solvent Recovery Services of New England Superfund Site in CT

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- Plume Stop and Aqua ZVI Application to address cVOC and PFAS contamination
- Target combined 5 compounds 70 ppt: PFOA, PFOS, PFNA, PFHxS, PFHpA
- Starting concentration: max 148ppt
- Applied Reagents in Trench and laterals
- Application July 23-25, 2018
- Aqua ZVI: 4,000 lbs
Plume Stop: 21,600 lbs

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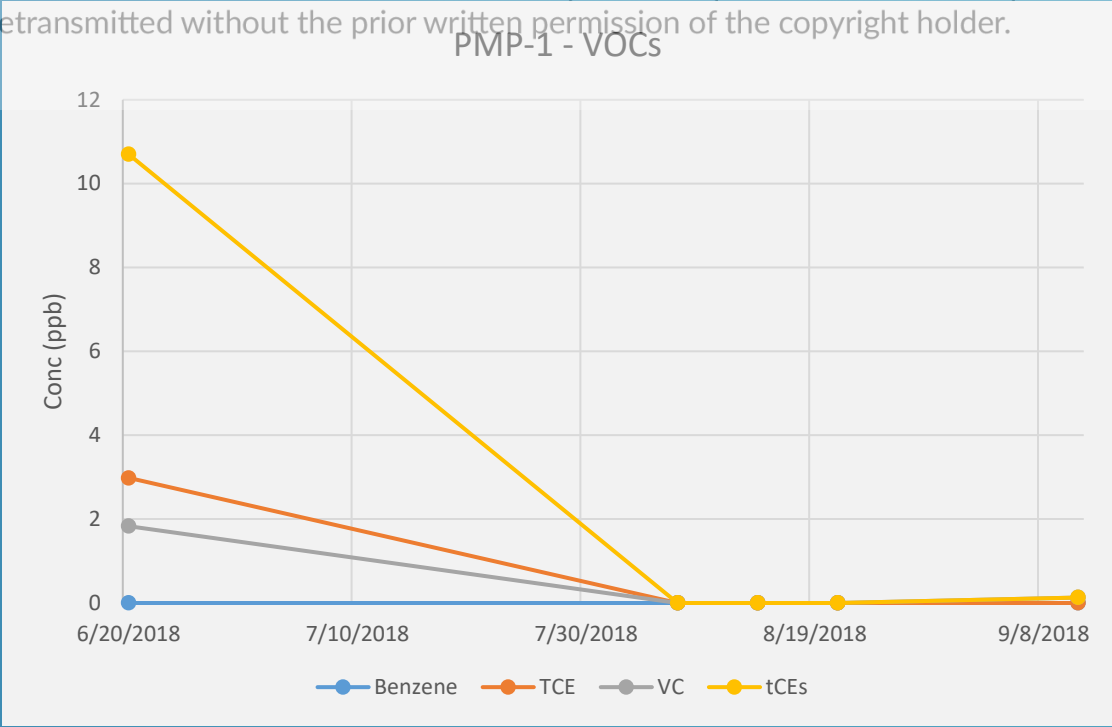
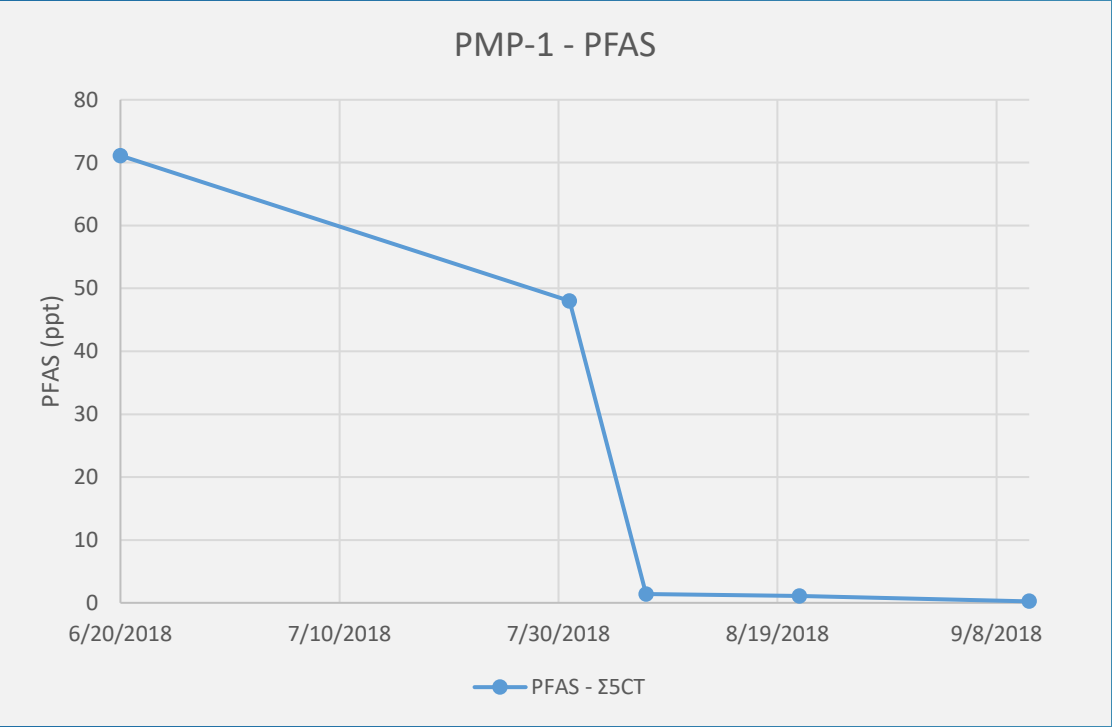


- 8,800 lbs of PlumeStop and 4,000 lbs of ZVI into the upgradient trench
- 12,800 lbs of PlumeStop into the downgradient trench (including four 50' distribution trenches)



Results from PMP-1 (within trench)

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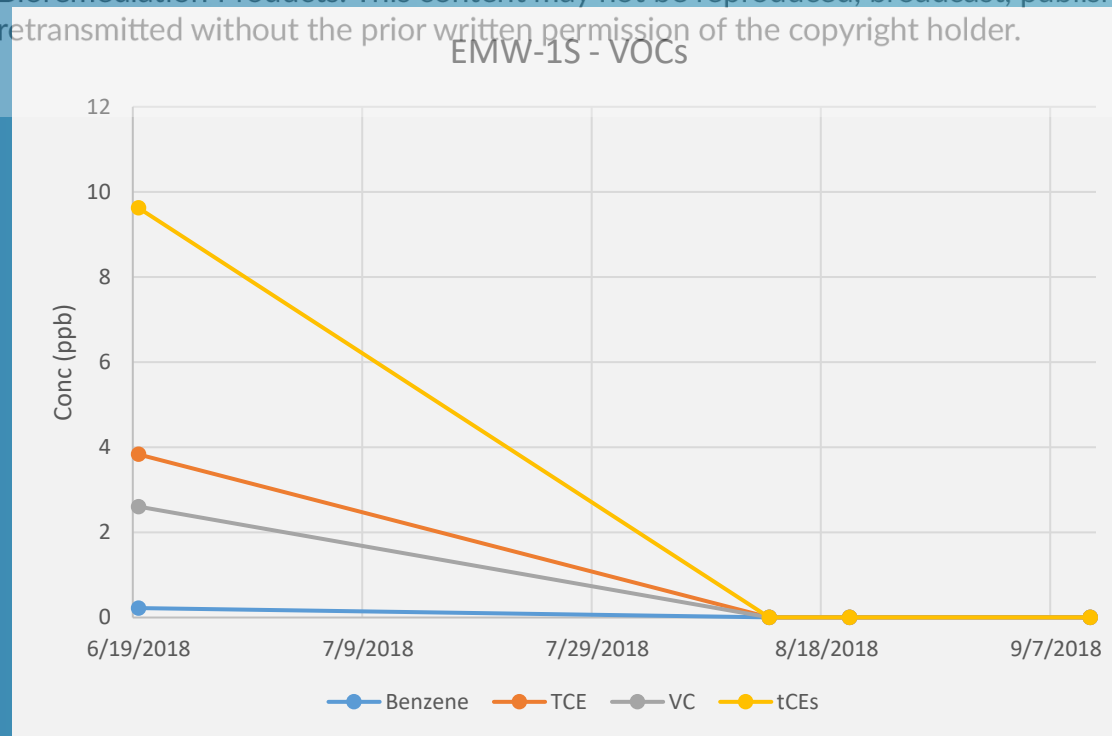
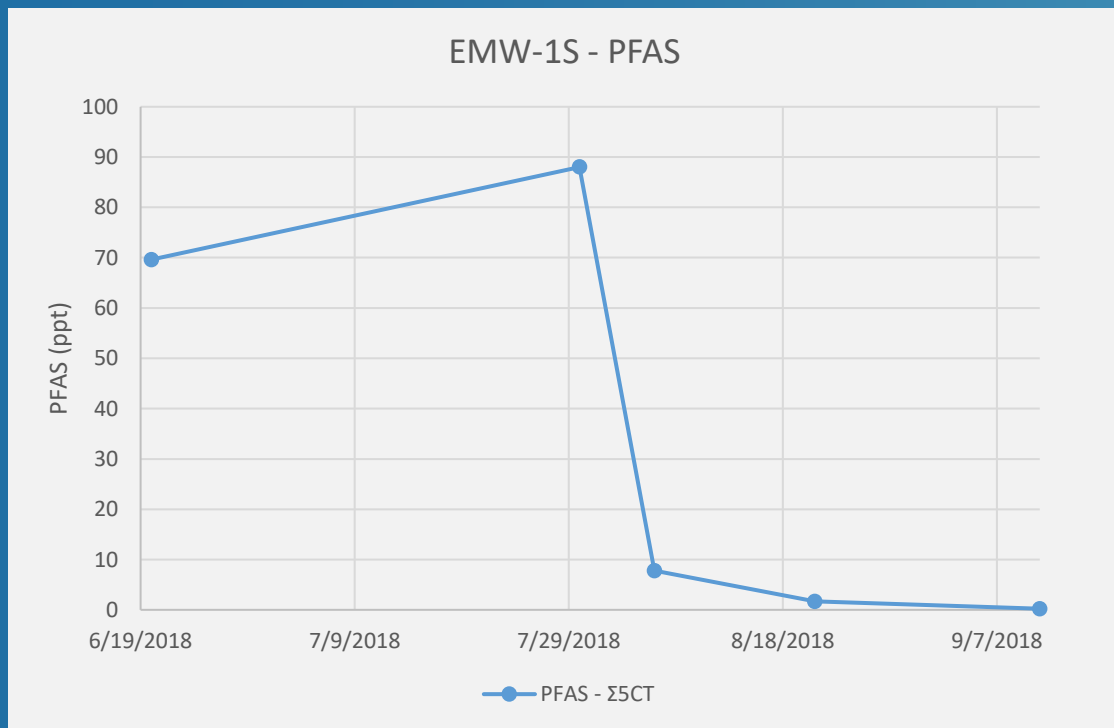


Σ5CT is sum of 5 PFAS compounds (PFOA, PFOS, PFNA, PFHpA, and PFHxS)



Results from EMW-1S (10 ft downgradient of trench)

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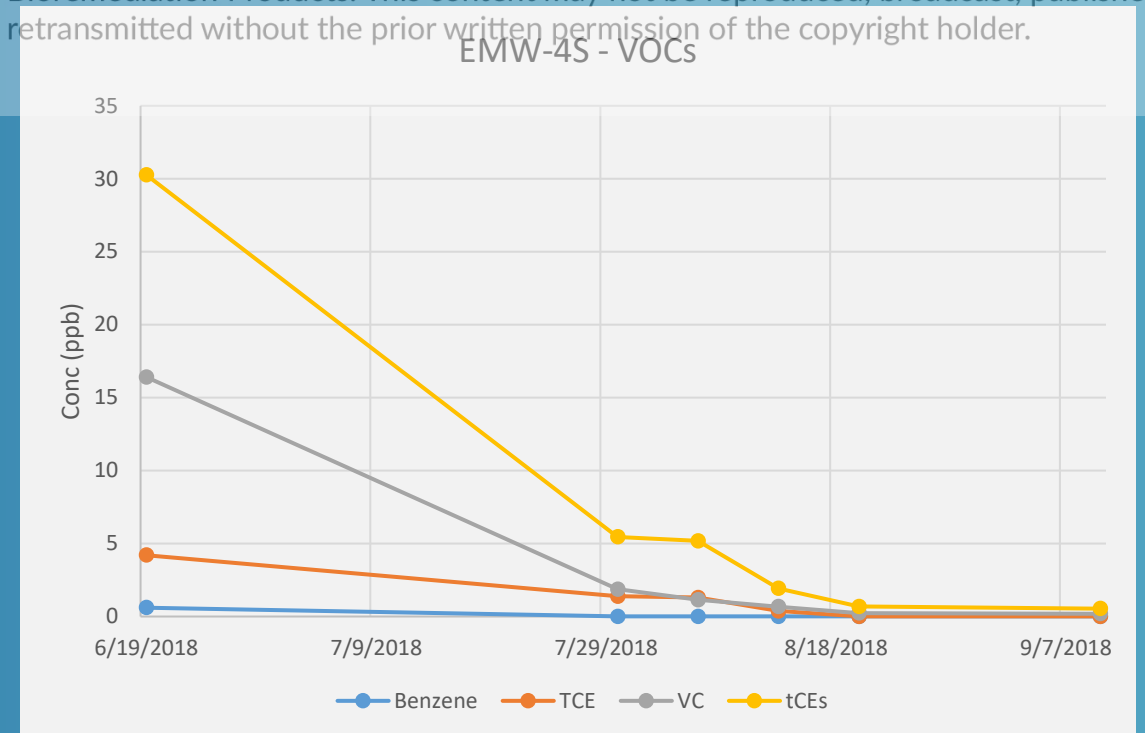
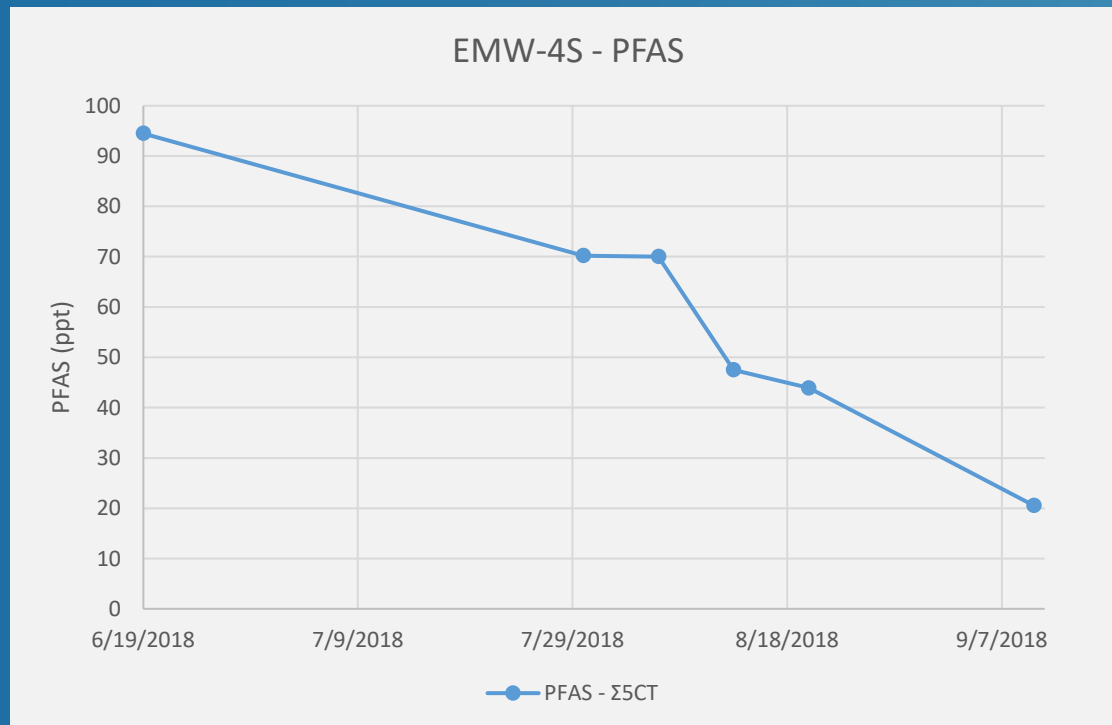


Σ5CT is sum of 5 PFAS compounds (PFOA, PFOS, PFNA, PFHpA, and PFHxS)

Results from EMW-4S (about 50 ft downgradient of trench)



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Σ5CT is sum of 5 PFAS compounds (PFOA, PFOS, PFNA, PFHpA, and PFHxS)

RESULTS



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- Rapid Reduction Target PFA compounds and cVOCs
- Water is not exceeding any EPA-determined downgradient triggers
- Anticipated cost savings \$400,000 per year
- Long terms success is based on allowing the valves to remain open and allow the trench to serve as a long-term permeable reactive barrier.
- Current results from the Plume Stop/Aqua ZVI treatment suggest it will be possible to turn off 12 pumping wells and reduce onsite treatment because water clean enough for discharge to sanitary sewer

CASE STUDY

Grayling Army Airfield



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Case Study Background

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Site Location: Camp Grayling Joint Maneuver Training Center

- Founded 1913
- 147,000 acres
- Largest National Guard training center in the country
- Home to the Grayling Army Airfield (900acres)

Contaminant Release History:

- Diesel, PCE/TCE, PFAS

Remediation History:

- Pump and Treat, air sparging/SVE

Case Study: Pilot Test



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Aquifer:

- Sand & Gravel with some clay layers
- ~250'/yr gw seepage velocity
- Treatment Interval 15-27'bgs

Contaminant levels:

- 10 µg/L PCE
- 130 ng/L Total PFAS (PFOS, PFHxS)

Sensitive Receptors:

- Residential areas
- Surface water bodies
- Property Boundary



Former Bulk Storage
Tanks Location

GAAF

W. North Down River Rd

Simple Plume Cut-Off Barrier

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Modeling in the Design Process



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PlumeForce™

- Long-Term Prediction Model
- Competitive Sorption and Degradation (if applicable)
- Compound Specific Isotherms
- VOCs, PFAS, etc.

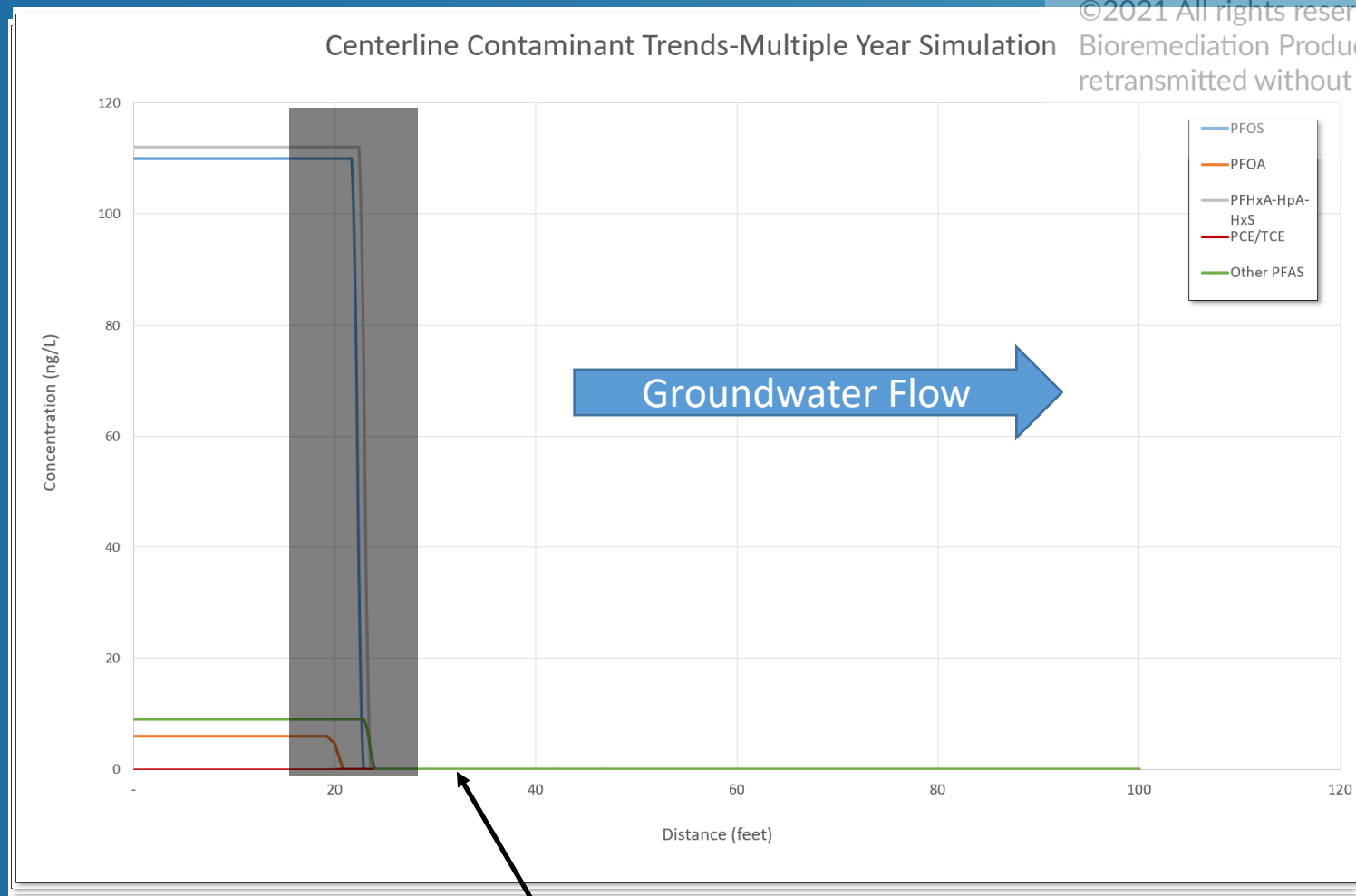
Considerations

- Soil Type/Porosity
- Groundwater Seepage Velocity/Mass Flux
- Vertical Variations
- Barrier Thickness
- Carbon Demand
- Time

Modeling in the Design Process



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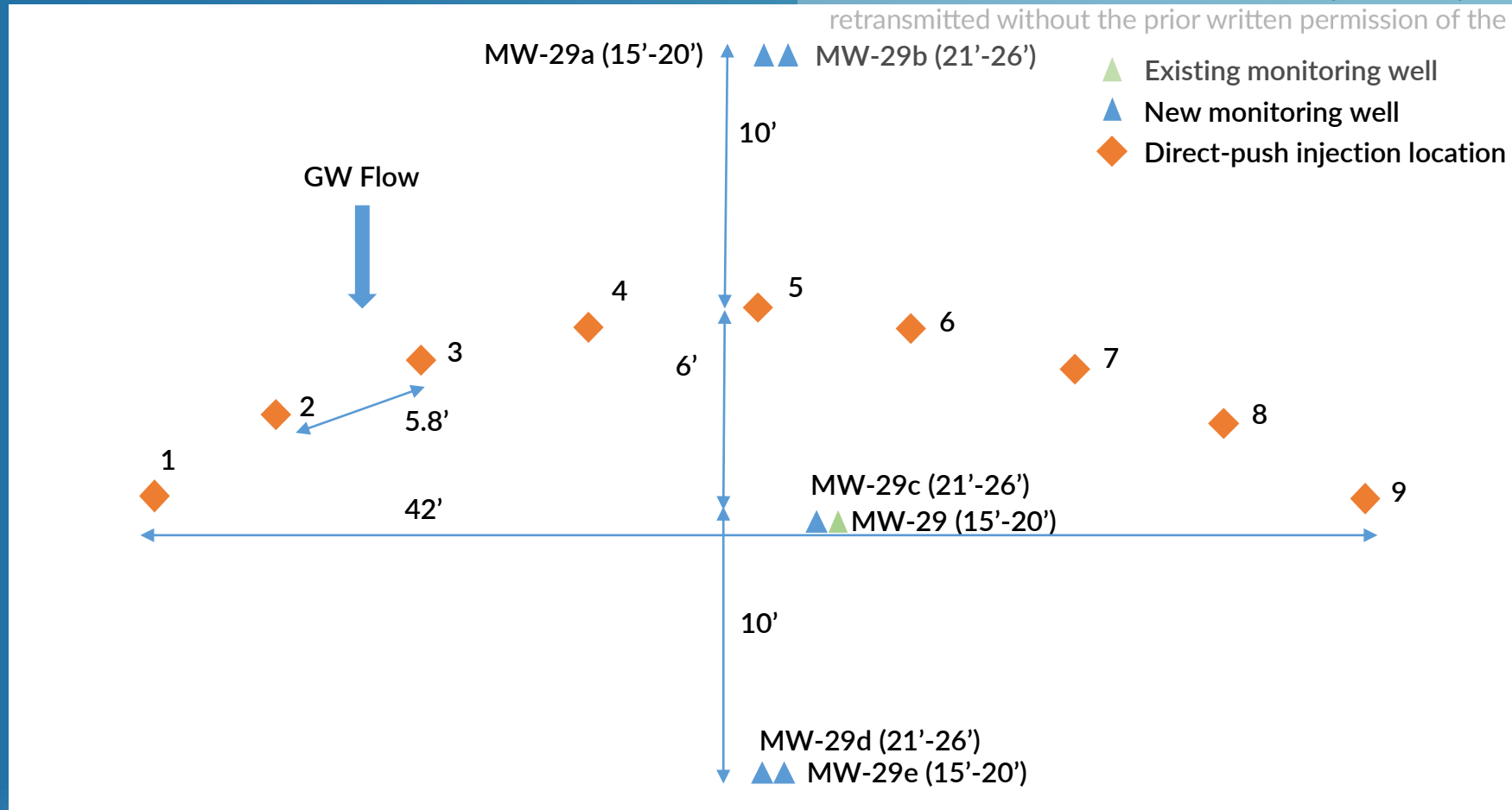
- Inputs**
- GW 219 feet/year
 - Infinite Source
 - PFOS 110 ng/L
 - PFOA 8 ng/L
 - PFHxA -HpA – HxS 112 ng/L
 - Other PFAS 9 ng/L
 - PCE 10 ug/L
 - No degradation of any PFAS compound or CVOC's
 - Time (>75yrs)

Field Test Layout



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Field Test Layout



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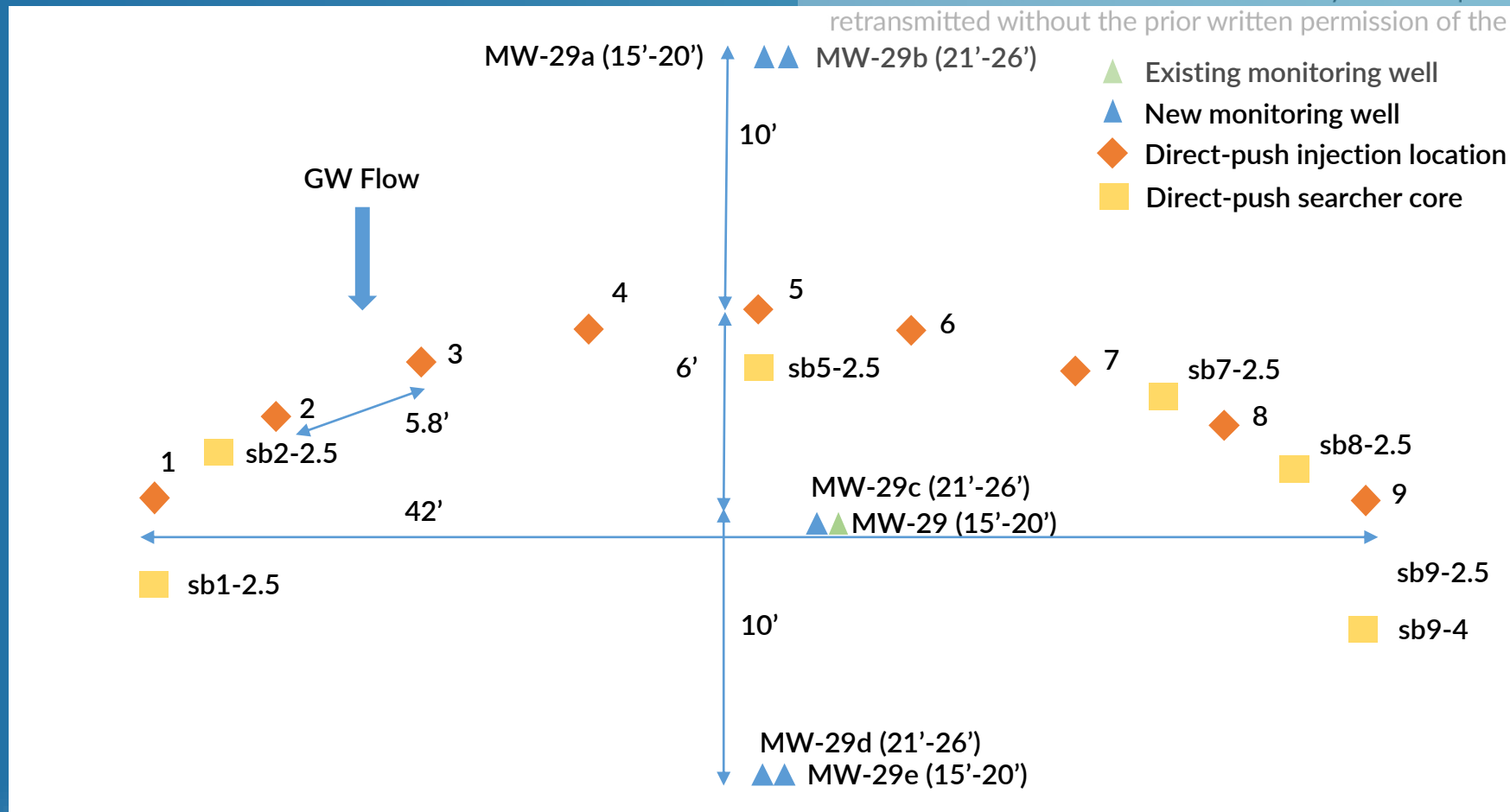


Field Test Layout



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CAC-Distribution Confirmation

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27 feet bgs

0 feet bgs

15 feet bgs

30 feet bgs



CAC-Distribution Confirmation

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27 feet bgs

0 feet bgs

15 feet bgs

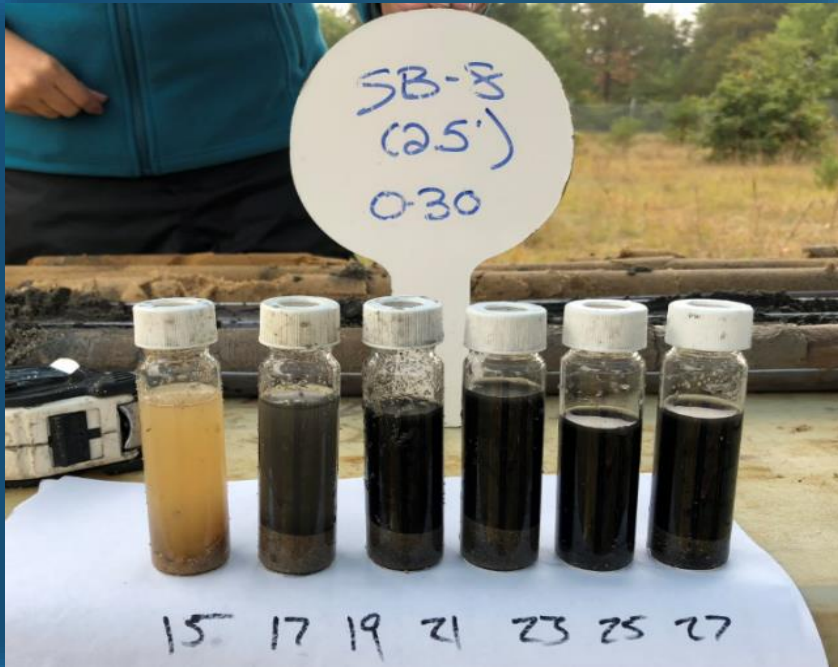
30 feet bgs



PlumeStop-Distribution Confirmation

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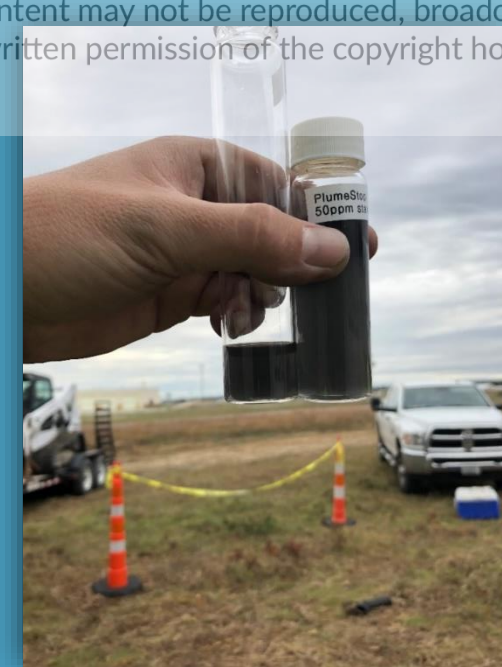
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Soil Vial Shake Test



MW-29c



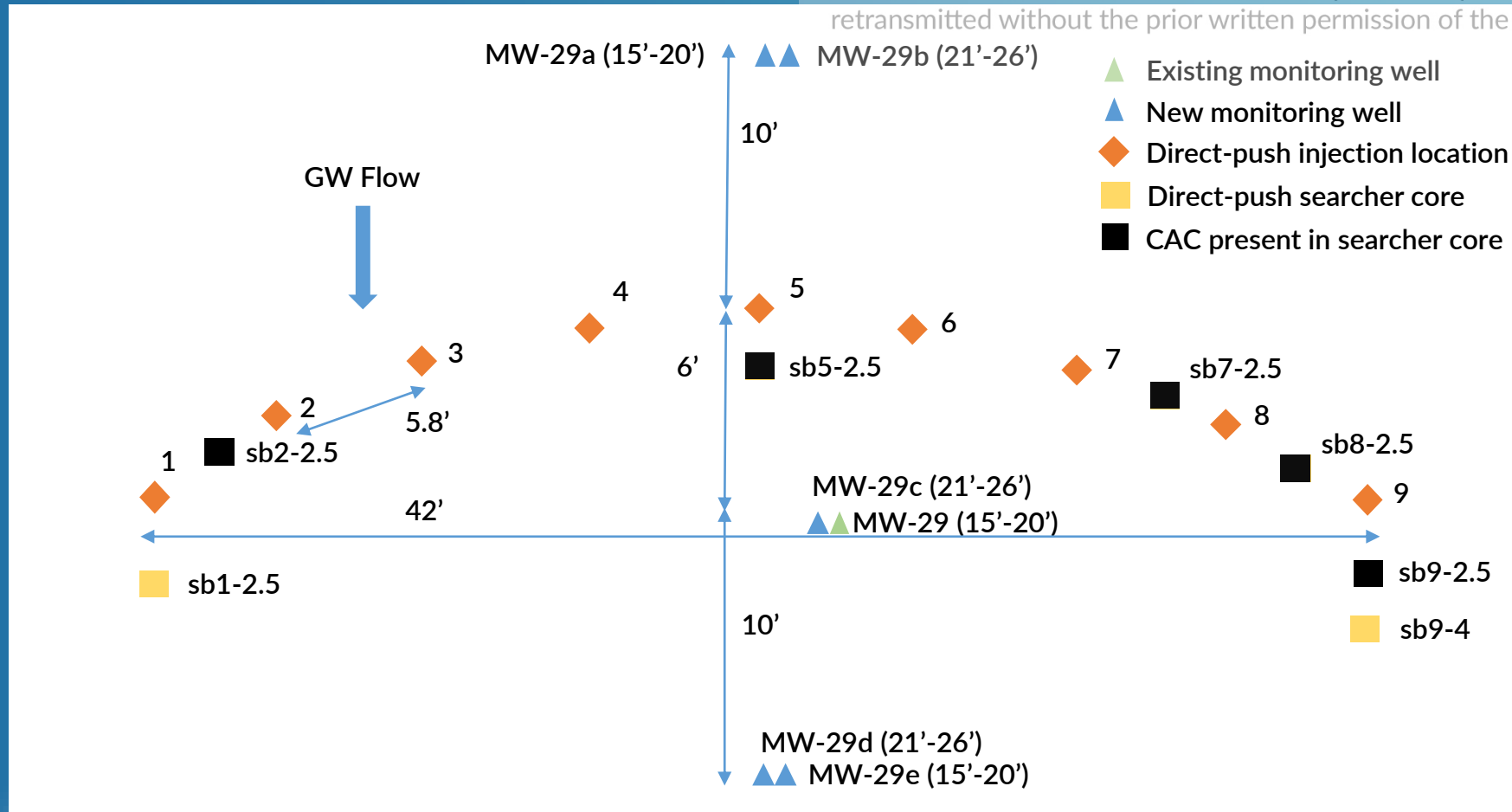
Field Test Kit

Field Test Layout



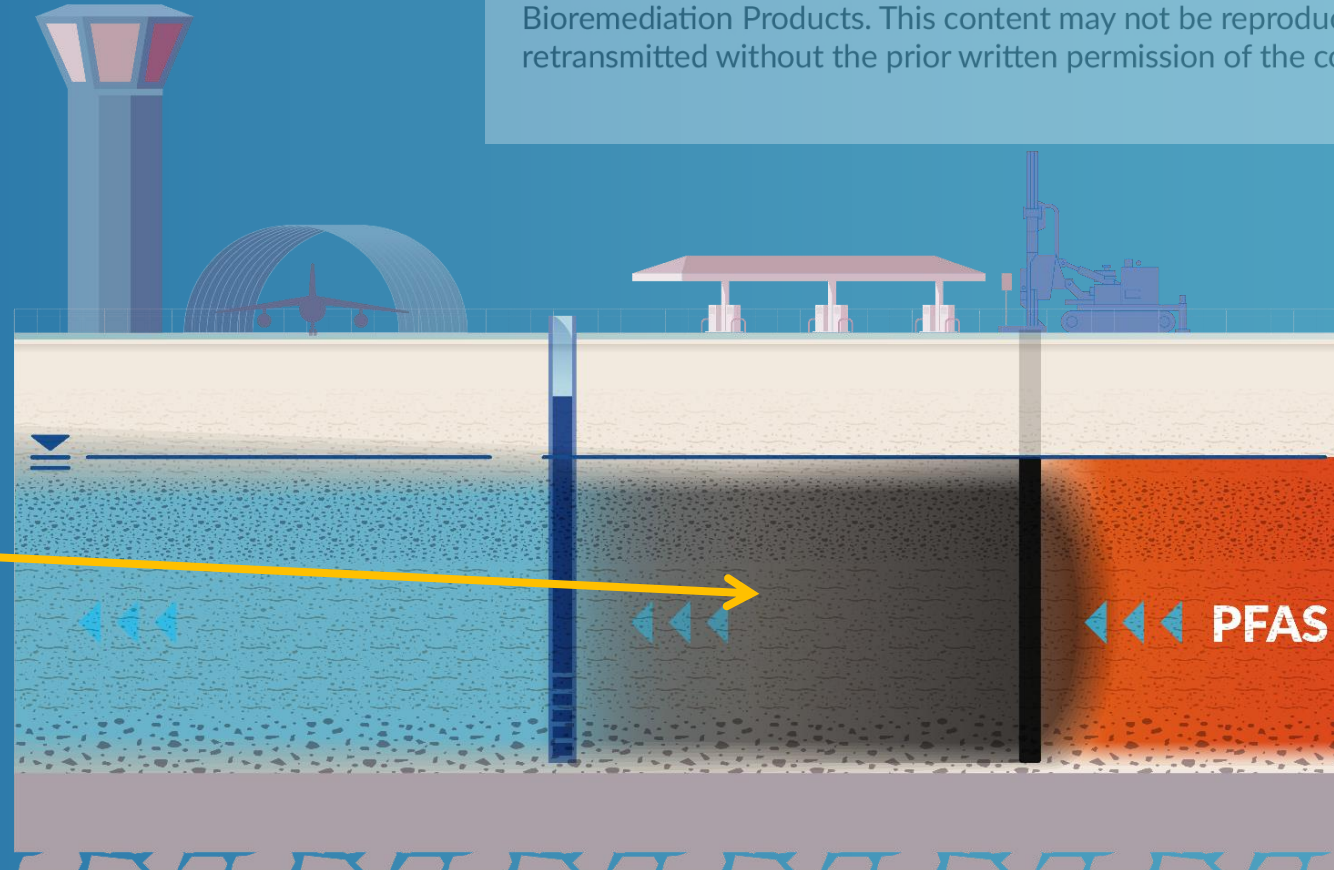
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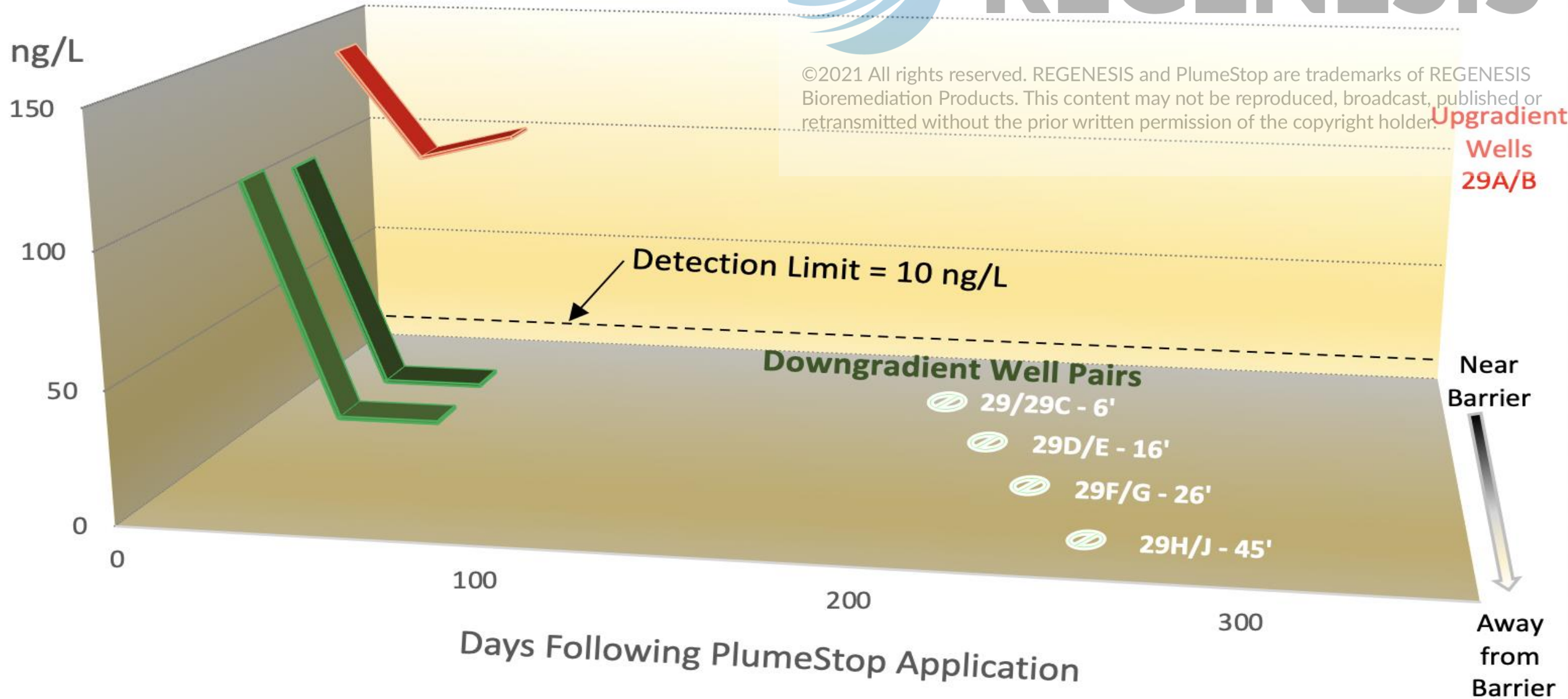
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Average Total PFAS in Monitoring Wells Upgradient and Downgradient of PlumeStop Barrier

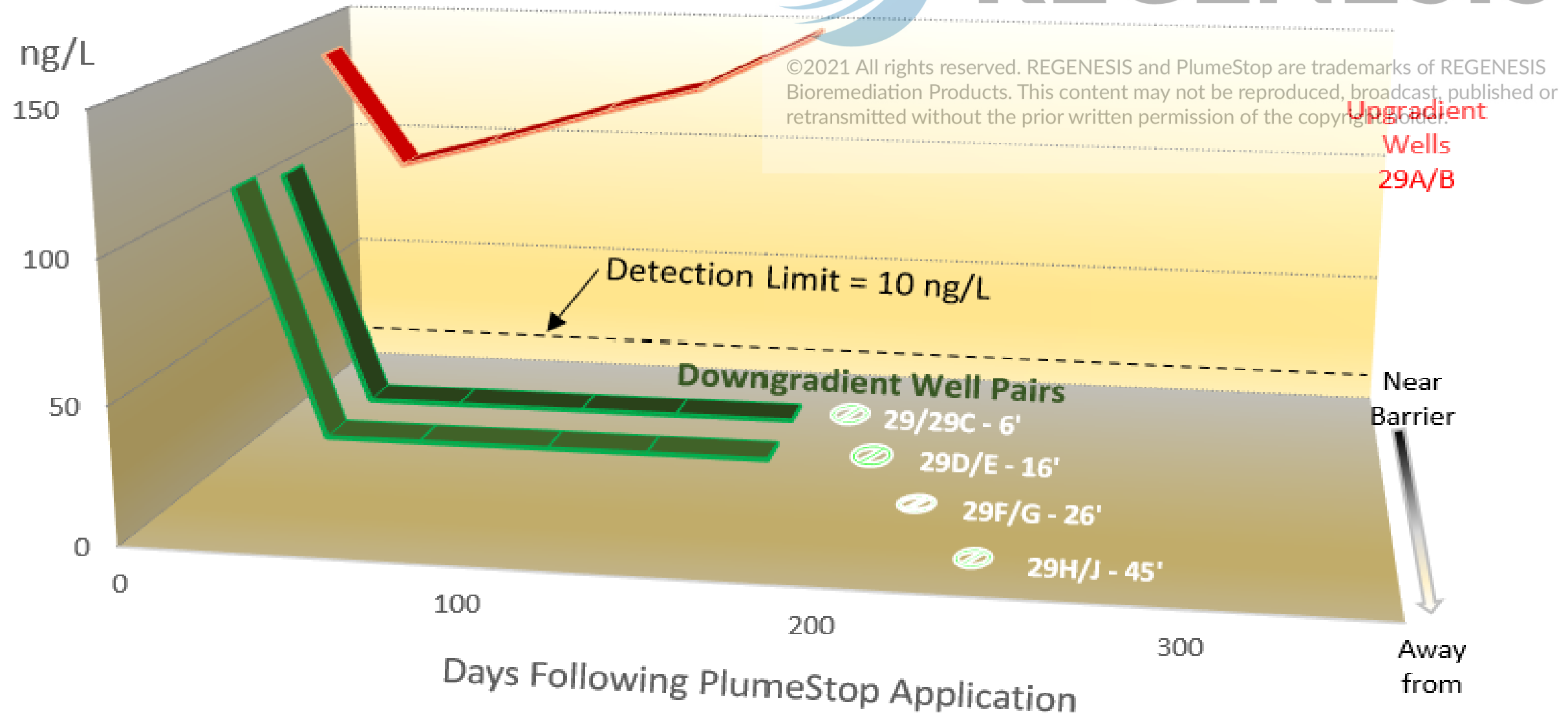


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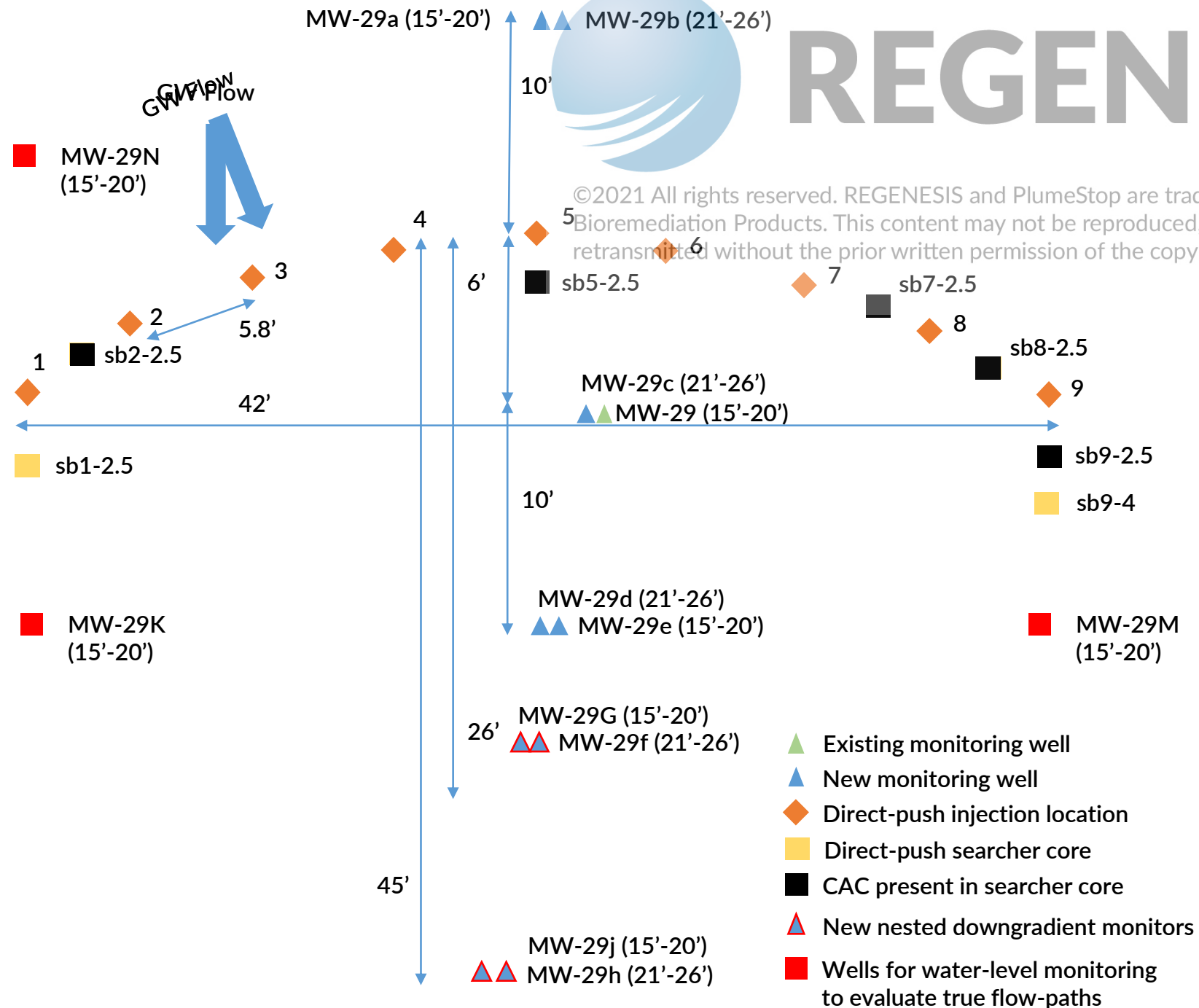


Average Total PFAS in Monitoring Wells Upgradient and Downgradient of PlumeStop Barrier

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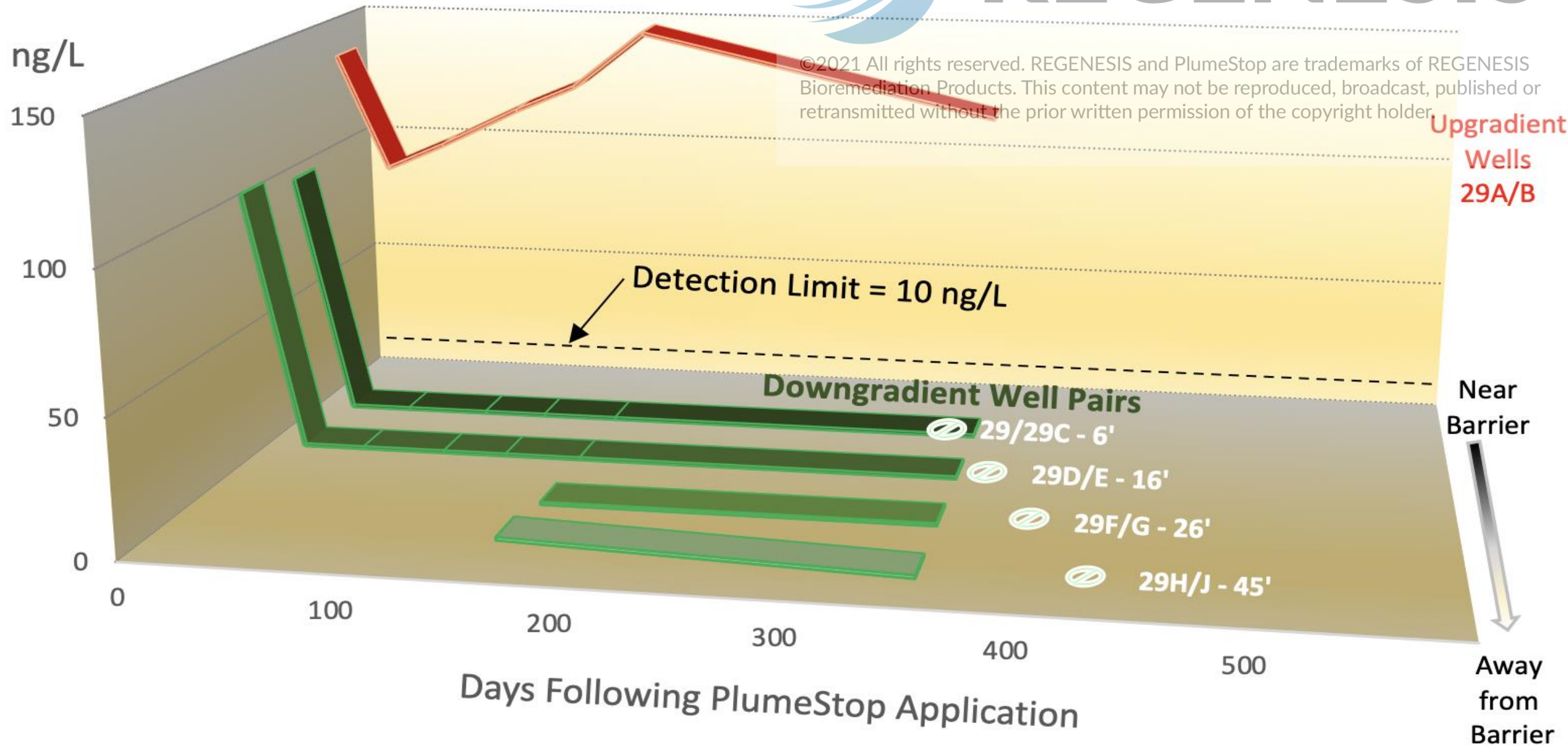


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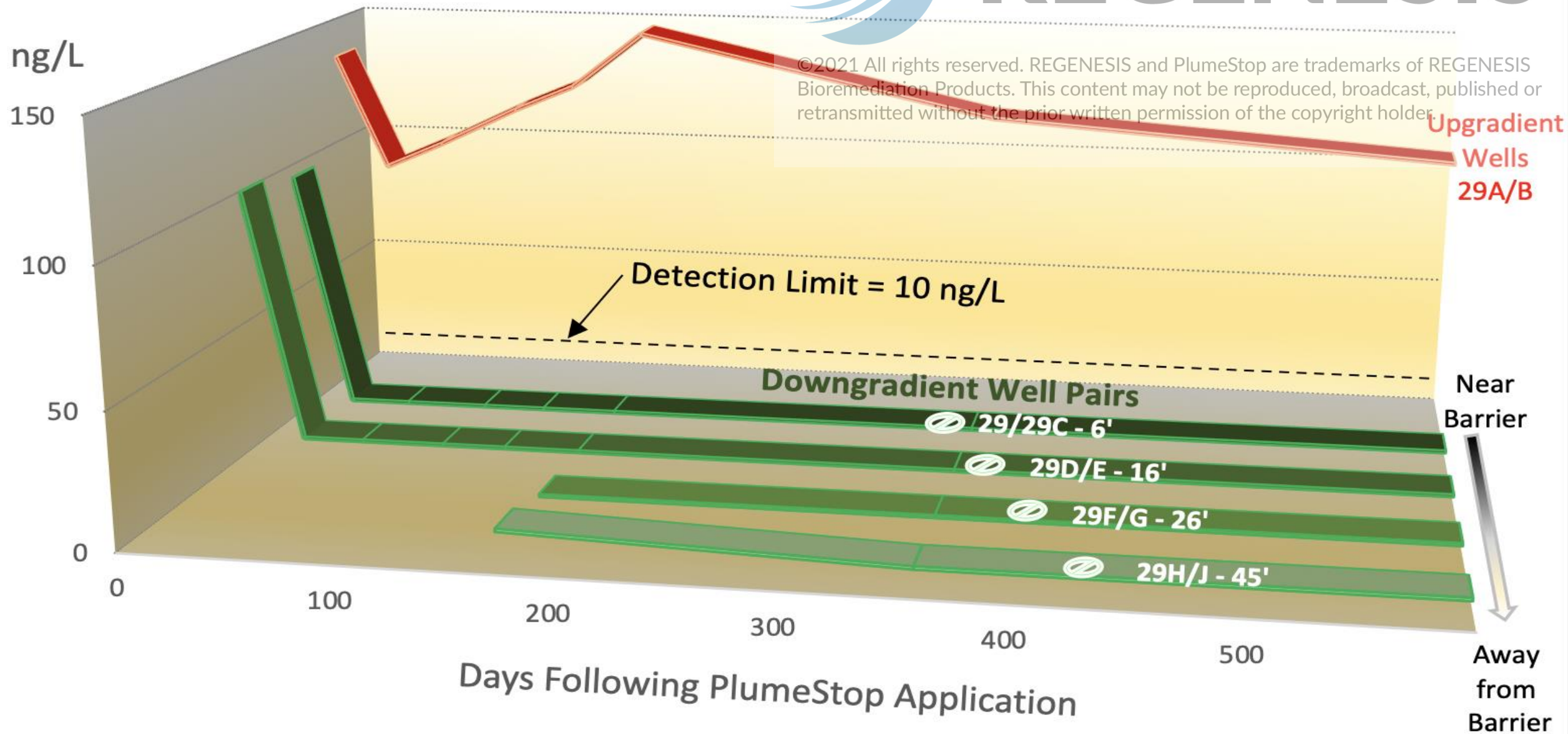
Average Total PFAS in Monitoring Wells Upgradient and Downgradient of PlumeStop Barrier

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Average Total PFAS in Monitoring Wells Upgradient and Downgradient of PlumeStop Barrier

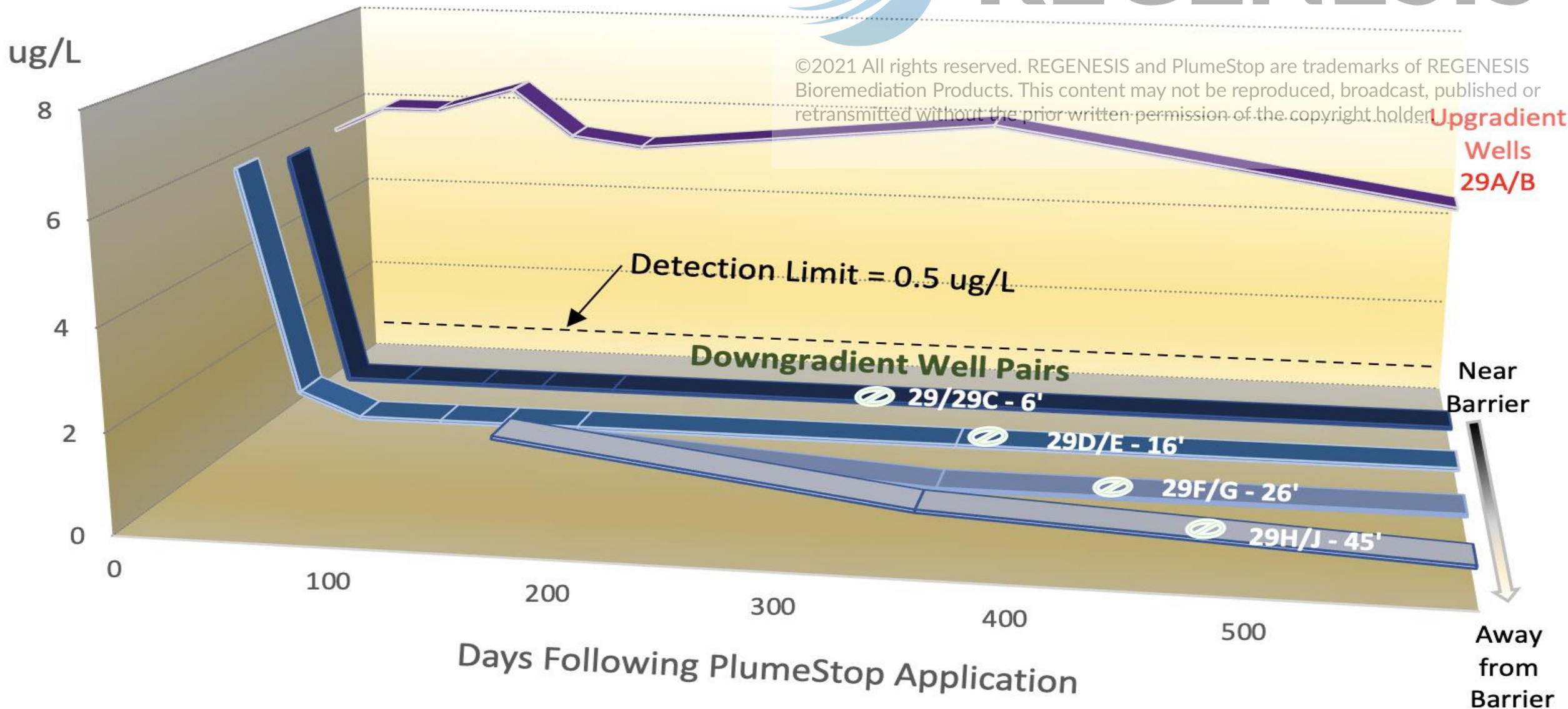
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Average Total PCE in Monitoring Wells Upgradient and Downgradient of PlumeStop Barrier



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Summary

- Very Successful Test
 - Verified distribution of CAC
 - Sustained reductions of PFAS and PCE over time
 - Anticipated to last for decades
 - Low cost alternative for possible remediation
- CAC provides a flexible, effective, *in situ* option to address PFAS
 - Passive plume control & containment
 - Prevent expansion of the problem
 - Manages the risk of PFAS in groundwater for years



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IN CLOSING

“The field crew was professional, efficient and worked hard to get our project completed on schedule”.

Gerlinde Wolf,
Environmental Engineer
AECOM

PlumeStop PFAS Sites



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114 PFAS Sites Worldwide

-  Completed Applications (16)
-  Scheduled Applications (4)
-  Design/Review Phase (94)

Advantages of PlumeStop Treatment

- Proven performance in the field
- Corroborated by third party research
- Highly effective at eliminating risk of PFAS *in situ*
- HIGHLY cost effective
 - A fraction of the cost of pump and treat
- No PFAS waste generated

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Cumulative Cost Comparison



LINKS TO PFAS RESOURCES

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Third Party Research and Press:

- <https://www2.regenesis.com/wiley-article-pfas-2020>
- <http://www2.regenesis.com/pfas-wiley-article>
- <https://genesis.com/wp-content/uploads/2019/02/Dayton-Daily-News-2020-07-20-01.pdf>
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General Links and Case Studies:

- www.pfastreatment.org
- <https://genesis.com/en/project/pilot-test-conducted-to-remove-pfas-risk/>
- <https://genesis.com/en/project/pfas-contaminants-reduced-to-non-detect/>
- <https://genesis.com/en/project/in-situ-remedy-addresses-pfas-risk-at-superfund-site/>
- <https://genesis.com/en/project/breakthrough-treatment-for-pfas/>
- <http://www2.regenesis.com/pfas-qa>
- <https://www2.regenesis.com/dod-pfas>



THANK YOU



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