Colloidal Activated Carbon Used to Enhance Natural Attenuation of PFAS at Airports Worldwide: A Multiple Site Review

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REGENESIS

Presentation Overview

- **Enhanced Attenuation of PFAS**
- **Effectiveness of CAC Treatment**
- **Case Studies**
  - Ever-changing Remediation Goals
  - Design & Implementation Process
  - Long-term Data

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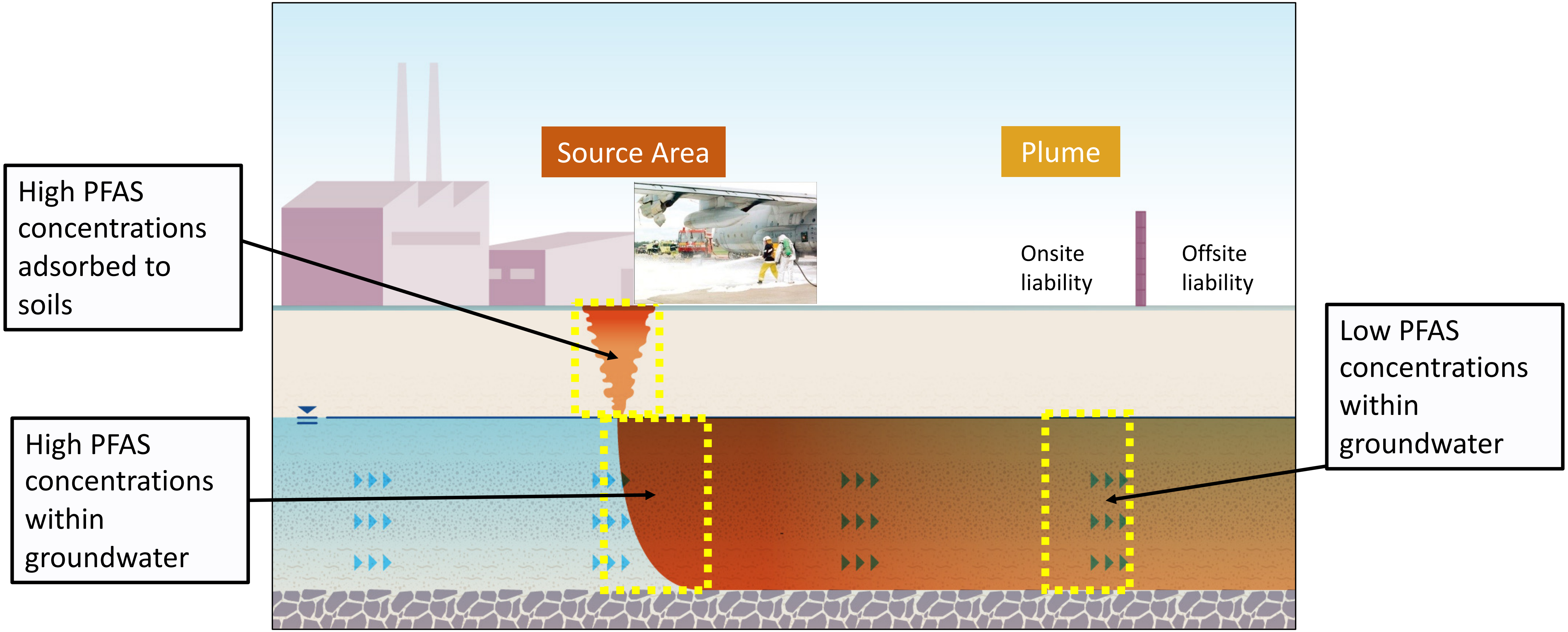
PFAS Sources/Plume System



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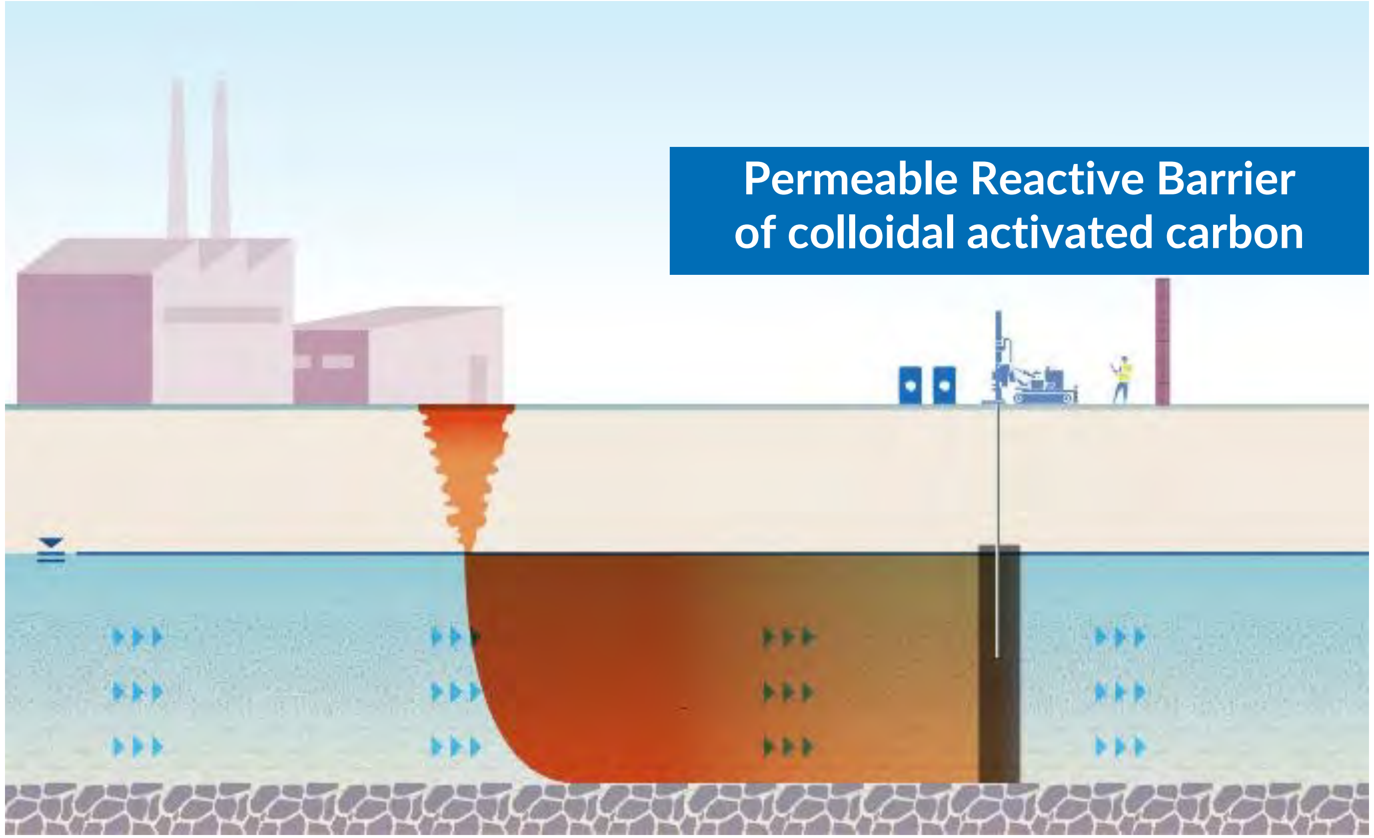
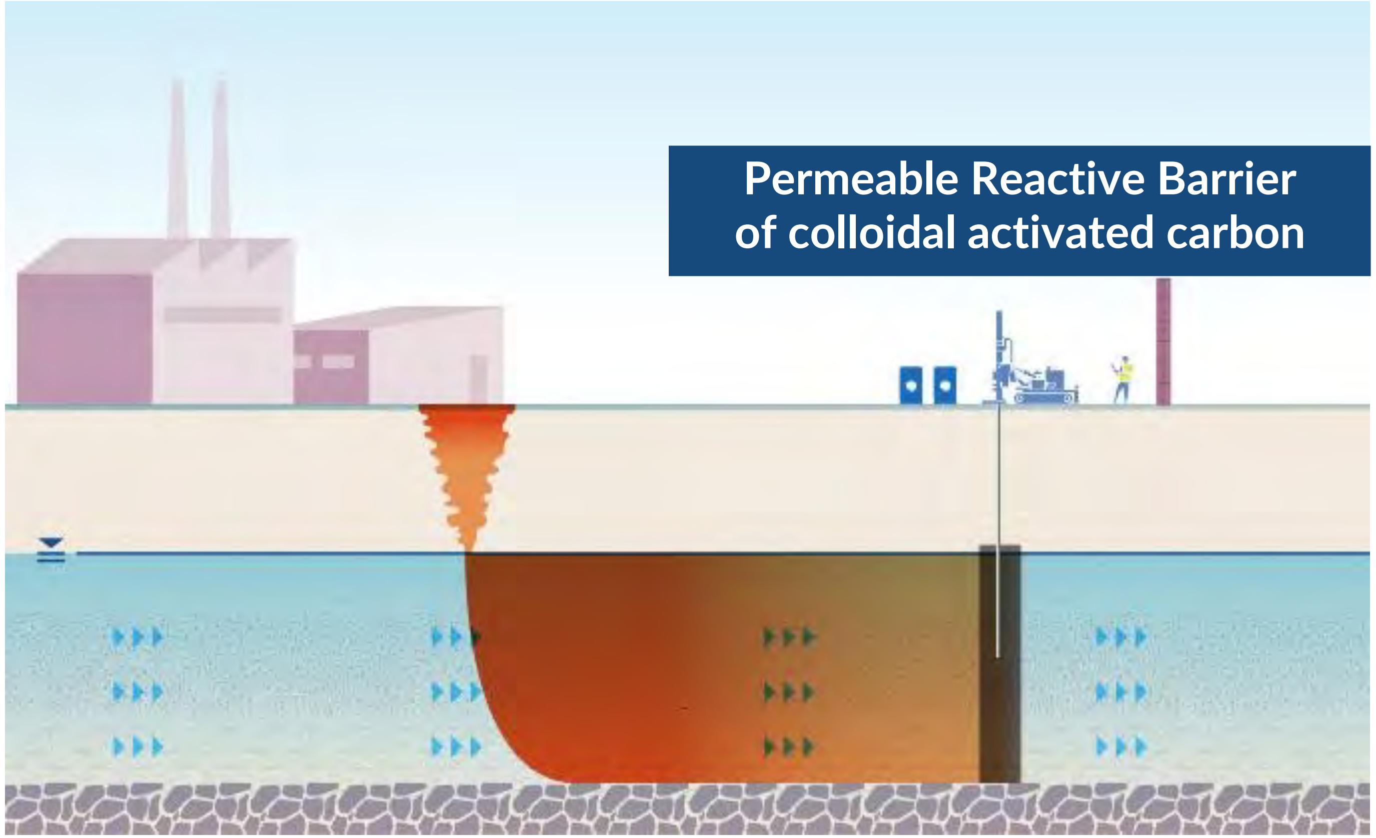
Plume Management Solution:
Enhanced Attenuation



"The result of applying an enhancement that **sustainably** manipulates a natural attenuation process, leading to an increased reduction in mass flux of contaminants."

Plume Management Solution:
Enhanced Attenuation



Common Questions:

Without contaminant destruction, how does this fit with remediation?

re·me·di·a·tion

/rəˌmēdēˈāSH(ə)n/

Noun

A Process used to reduce or eliminate the risk for humans and the environment that may result from exposure to harmful chemicals

Source: ITRC

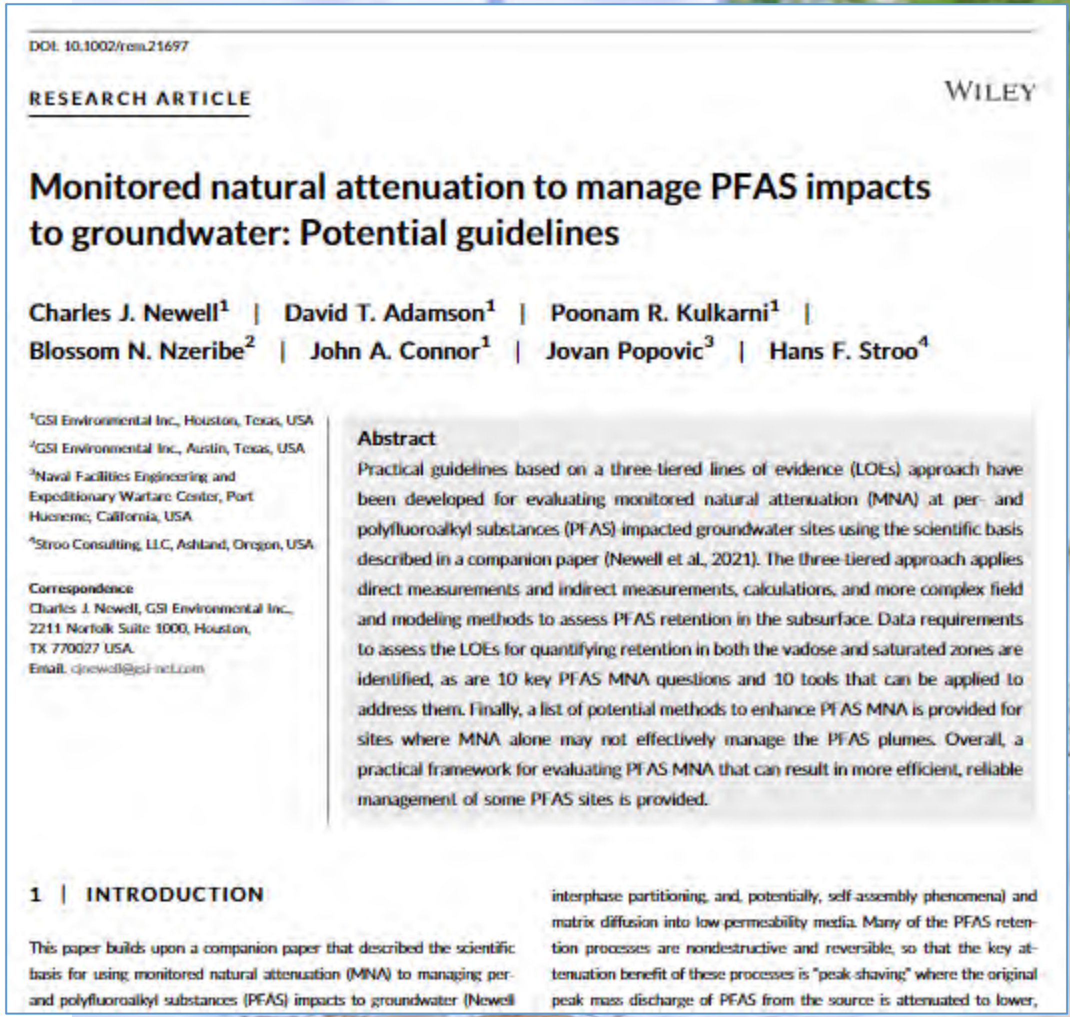
Eliminating Risk

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

US EPA: **Natural attenuation processes may reduce the potential risk posed by site contamination in three ways:**

1. Transformation of contaminants to a less toxic form
2. Reduction of contaminant concentrations
3. **Reduction of contaminant mobility and bioavailability**

Colloidal activated carbon adsorbs PFAS *in situ*, reducing mobility and exposure



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RESEARCH ARTICLE

WILEY

Monitored natural attenuation to manage PFAS impacts to groundwater: Potential guidelines

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Abstract
Practical guidelines based on a three-tiered lines of evidence (LOEs) approach have been developed for evaluating monitored natural attenuation (MNA) at per- and polyfluoroalkyl substances (PFAS) impacted groundwater sites using the scientific basis described in a companion paper (Newell et al., 2021). The three-tiered approach applies direct measurements and indirect measurements, calculations, and more complex field and modeling methods to assess PFAS retention in the subsurface. Data requirements to assess the LOEs for quantifying retention in both the vadose and saturated zones are identified, as are 10 key PFAS MNA questions and 10 tools that can be applied to address them. Finally, a list of potential methods to enhance PFAS MNA is provided for sites where MNA alone may not effectively manage the PFAS plumes. Overall, a practical framework for evaluating PFAS MNA that can result in more efficient, reliable management of some PFAS sites is provided.

1 | INTRODUCTION

This paper builds upon a companion paper that described the scientific basis for using monitored natural attenuation (MNA) to managing per- and polyfluoroalkyl substances (PFAS) impacts to groundwater (Newell

interphase partitioning, and, potentially, self-assembly phenomena) and matrix diffusion into low permeability media. Many of the PFAS retention processes are nondestructive and reversible, so that the key attenuation benefit of these processes is "peak-shaving" where the original peak mass discharge of PFAS from the source is attenuated to lower,

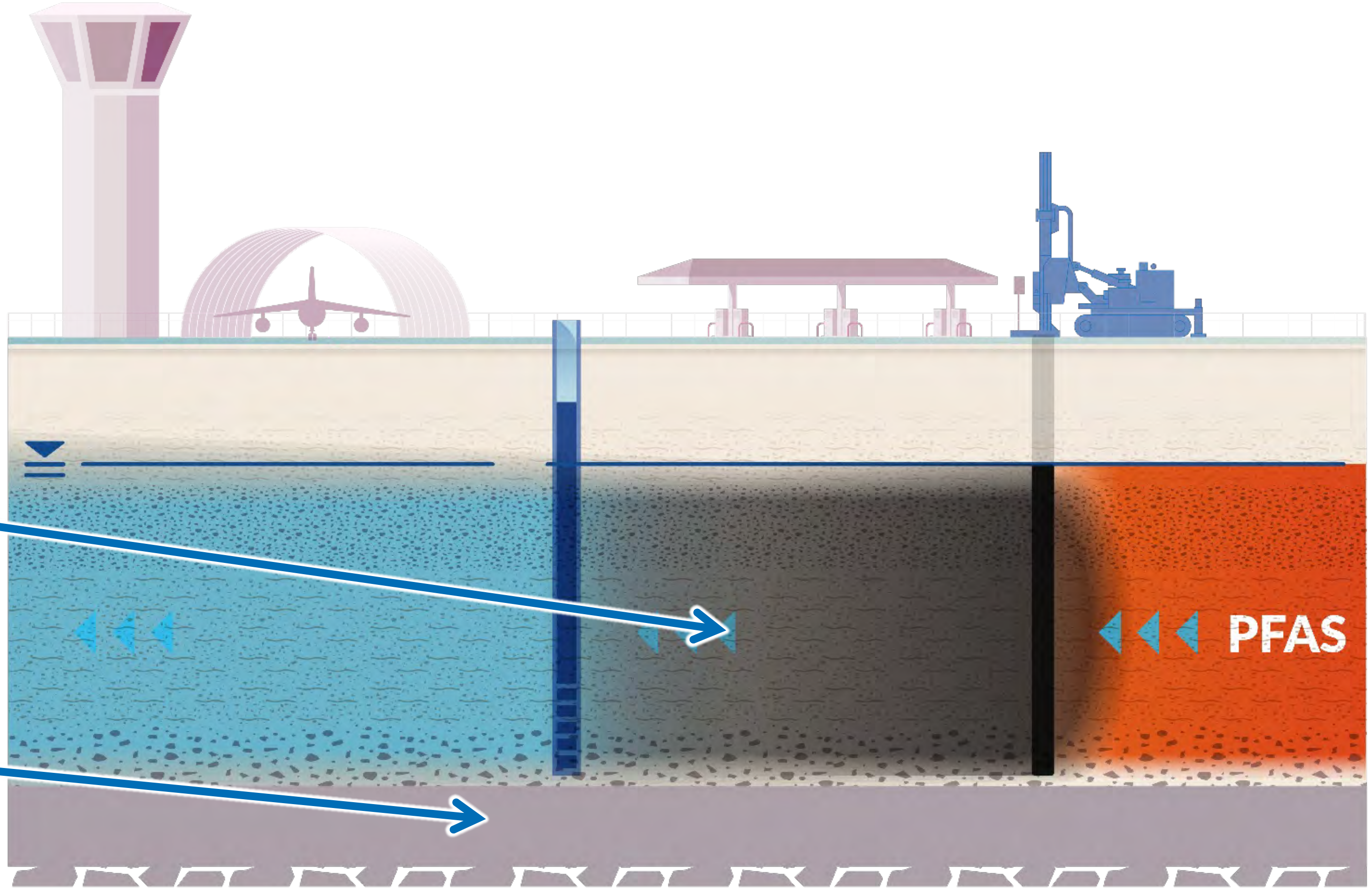
U.S. EPA. Use of Monitored Natural Attenuation for Inorganic Contaminants at Superfund Sites, Directive 9283.1-36. Published online 2015.
Newell CJ, et al. Monitored Natural Attenuation to Manage PFAS Impacts to Groundwater: Scientific Basis. Groundwater Monitoring & Remediation. 2021;41(4):76-89.
Newell CJ, et al. Monitored natural attenuation to manage PFAS impacts to groundwater: Potential guidelines. Remediation Journal. 2021;31(4):7-17.
ER21-5198. Accessed December 15, 2021. https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/ER21-5198/ER21-5198.

Colloidal Activated Carbon

- Form of Activated Carbon
- Particle Sizes 1 – 2 µm
- Suspended as a colloid in a polymer solution
- Distributes Widely Under Low Pressure
- Provides extremely fast sorption sites
- Converts underlying geology into purifying filter

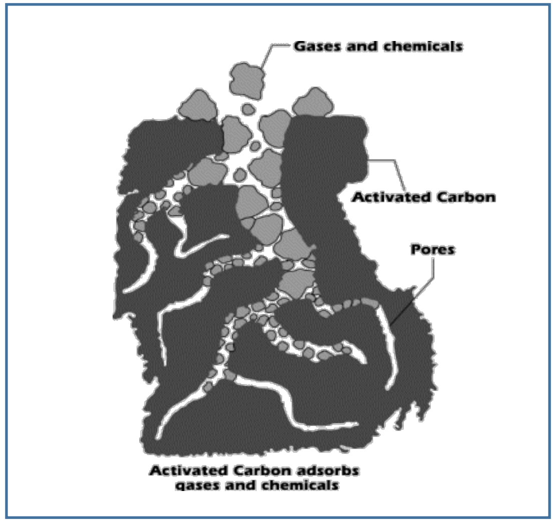
PLUME STOP
Liquid Activated Carbon

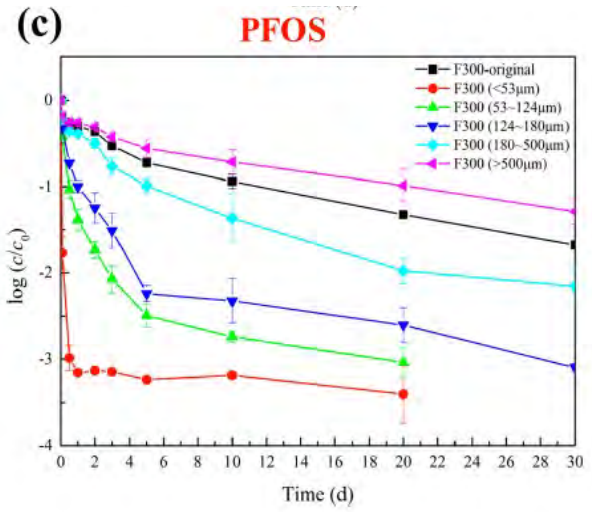
Treatment of Flux Zones and Control of Back Diffusion & COC Migration



Colloidal Activated Carbon

- **Optimized PFAS sorption**
  - Smaller particles provide more exterior surface
  - Shorter distance to all the sorption sites compared to PAC or GAC
  - Results in rapid and highly efficient sorption





Granular Activated Carbon (>500µm)

- **Limited surface area exposed to solute**
- **Slow, incomplete sorption**

Colloidal Activated Carbon (1-2µm)

- **More rapid and complete use of sorption sites**
- **Faster more effective sorption of PFAS**

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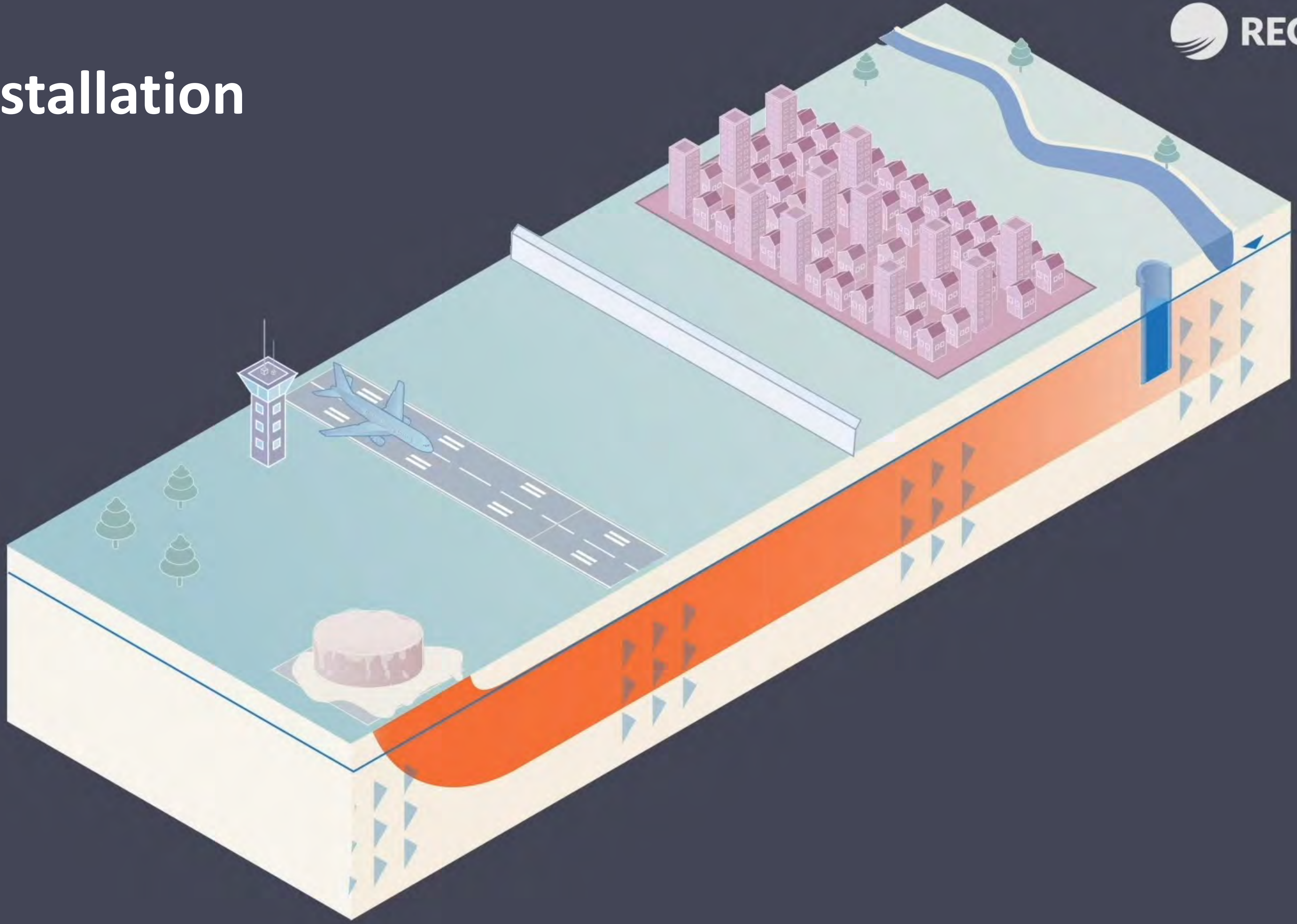
Source: Xiao, Ulrich, Chen & Higgins. Environ. Sci. Technol. 2017, 51, 6342-6351

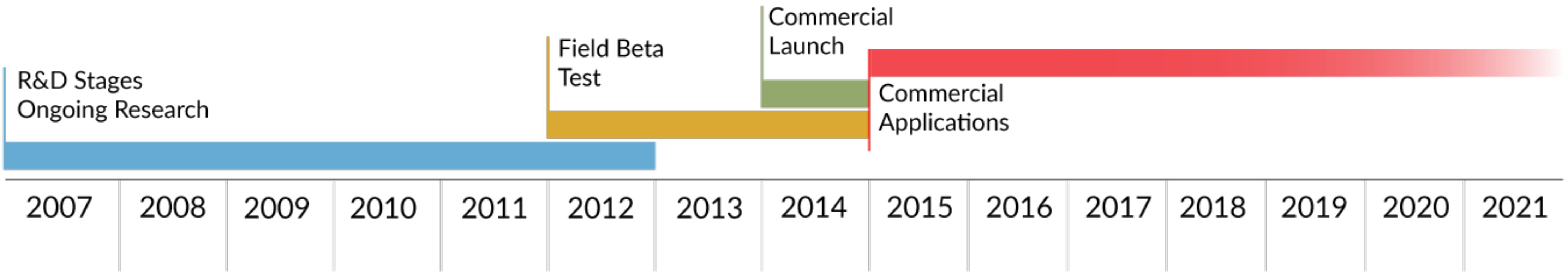
CAC Installation



5 Year Research and Development Process

The R&D process was exhaustive, spanning five years and resulting in the issuance of seven patents for the innovations that make PlumeStop possible.

PLUME STOP®
Liquid Activated Carbon



Current Research and Development Efforts

- **Field Demonstration of CAC for *In Situ* Sequestration of PFAS**
  - NESDI project 569 (APTIM)

- **Validation of CAC for Preventing the Migration of PFAS**
  - Principal Investigator: Paul Hatzinger

- **An Investigation of Factors Affecting *In Situ* PFAS Immobilization by Activated Carbon**
  - Principal Investigator:
    Dr. Neil Thompson, University of Waterloo

- **Additional Support of Domestic and International Research Projects in Academia**

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How does CAC distribute in the subsurface?

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PlumeStop

PLUME STOP™
Liquid Activated Carbon

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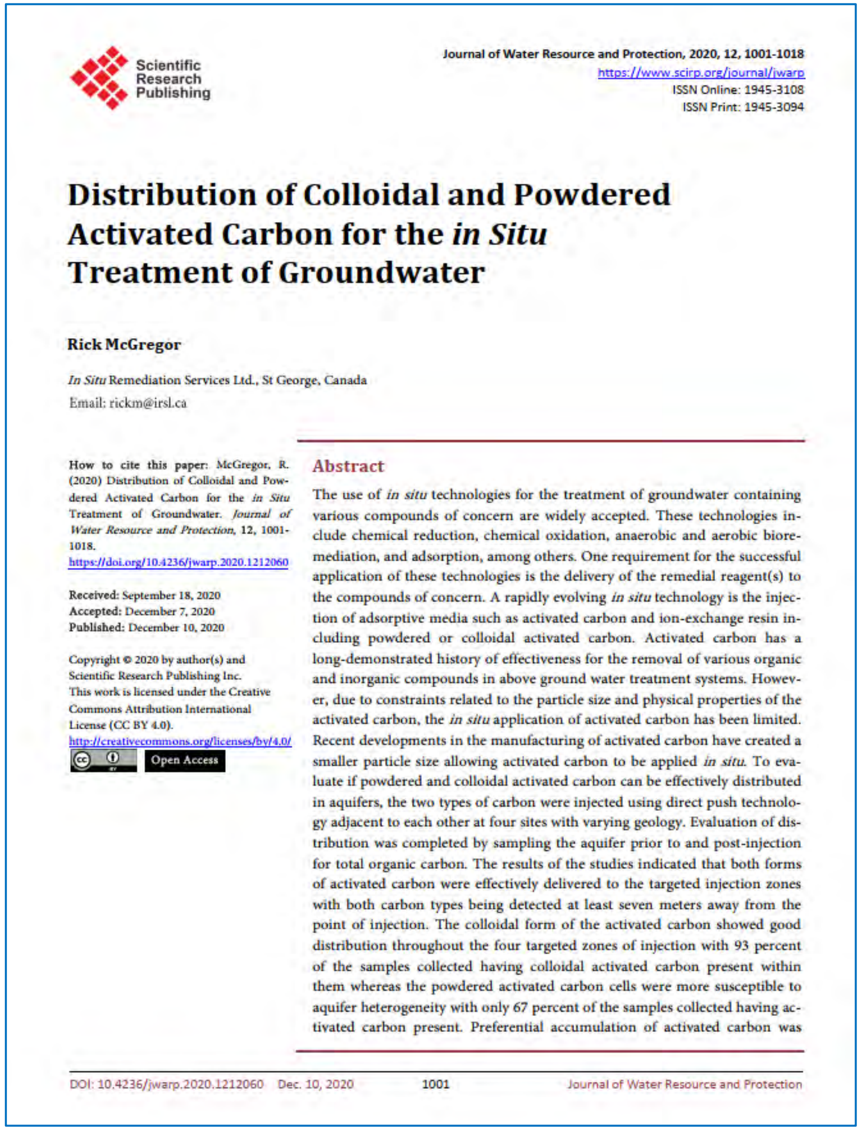
Reagent Distribution Research

CAC vs PAC Distribution Study

- **4 sites, two 10x10m test cells each – 8 plots**
- **~65 soil samples per plot to find AC (520 total)**



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Distribution of Colloidal and Powdered Activated Carbon for the *in Situ* Treatment of Groundwater

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https://doi.org/10.4236/jwarp.2020.1212060

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Abstract

The use of *in situ* technologies for the treatment of groundwater containing various compounds of concern are widely accepted. These technologies include chemical reduction, chemical oxidation, anaerobic and aerobic bioremediation, and adsorption, among others. One requirement for the successful application of these technologies is the delivery of the remedial reagent(s) to the compounds of concern. A rapidly evolving *in situ* technology is the injection of adsorptive media such as activated carbon and ion-exchange resin including powdered or colloidal activated carbon. Activated carbon has a long-demonstrated history of effectiveness for the removal of various organic and inorganic compounds in above ground water treatment systems. However, due to constraints related to the particle size and physical properties of the activated carbon, the *in situ* application of activated carbon has been limited. Recent developments in the manufacturing of activated carbon have created a smaller particle size allowing activated carbon to be applied *in situ*. To evaluate if powdered and colloidal activated carbon can be effectively distributed in aquifers, the two types of carbon were injected using direct push technology adjacent to each other at four sites with varying geology. Evaluation of distribution was completed by sampling the aquifer prior to and post-injection for total organic carbon. The results of the studies indicated that both forms of activated carbon were effectively delivered to the targeted injection zones with both carbon types being detected at least seven meters away from the point of injection. The colloidal form of the activated carbon showed good distribution throughout the four targeted zones of injection with 93 percent of the samples collected having colloidal activated carbon present within them whereas the powdered activated carbon cells were more susceptible to aquifer heterogeneity with only 67 percent of the samples collected having activated carbon present. Preferential accumulation of activated carbon was

McGregor, R.(2020) Distribution of Colloidal and Powdered Activated Carbon for the in Situ Treatment of Groundwater. Journal of Water Resource and Protection, 12, 1001-1018.

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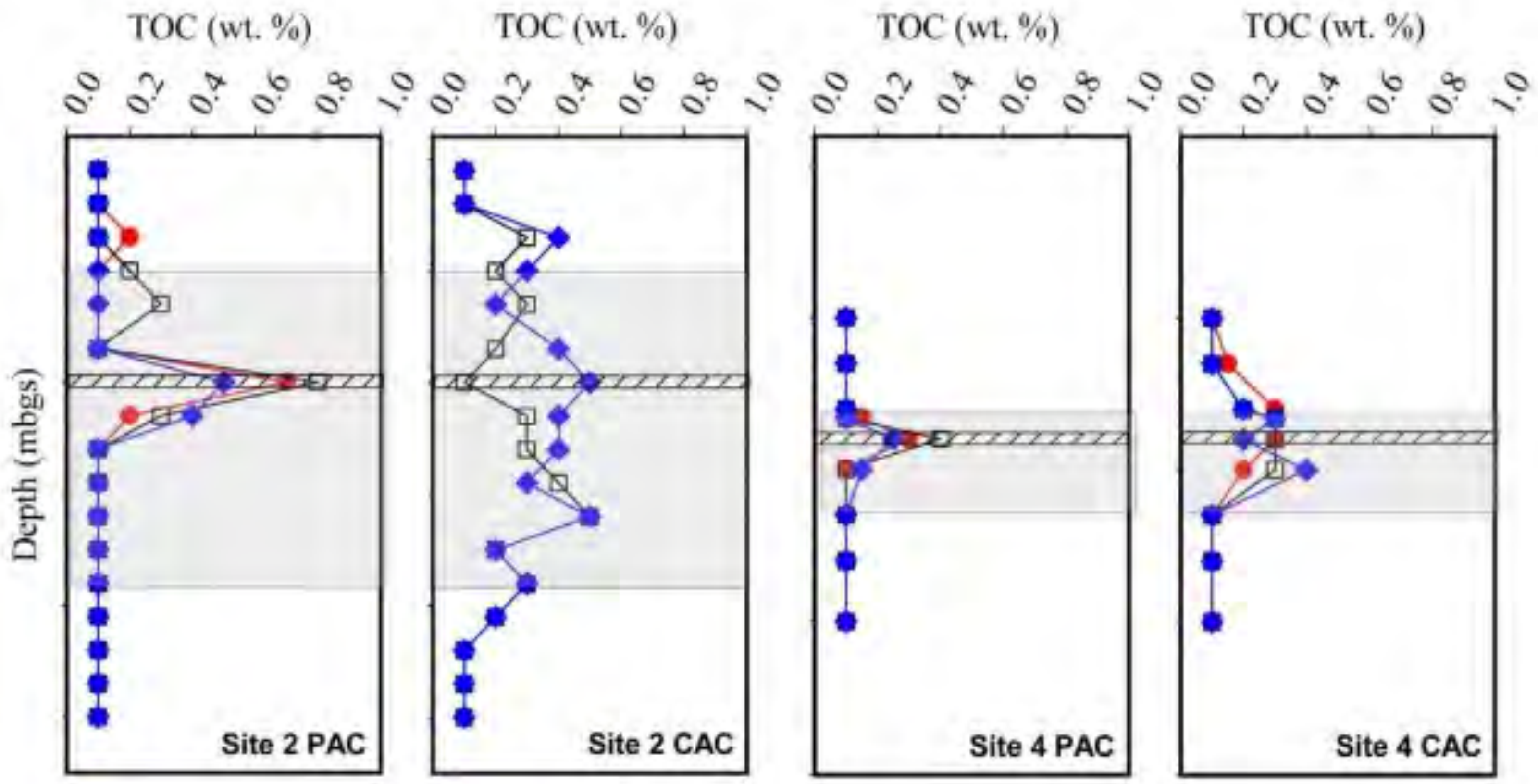
Reagent Distribution Research



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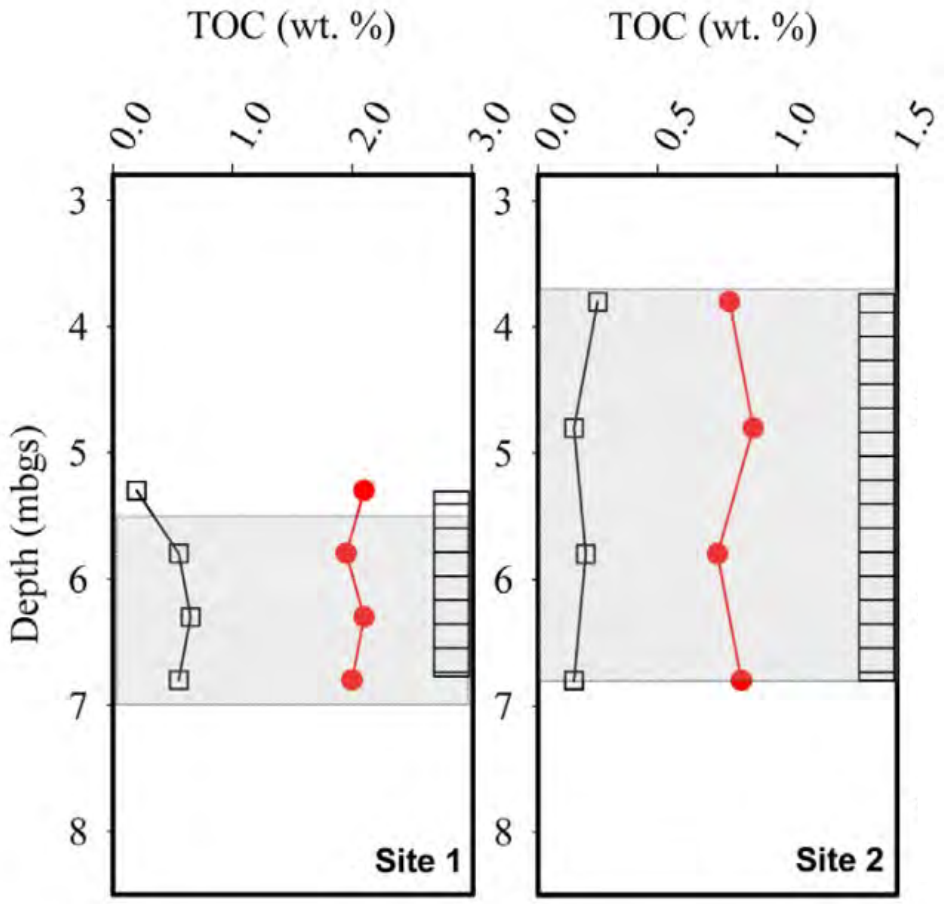
Accumulation of Carbon within the Well Sand-pack?

PAC:

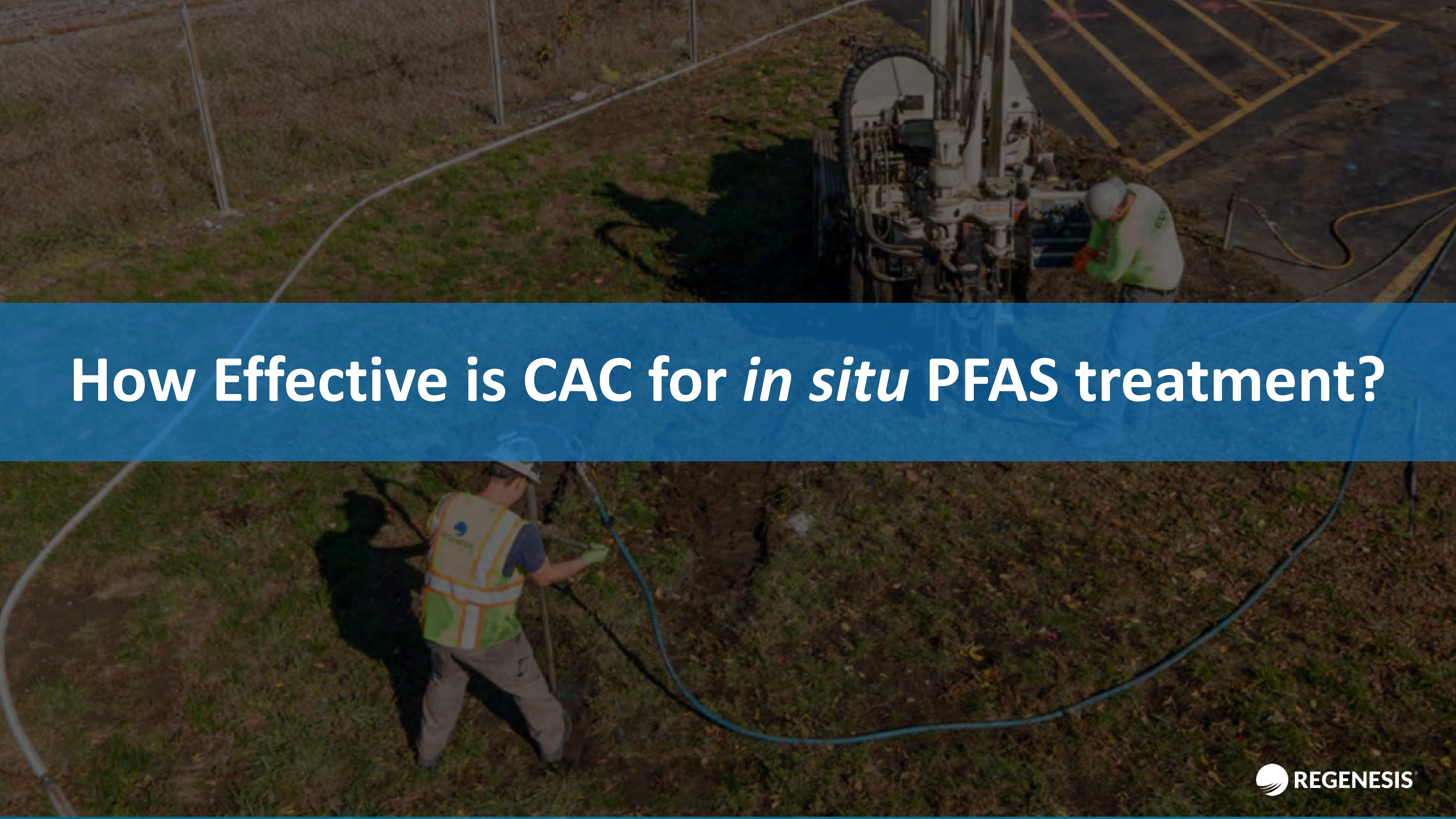
- TOC at 1.65 weight percent
- +224% mean TOC of the surrounding targeted injection zone

CAC:

- TOC at 0.65 weight percent
- -35% mean TOC of the surrounding targeted injection zone



How Effective is CAC for *in situ* PFAS treatment?



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DOI: 10.1002/rem.21741

RESEARCH ARTICLE

WILEY

Longevity of colloidal activated carbon for in situ PFAS remediation at AFFF-contaminated airport sites

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…g information
…ater Solutions, Ontario Centers for …nce, and Natural Sciences and …ering Research Council

Abstract

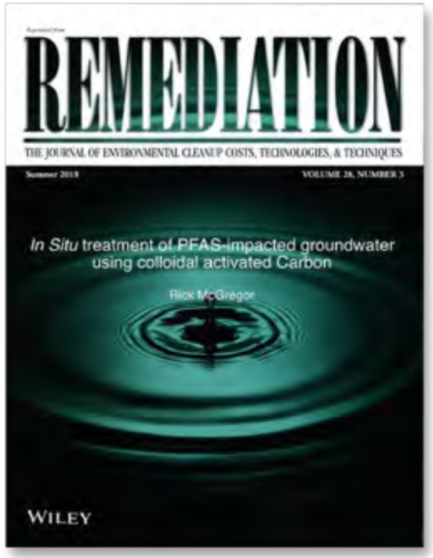
A review of state per- and polyfluoroalkyl substances (PFAS) guidelines indicates that four long-chain PFAS (perfluorooctanesulfonic acid [PFOS] and perfluorooctanoic acid [PFOA] followed by perfluorohexanesulfonic acid [PFHxS] and perfluorononanoic acid [PFNA]) are the most frequently regulated PFAS compounds. Analysis of 17 field-scale studies of colloidal activated carbon (CAC) injection at PFAS sites indicates that in situ CAC injection has been generally successful for both short- and long-chain PFAS in the short-term (0.3–6 years), even in the presence of low levels of organic co-contaminants. Freundlich isotherms were determined under competitive sorption conditions using a groundwater sample from an aqueous film-forming foam (AFFF)-impacted site. The median concentrations for these PFAS of interest at 96 AFFF-impacted sites were used to estimate influent concentrations for a CAC longevity model sensitivity analysis. CAC longevity estimates were shown to be insensitive to a wide range of potential cleanup criteria based on modeled conditions. PFOS had the greatest longevity even though PFOS is present at higher concentrations than the other species because the CAC sorption affinity for PFOS is considerably higher than PFOA and PFHxS. Longevity estimates were directly proportional to the CAC fraction in soil and the Freundlich K_F, and were inversely proportional to the influent concentration and average groundwater velocity.

Grant Carey

Independent assessment of PFAS CAC applications at Airport Sites

- PoreWater Solutions
- InSitu Remediation Services Ltd
- University of Waterloo
- University of Toronto

- *Treatment Expected to last decades*
- *Source reductions extend longevity*



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Paper Highlights

- Airports PFAS Sites (96 reviewed)
  - 82% dominated by PFOS and PFHxS (Grayling)
  - Preferentially sorbed to AC
- 17 Field Sites show Success with Co-Contaminants PHC/VOC (Grayling)
- *In Situ* CAC has much Longer Breakthrough Time vs. *ex situ* AC
  - particle size and extended retention
- Longevity Impacted Mostly by Incoming Mass Flux

TABLE 1a CAC field studies with a measured fraction of CAC in soil (f_{cac})

Field site ID	Reference	Maximum detected PFAS groundwater concentrations before CAC injection(µg/L)	Maximum concentrations of co-contaminants before CAC injection (µg/L)	Soil type	Measuredf_{cac}	Description of monitoring network within the CAC adsorption zone	No. of postinjection monitoring events	Postinjectionmonitoring events (days after injection)	Summary of postinjection PFAS monitoring results
1	McGregor (2018), Carey et al. (2019)	PFOA: 3.26 and PFOS: 1.45	BTEX: 300 GRO: 2000 DRO: 3500	Silty sand	0.02%	Four monitoring wells	11	79, 175, 298, 350, 449, 533, 689, 1050, 1415, 1780, 2145	No detections of PFAS in the CAC adsorption zone over first 10 postinjection monitoring events (5 years), with the exception of a single well with low detections of PFOS and PFUnA at t = 533 days (40 and 20 ng/L, respectively). First five monitoring events included lab analysis for only PFOS and PFOA; lab analysis in the last six events included a full suite of PFAAs. In Event 11 (6 years), the detection limits were lowered to about 1 ng/L, and several PFAS were observed slightly above the new detection limits in this last event.
2	McGregor, 2020a	PFBA: 6.2; PFPeA: 24.0; PFHxA: 16.1; PFHpA: 6.08; PFOA: 0.45; and PFNA: 0.14	Petroleum hydrocarbons: 3500	Fine-grained sand	0.08%	Three monitoring wells and one well multilevel with three screened intervals	5	92, 184, 278, 366, 549	No detections of PFAS in the CAC adsorption zone over all five postinjection monitoring events (1.5 years).
3	McGregor and Benevento (2021)	PFBA: 6.405; PFPeA: 24.0; PFHxA: 15.74; PFHpA: 7.25; PFOA: 0.91; PFNA: 0.165; and PFOS: 2.105	Total BTEX: 6160	Silty sand and sand	0.76%	Three multilevel wells (two wells with seven screened intervals, and one well with three screened intervals)	3	182, 273, 366	No detections of PFAS in the CAC adsorption zone in unconsolidated media over all three postinjection monitoring events (1 year).
4	McGregor and Zhao (2021)	PFBA: 0.795; PFPeA: 12.8; PFHxA: 3.24; PFOA: 0.95; and PFOS: 2.14	TCE: 985 cis-1,2-DCE: 258 vinyl chloride: 54	Silty sand	0.07%	Three monitoring wells	5	122, 248, 362, 547, 724	No detections of PFAS in the CAC adsorption zone over all five postinjection monitoring events (2 years).

Abbreviations: BTEX, benzene, toluene, ethylbenzene, and xylenes; CAC, colloidal activated carbon; DCE, dichloroethene; DRO, diesel range organics; GRO, gasoline range organics; PFAS, per- and polyfluoroalkyl substances; PFBA, perfluorobutanoic acid; PFHpA, perfluoroheptanoic acid; PFHxA, perfluorohexanesulfonic acid; PFNA, perfluorononanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonic acid; PFPeA, perfluoropentanoic acid; PFUnA, perfluoroundecanoic acid; TCE, trichloroethene.

Summary REGENESIS AIRPORT Projects

		PFOA/PFOS max (ug/L)	Results
MA airport	barrier		Met remediation Goals in 3 months
Camp Grayling Air Field	barrier	ND/.06	Met Remediation Goals, maintained 4+ years
MI airport	barrier	0.024/.511	Met Remediation Goals in 3 months
UK Int airport	barrier	.316/.014	Met remediation goals
UK commercial airport	barrier	5.66/.62	Met Remediation Goals, project under Plume Shield Warranty
Fairbanks AK	barrier	.24/.28	Met Remediation Goals, maintained 2+ years
Federal Facility Airport	grid		Met Remediation Goals
Ontario	barrier	0.042/1.5	downgradient wells trending downward 50% reduction observed, does not have near barrier well
NY airport	barrier	0.172/.823	waiting for data

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Source Zone Treatment

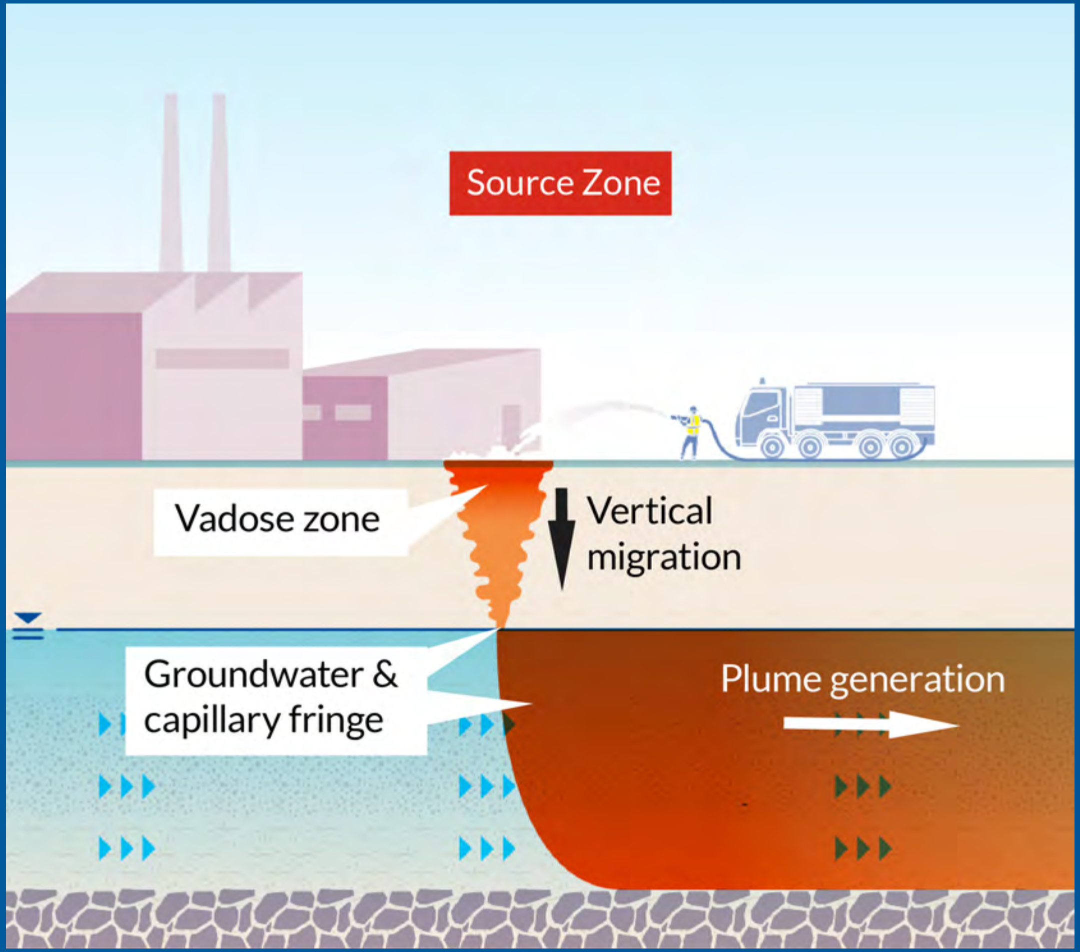
Plume Management Solution: Source Zones

What is the Goal

- Manage soils in place
- Promote ENA of groundwater plume
- Long-term reduction in PFAS mass discharge

Achieving the goal by

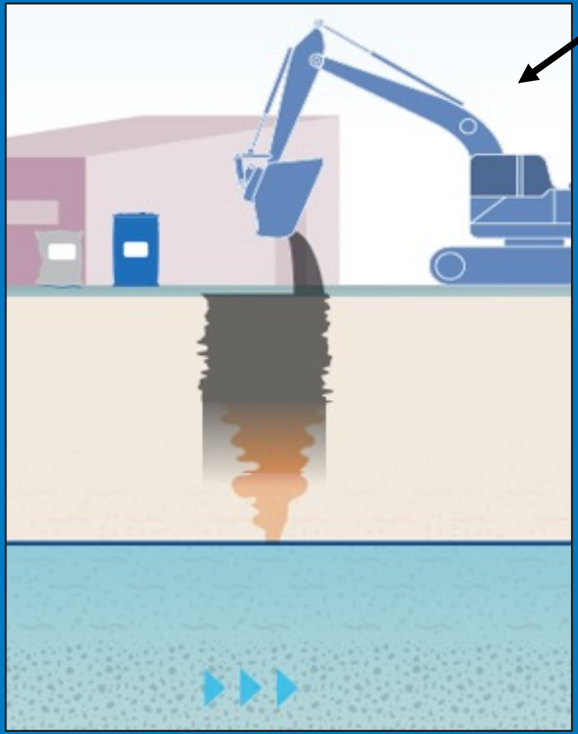
- Leachability reduction of vadose soils
- Infiltration reduction of vadose soils
- Prevent residual PFAS moving downward with horizontal barriers



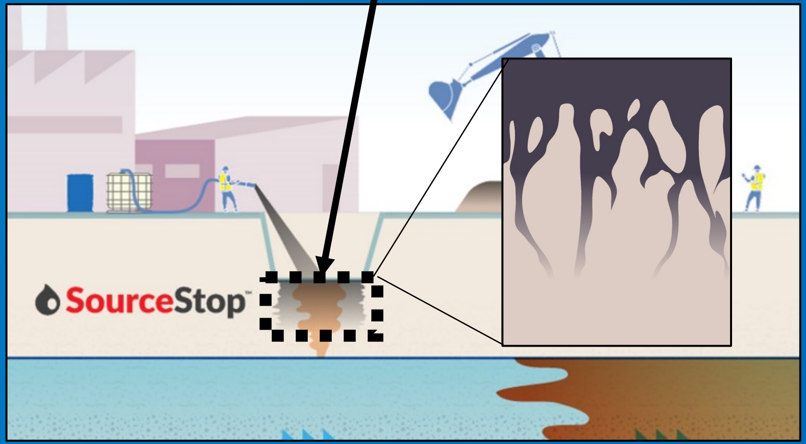
Source Application Approaches

Source Treatment Application Methods

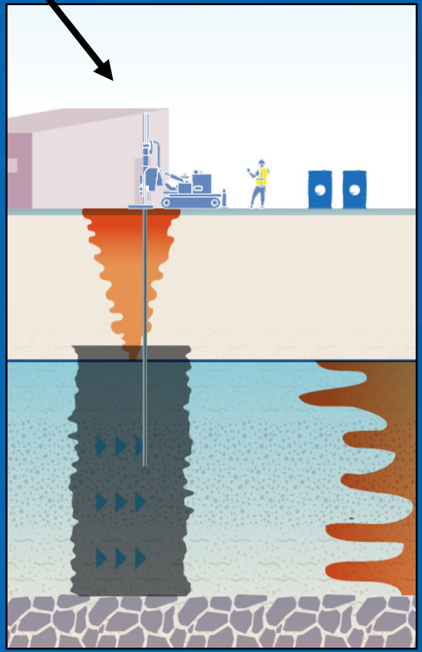
Mechanical Soil Mixing with Bulk Amendments
- Reduce leachability
- Reduce permeability (infiltration)



Horizontal Barrier
- Reduce leachability
- Immobilize PFAS mass migrating downward



Groundwater Treatment
- Direct injection

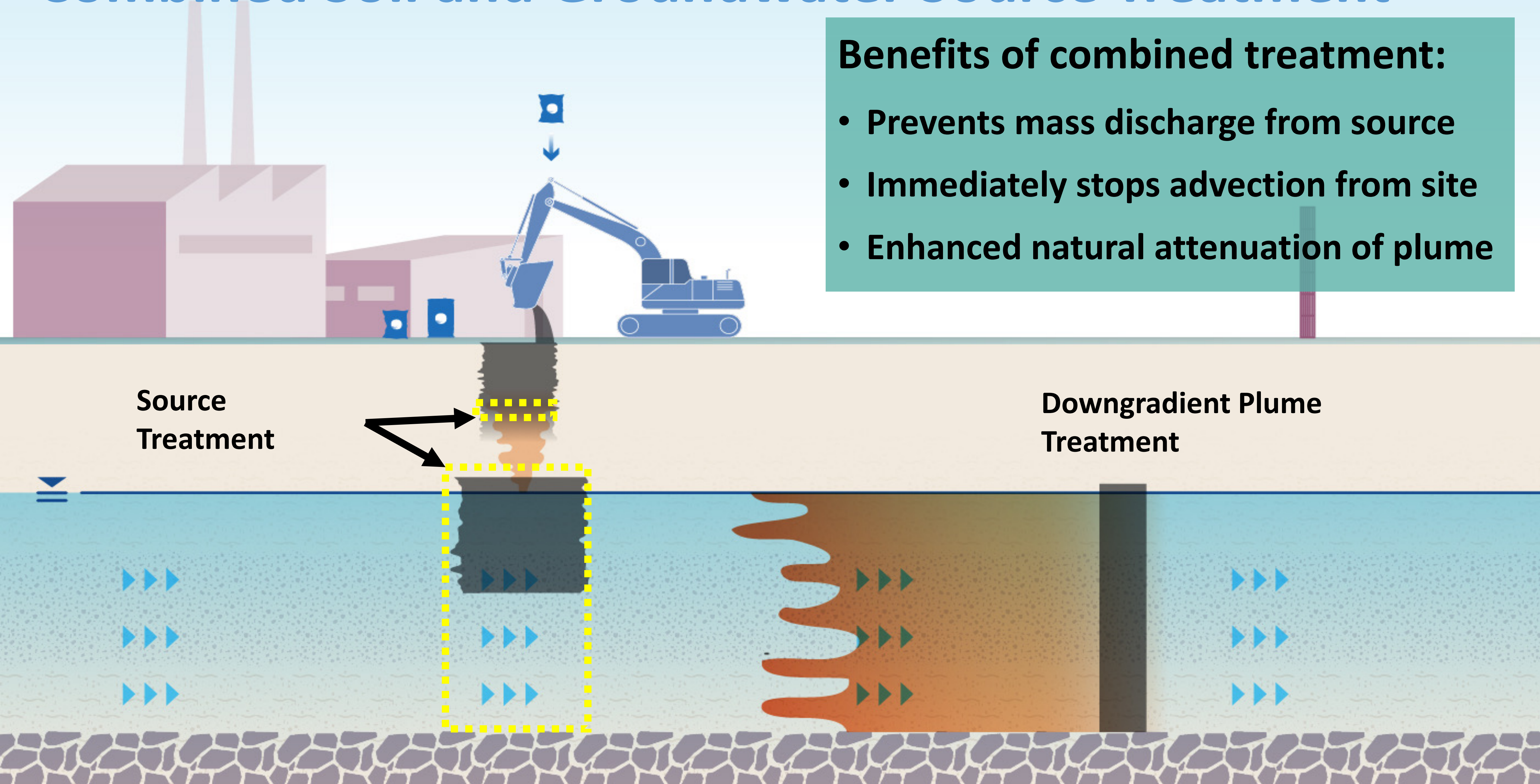


Combining Source and Plume Treatment

Combined Soil and Groundwater Source Treatment

Benefits of combined treatment:

- Prevents mass discharge from source
- Immediately stops advection from site
- Enhanced natural attenuation of plume



Case Study #1

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Grayling Army Airfield

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Background

- Founded 1913
- 147,000 Acres
- Largest National Guard Training Center in the Country
- Home to Grayling Army Airfield (900 Acres)
- Contaminant Release History:
  - Diesel, PCE/TCE, PFAS
- Remediation History:
  - Pump and Treat, Air Sparging/SVE

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Case Study: Pilot Test

Former Bulk Storage Tanks Location

Site Details

GW Velocity	~250 ft/yr
Vertical Treatment Interval	15’-27’ bgs.
Injection Points	9
Soil Type	Coarse, Medium to Fine Sand with Clay at 27’ bgs
Sensitive Receptors	Residences, Surface water bodies, Property Boundary
Contaminants of Concern	8 µg/L PCE and 130 ng/L Total PFAS, Primarily PFOS & PFHxS

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Ever-changing Remediation Goals

- **Fall 2018: 70ppt Total PFOS/PFOA USEPA Health Advisory Level**
- **August 2020: Michigan MCLs**
- **March 2023: Proposed USEPA MCLs**

Summary

EPA is proposing a National Primary Drinking Water Regulation (NPDWR) to establish legally enforceable levels, called Maximum Contaminant Levels (MCLs), for six PFAS in drinking water. PFOA and PFOS as individual contaminants, and PFHxS, PFNA, PFBS, and HFPO-DA (commonly referred to as GenX Chemicals) as a PFAS mixture. EPA is also proposing health-based, non-enforceable Maximum Contaminant Level Goals (MCLGs) for these six PFAS.

Compound	Proposed MCLG	Proposed MCL (enforceable levels)
PFOA	Zero	4.0 parts per trillion (also expressed as ng/L)
PFOS	Zero	4.0 ppt
PFNA	1.0 (unitless) Hazard Index	1.0 (unitless) Hazard Index
PFHxS		
PFBS		
HFPO-DA (commonly referred to as GenX Chemicals)		

Source: https://www.michigan.gov/pfasresponse/drinking-water/mcl
Source: https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

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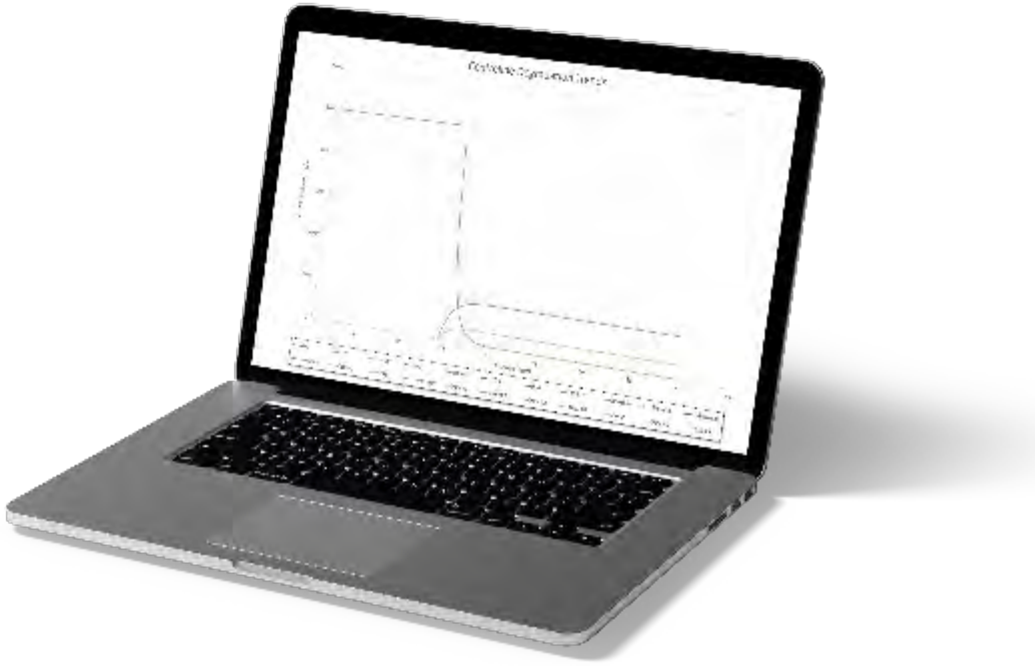
Simple Plume Cut-Off Barrier

Modeling in the Design Process

- **Key Factors:**
  - Target contaminant of concern
    - VOCs, PFAS, etc.
    - Compound Specific Isotherms
  - Contaminant Mass Flux
  - Non-target compounds present
  - Competitive Sorption and Degradation (if applicable)
- **Model Considerations:**
  - Carbon Dose
  - Vertical Variations
  - Barrier Thickness
  - Time

PlumeForce™
Modeling Tool

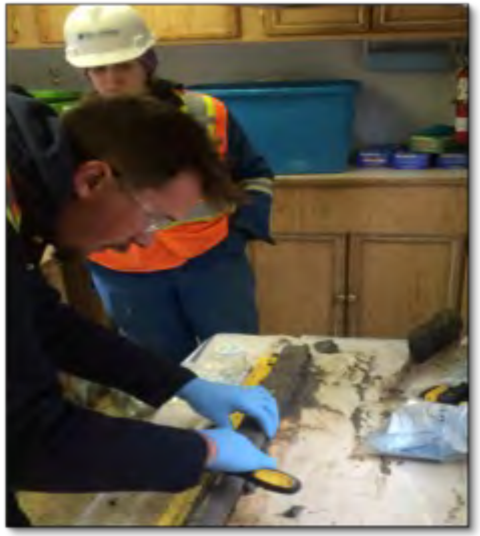


Design Verification Testing

- Subsurface investigation specific to application requirements
- Separate mobilization ahead of the principal application

Delineation for risk ≠ delineation for remediation

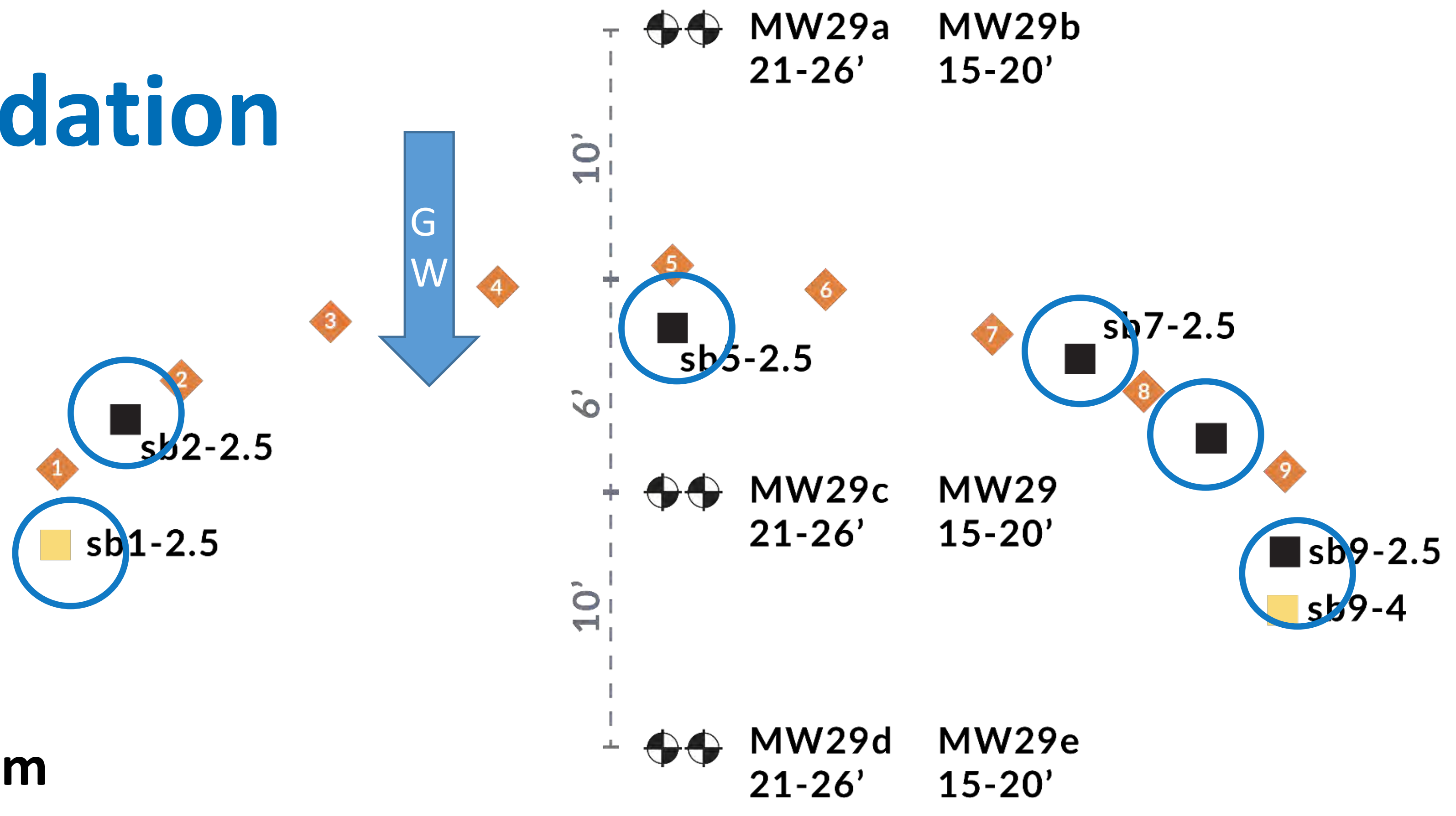
- Detailed stratigraphy, feasible flow rates, appropriate tooling, aquifer response to injection (clean water)
- Informs design refinement and placement optimization
- Injection Test, Soil Cores, High Resolution Sensing Tools, FluxTracer™



Pilot Test Layout

- 9 Direct-Push Injection Points
- Paired Wells UG & DG
- Bottom up DPT Injection using 3’ retractable screens
- ~8500-gallons of CAC Solution
- Avg. injection pressure of 16 psi
- Avg. flow rate of 6.45 gpm

Placement Validation



- Planned field steps to confirm and optimize CAC distribution
- Pre- and Post-Soil Cores
- Piezometers

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Application Fieldwork

- **Placement Validation**
  - Conducted during application
  - *Has the injected CAC gone where we intended it to?*
  - Soil cores, temporary piezometers, carbon concentrations

- **Real-time adjustment to situations encountered**
  - Designer is frequently in the field
  - Deep CSM familiarity – alert to discrepancies
  - Full project team involvement

CAC-Distribution Confirmation

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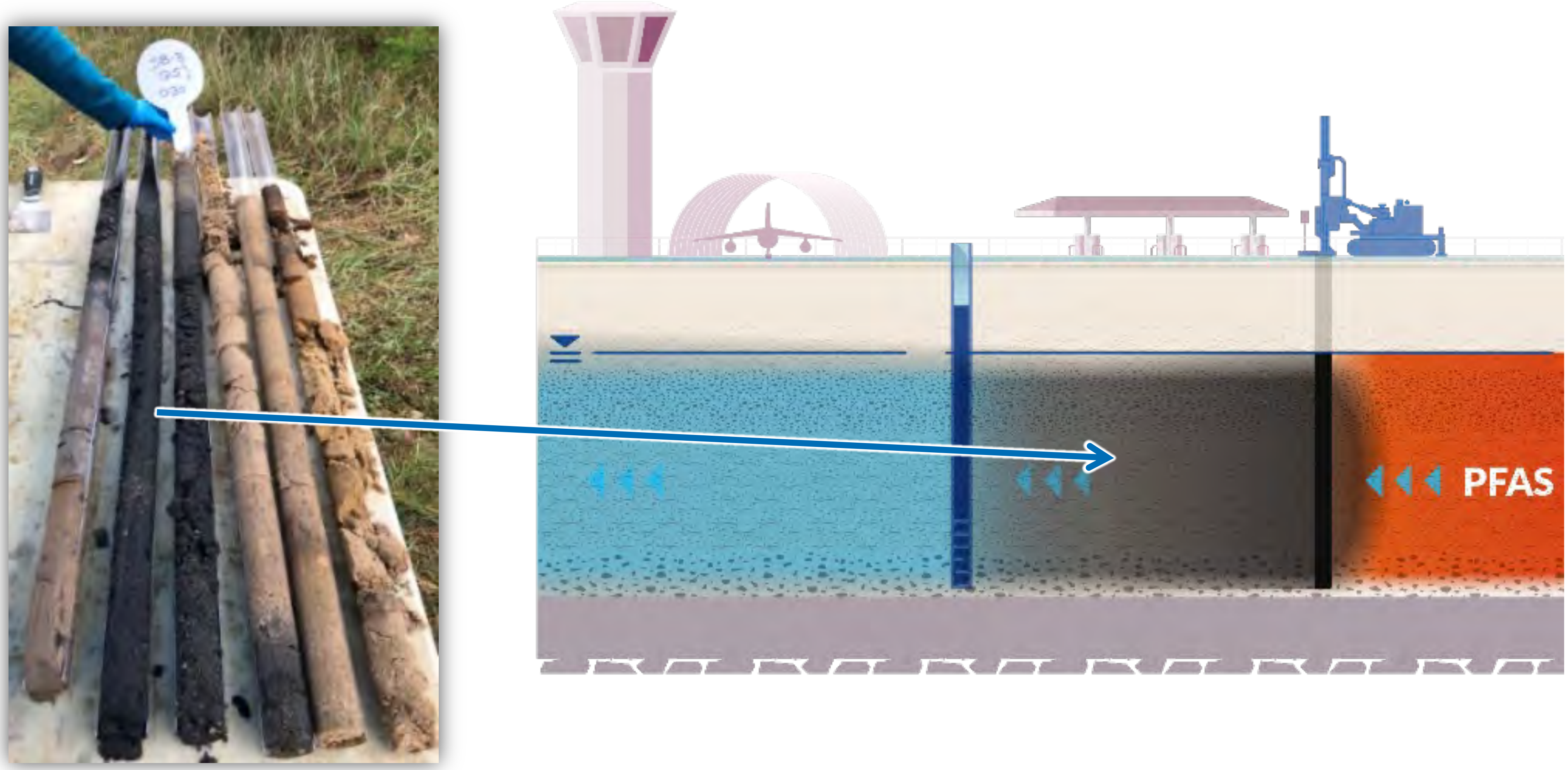
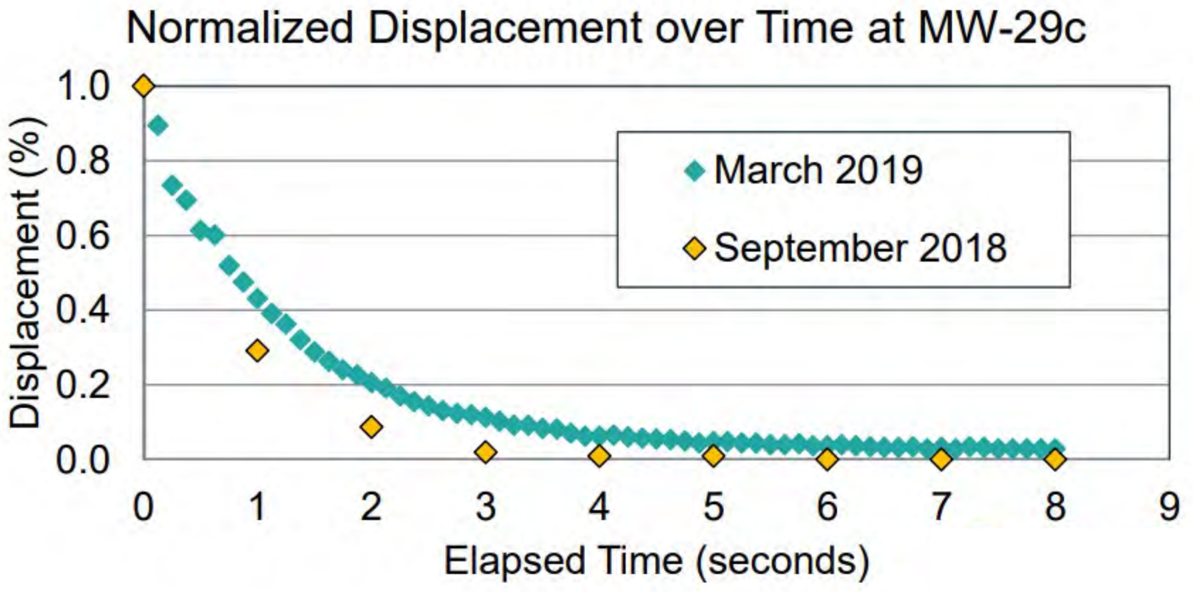
CAC-Distribution Confirmation



Did the CAC Application change the Characteristics of the Site?

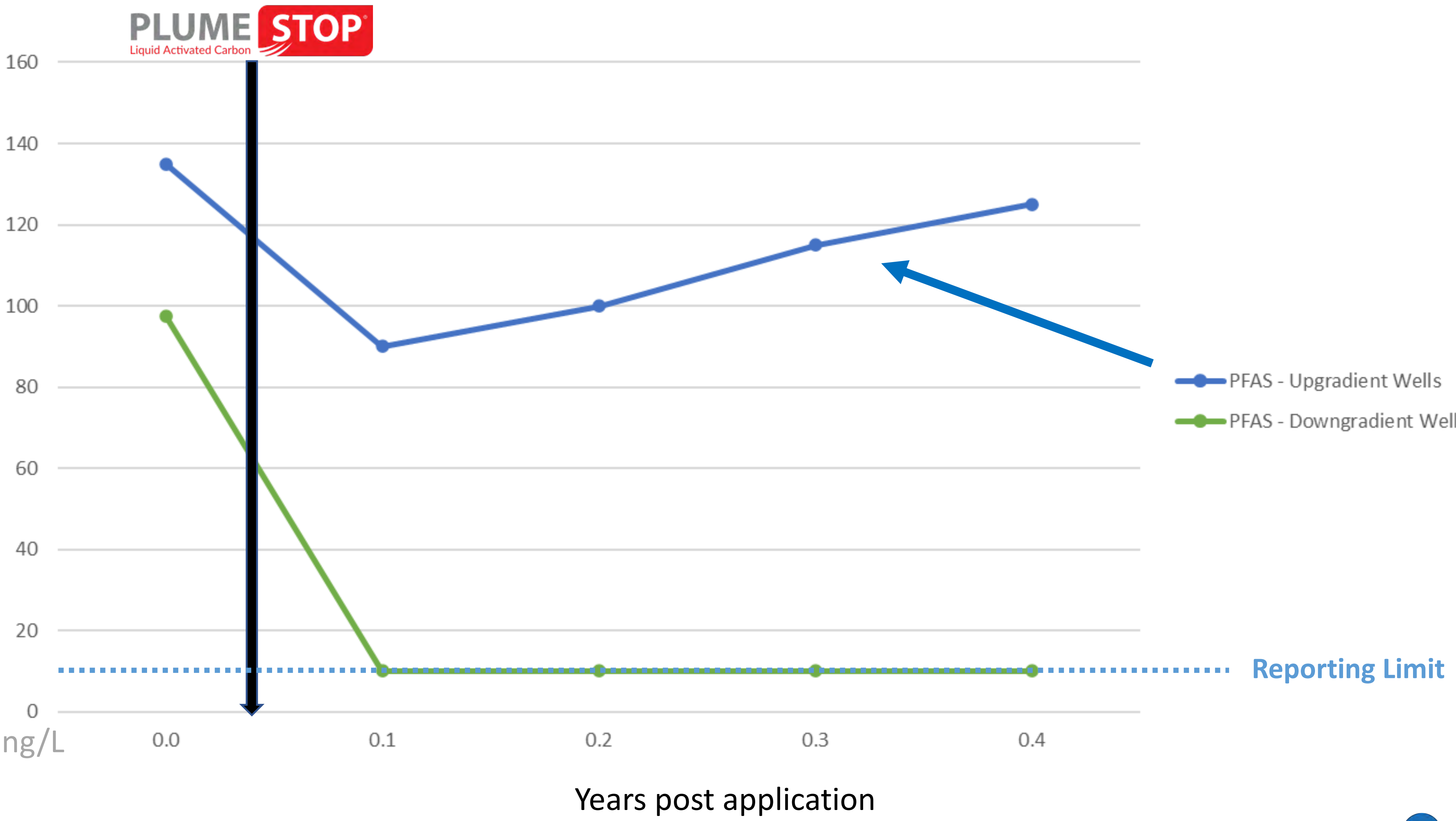
Pre-/Post-Injection Slug Test Results Relatively Unchanged



Source: Mankowski, Len, VP of Geology WSP, AIPG Presentation February 2020, https://cdn.ymaws.com/aipg.org/resource/resmgr/documents/events/seminars/2020_wi_pfas_seminar/mankowski_len.pdf

Analytical Results

Average Total PFAS Concentrations in Upgradient and Downgradient Well Pairs



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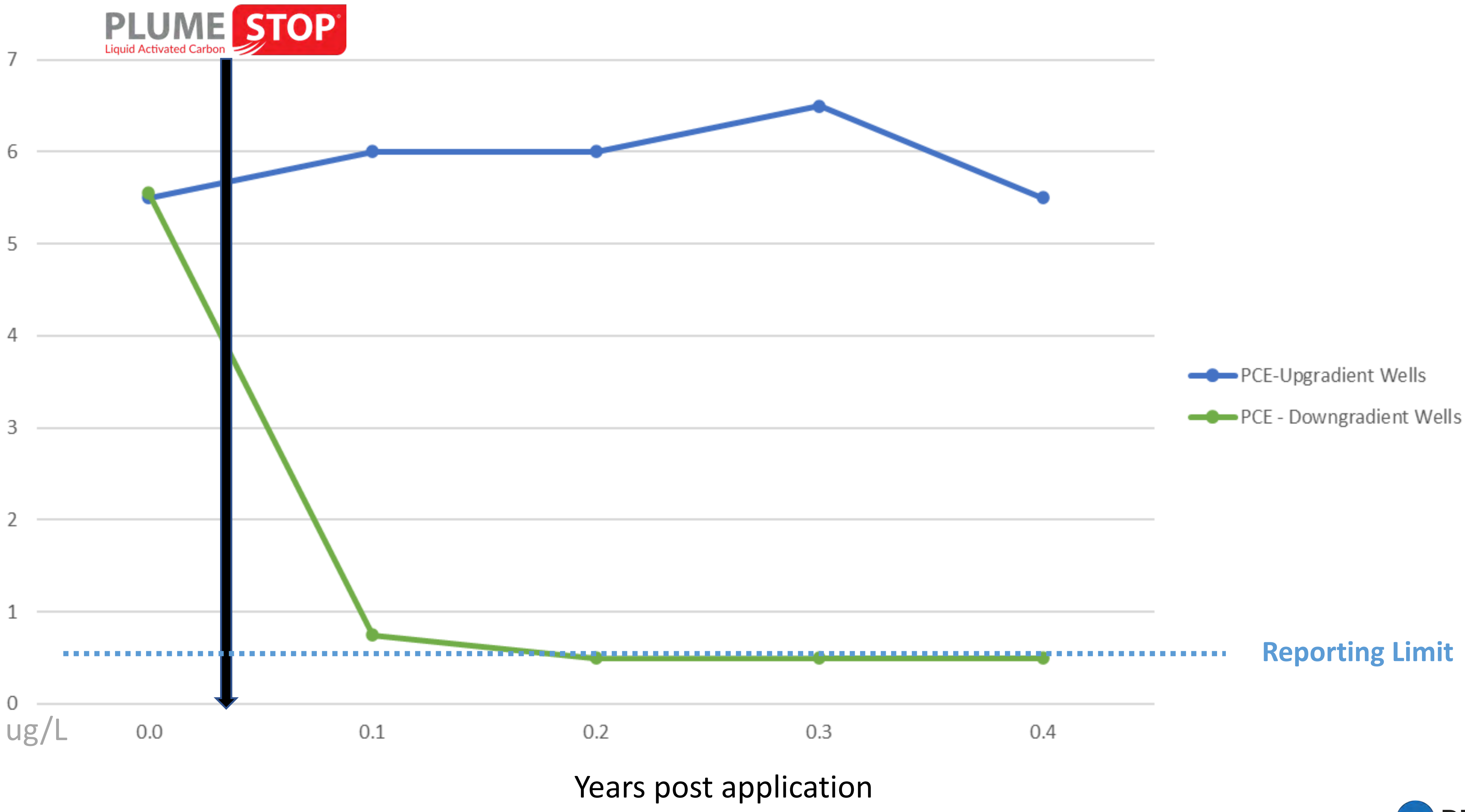
Average PCE Concentrations in Upgradient and Downgradient Well Pairs



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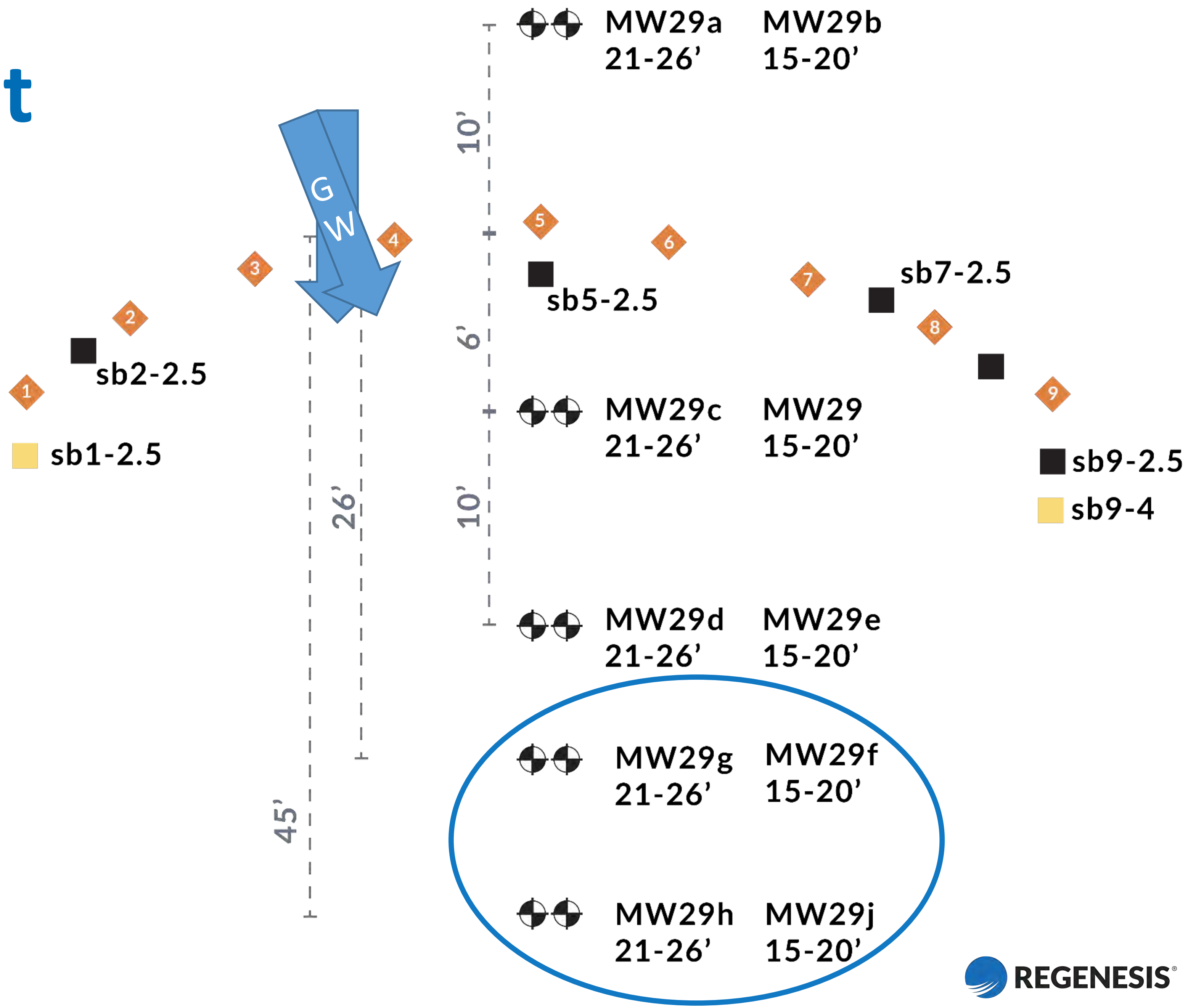
Pilot Test Layout

- **At 6 Months we Added Four Downgradient Wells**



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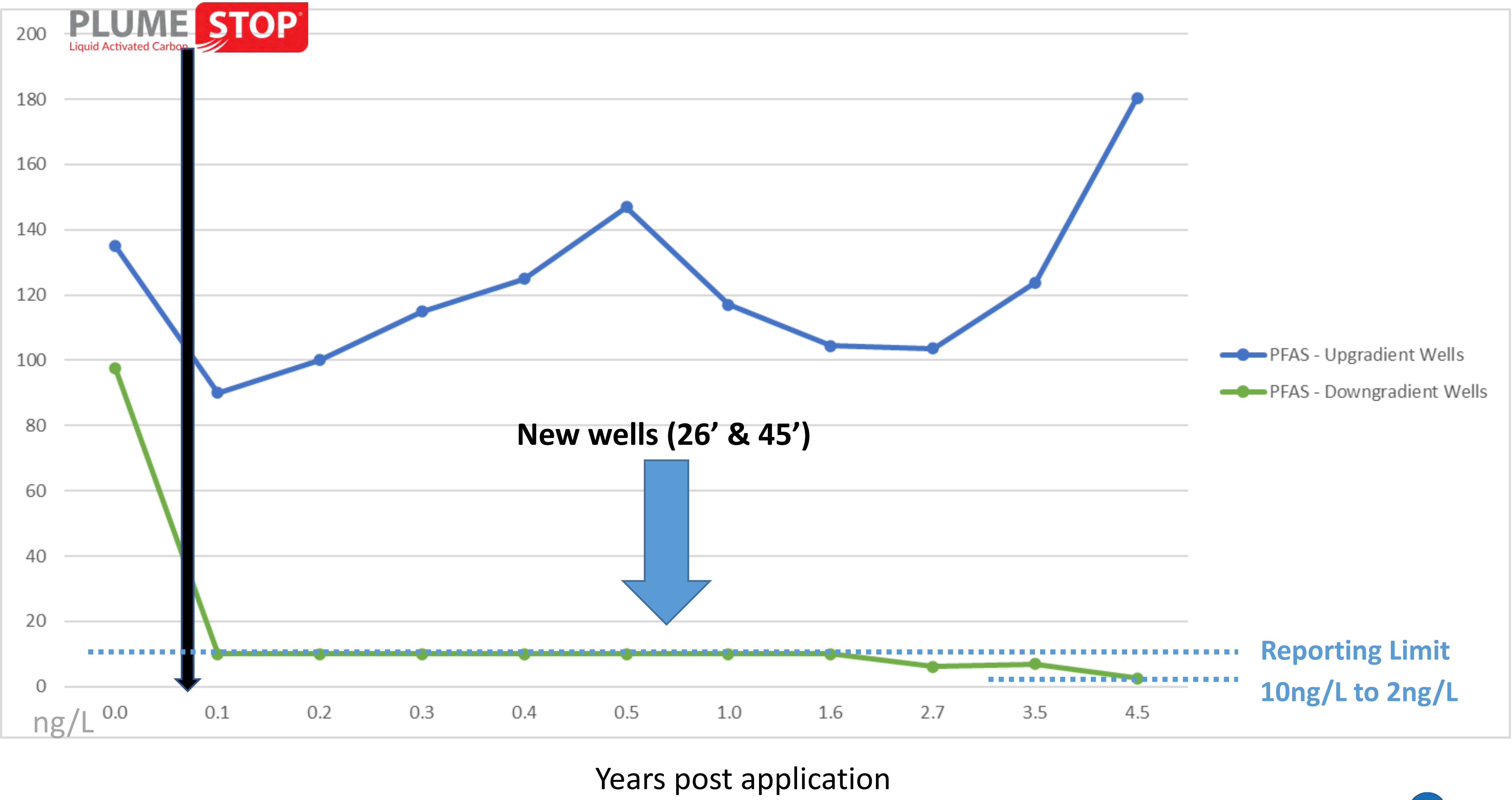
Average PFAS Concentrations in Upgradient and Downgradient Well Pairs



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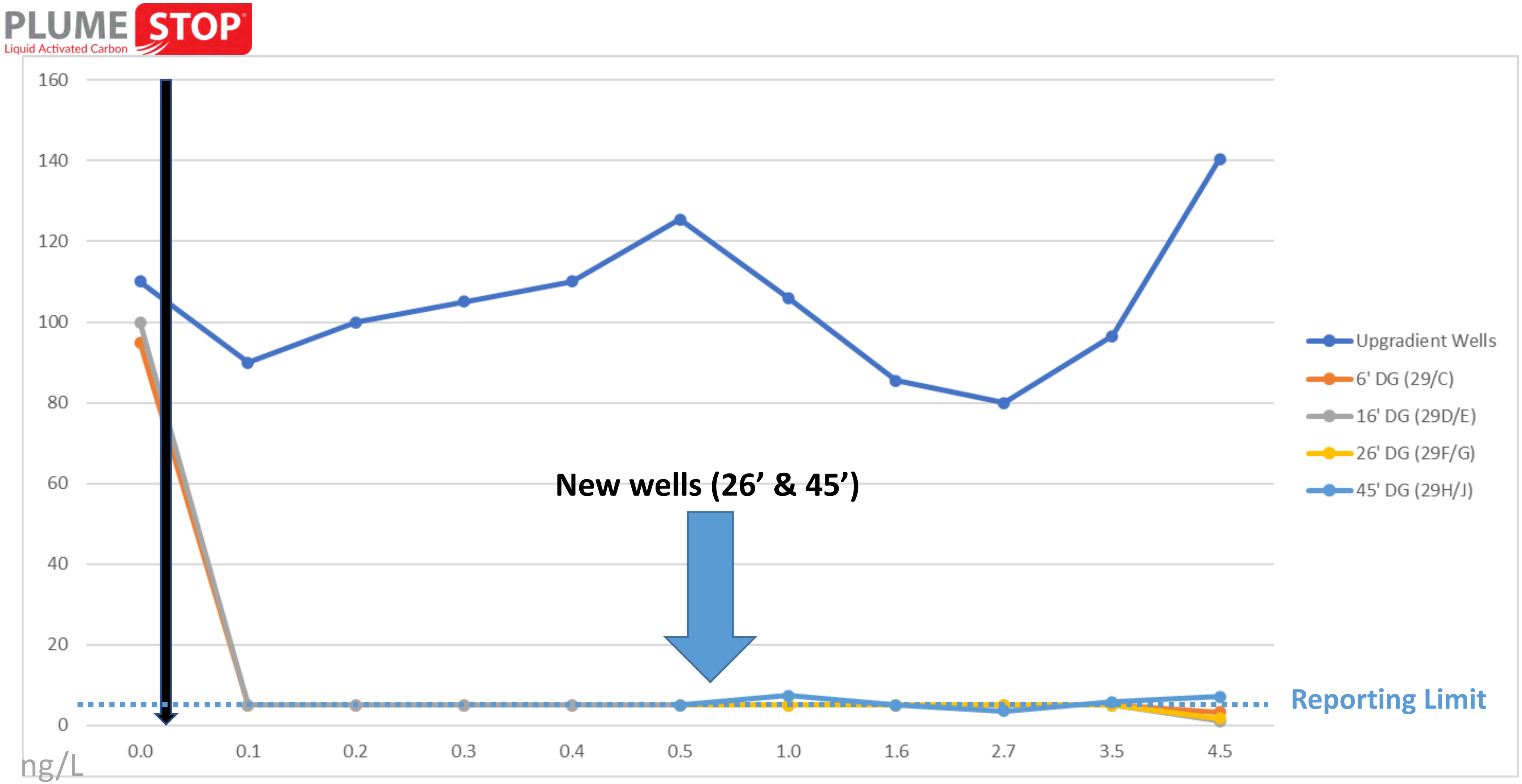
Average Total PFHxS/PFOS Concentrations in Upgradient & Downgradient Wells Pairs



Years post application

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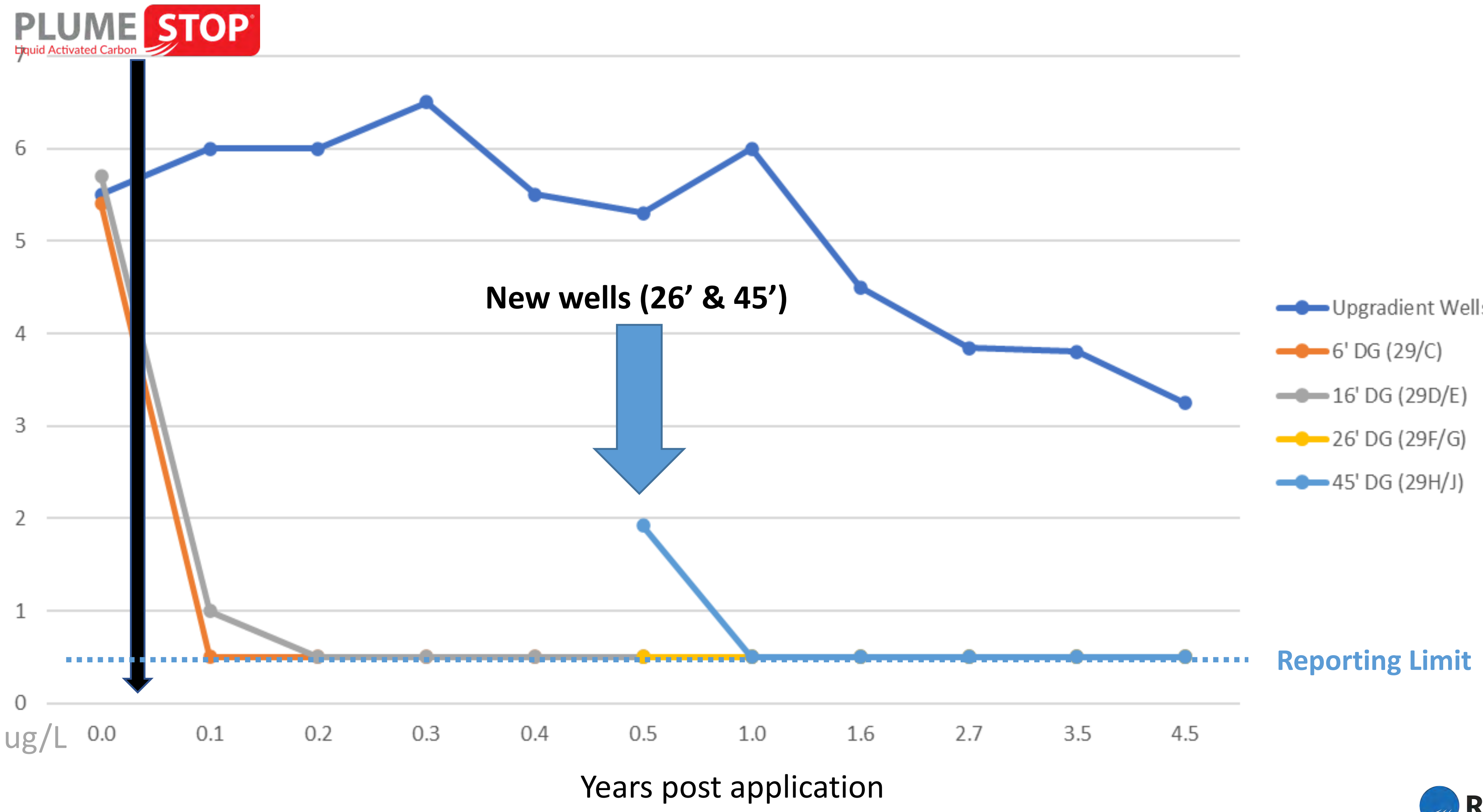
Average PCE Concentrations in Upgradient and Downgradient Wells Pairs



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Case Study #2

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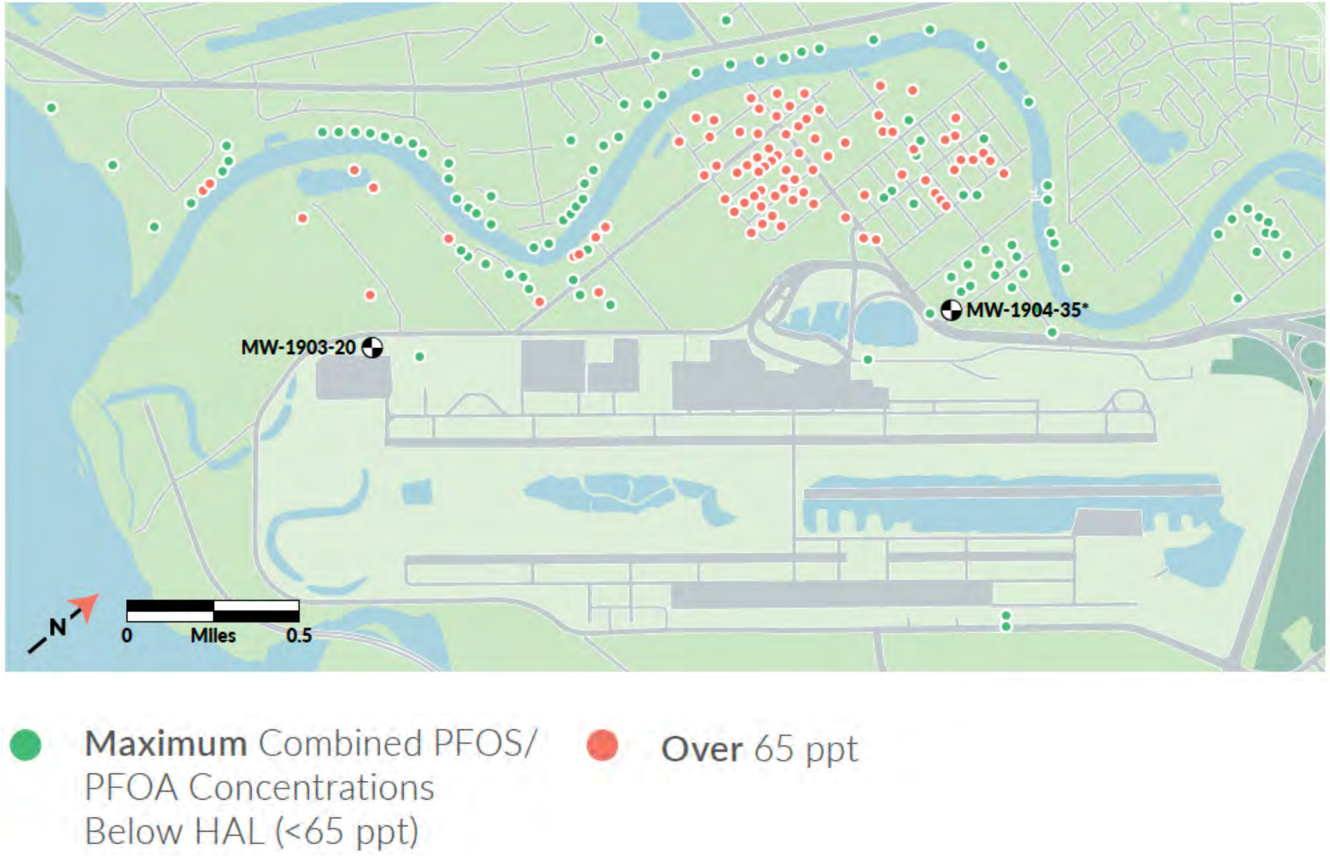
Case Study:
Fairbanks International Airport

- PFAS detected onsite
- FIA responded immediately
- Properties connected to municipal water line



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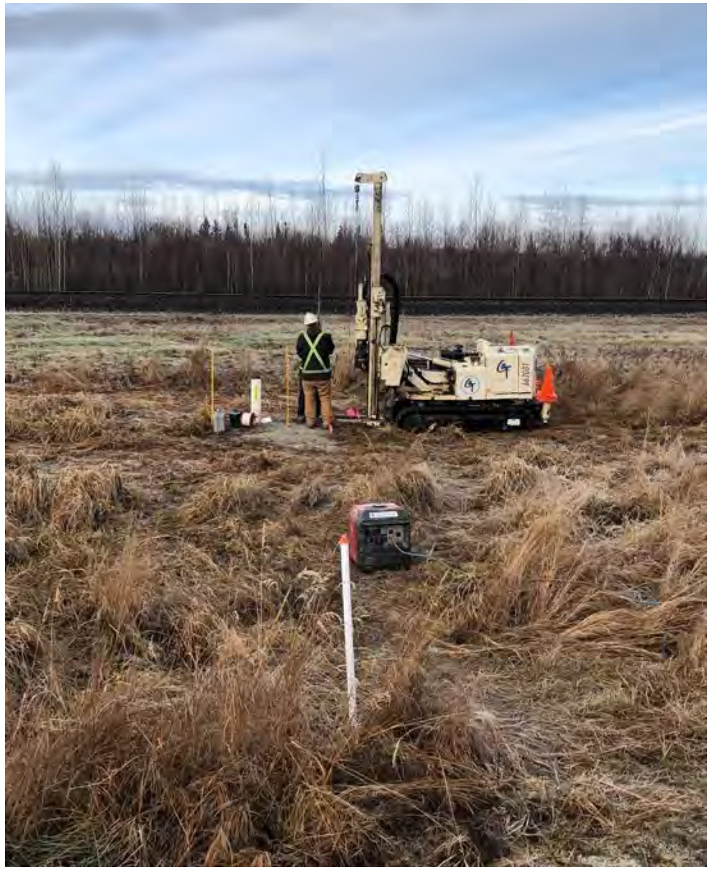
PlumeStop Application

- **Purpose:**
  - Treatment designed to address PFOS, PFOA, PFHpA, PFHxS, and PFNA
- **Objectives**
  - Inject PlumeStop to address contamination in vicinity of MW1902-20
  - Monitor PFAS levels in MW for minimum of one year
  - Extend barrier 2023



PlumeStop Pilot Study - Application

PlumeStop Application – Injection Controls

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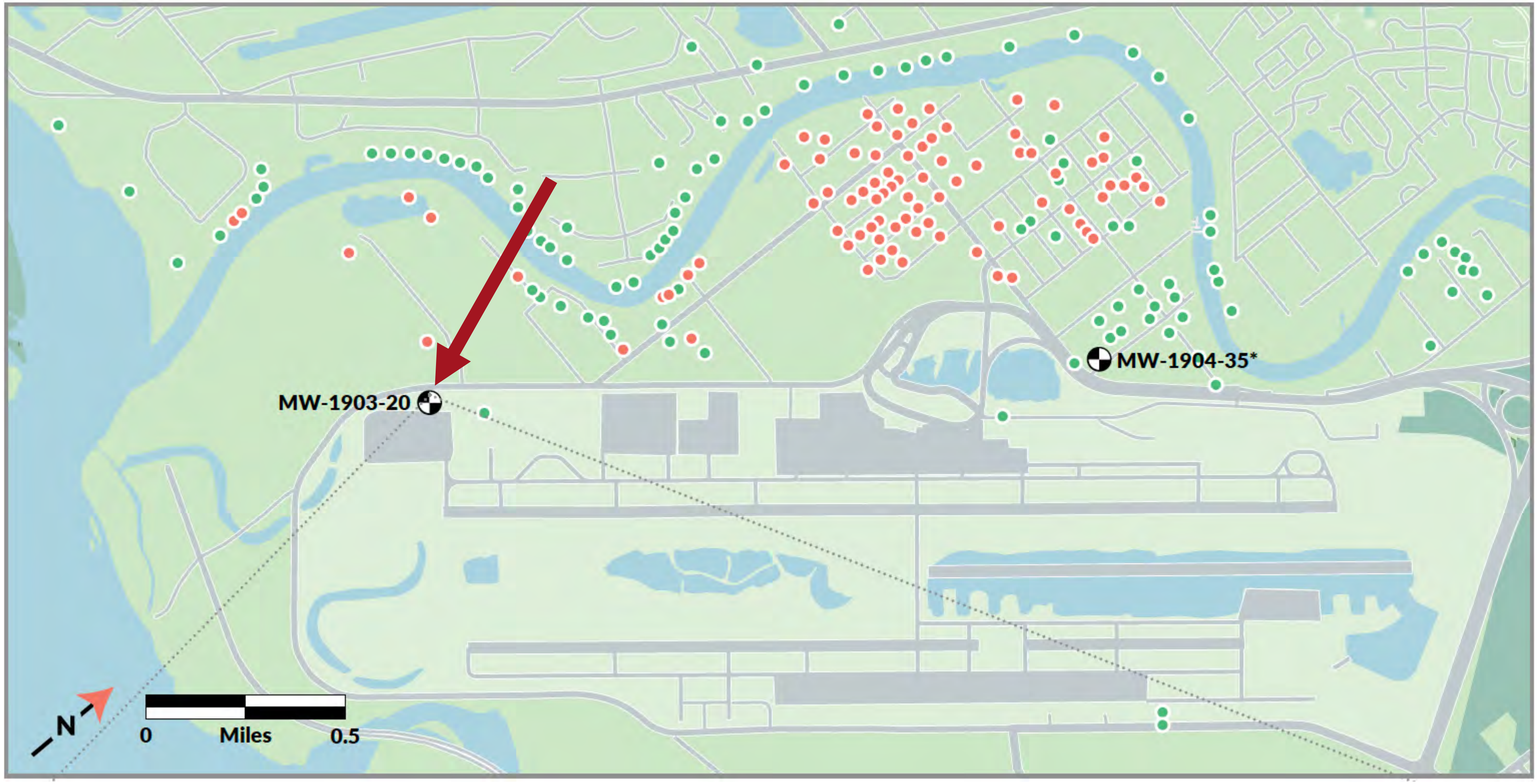
Injection Locations



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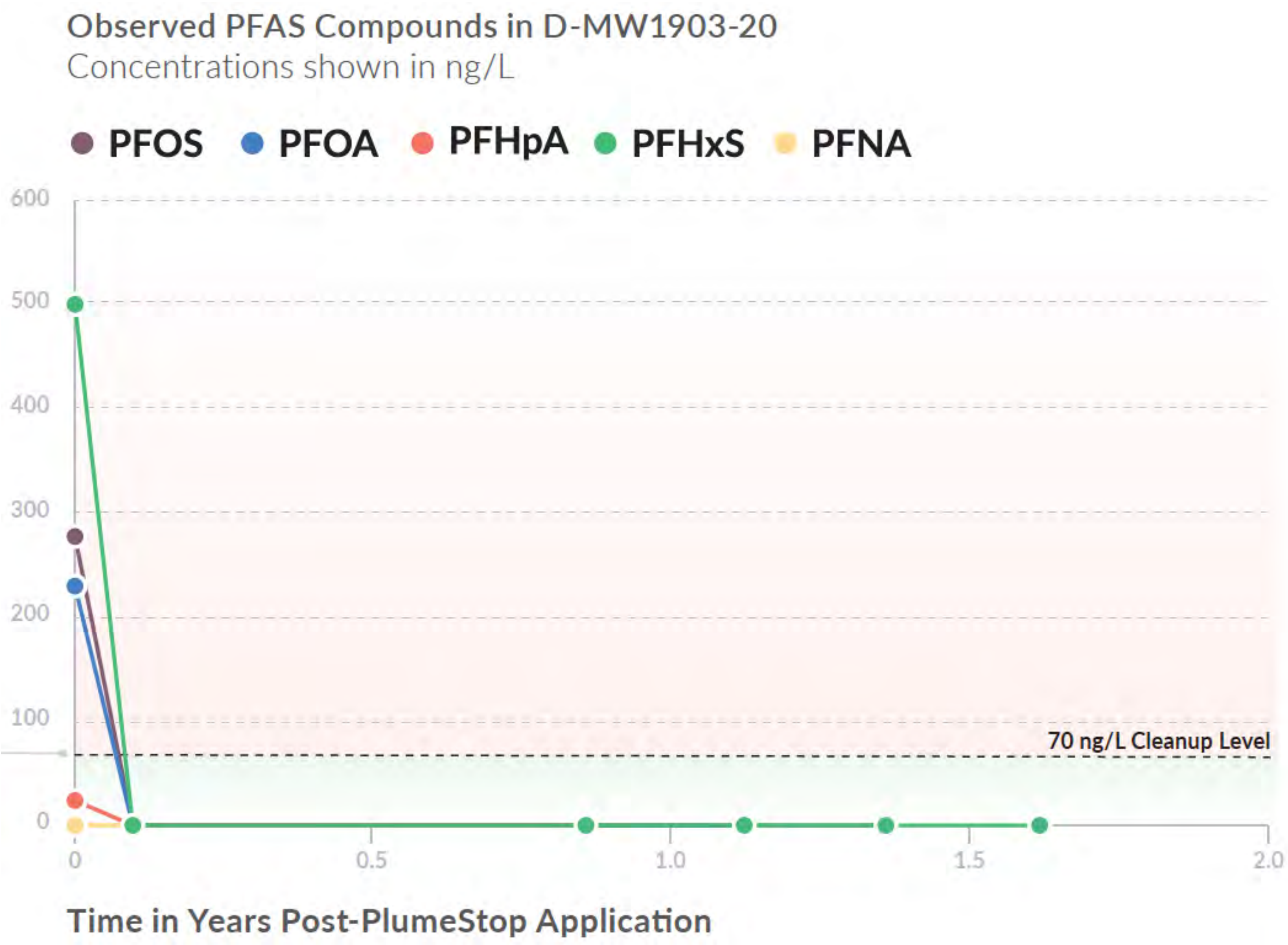
Results

Baseline Sampling

- **PFOS = 270 ng/L**
- **PFOA = 240 ng/L**
- **PFHxS = 530 ng/L**
- **PFHxA = 200 ng/L**
- **PFBS = 100 ng/L**
- **PFBA = 24 ng/L**

June 2021 – Removal Rates

- **PFOS = 100%**
- **PFOA = 100%**
- **PFHxS = 100%**
- **PFHpA = 100%**
- **PFNA = ND**



Case Study #3

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Martha's Vineyard Airport Selects PlumeStop to Address PFAS

Cost-Effective *In Situ* Approach Addresses PFAS Risk with No Greenhouse Gases or Hazardous Waste

TETRA TECH REGENESIS

Martha’s Vineyard Airport Selects PlumeStop to Address PFAS

- Martha’s Vineyard Airport is centrally located on an island off the coast of Massachusetts.
- AFFF leached into the underlying groundwater impacting it with PFAS and plume extends beyond airport property boundaries
- Private water wells supplying drinking water to residents at risk

TETRA TECH REGENESIS®

Remedy Selection

Remediation Goal:

- Prevent further PFAS movement away from the site
- Prevent PFAS exposures to downgradient residents
- Achieve regulatory standard:
  20 ppt sum of:
  PFOA, PFOS, PFHxS, PFNA, PFBS, PFDA
- **15+ year Design single application**

Key factors in the selection included:

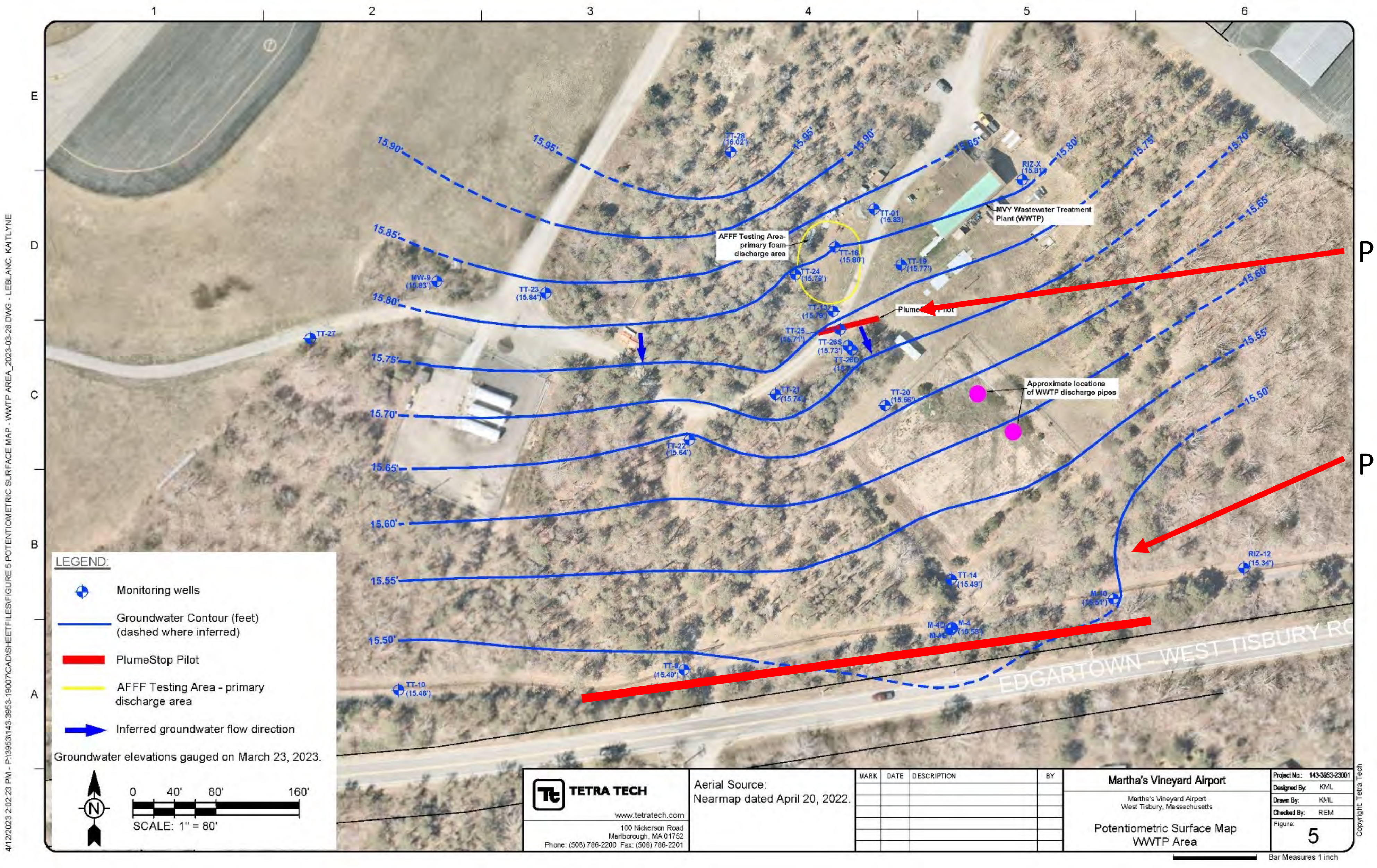
- Avoiding greenhouse gas emissions
- Avoiding PFAS hazardous waste disposal
- Cost

Application and Results

- PlumeStop applied in December 2022
- Currently in performance monitoring period
- Barrier designed to immobilize PFAS for decades, reducing potential exposure risk to nearby residents
- Plan to Expand barrier

PlumeStop PRB Application Details

Contaminants of concern	PFAS
Treatment Zone Geology	Coarse sand, with some silt and clay
Barrier length	60 linear feet
Target treatment zone	30 to 40 feet bgs
Injection configuration	24 pts, 5-feet spacing, two rows
PlumeStop applied	9,200 pounds/10,044 gallons



Phase 1application

Phase 2 application

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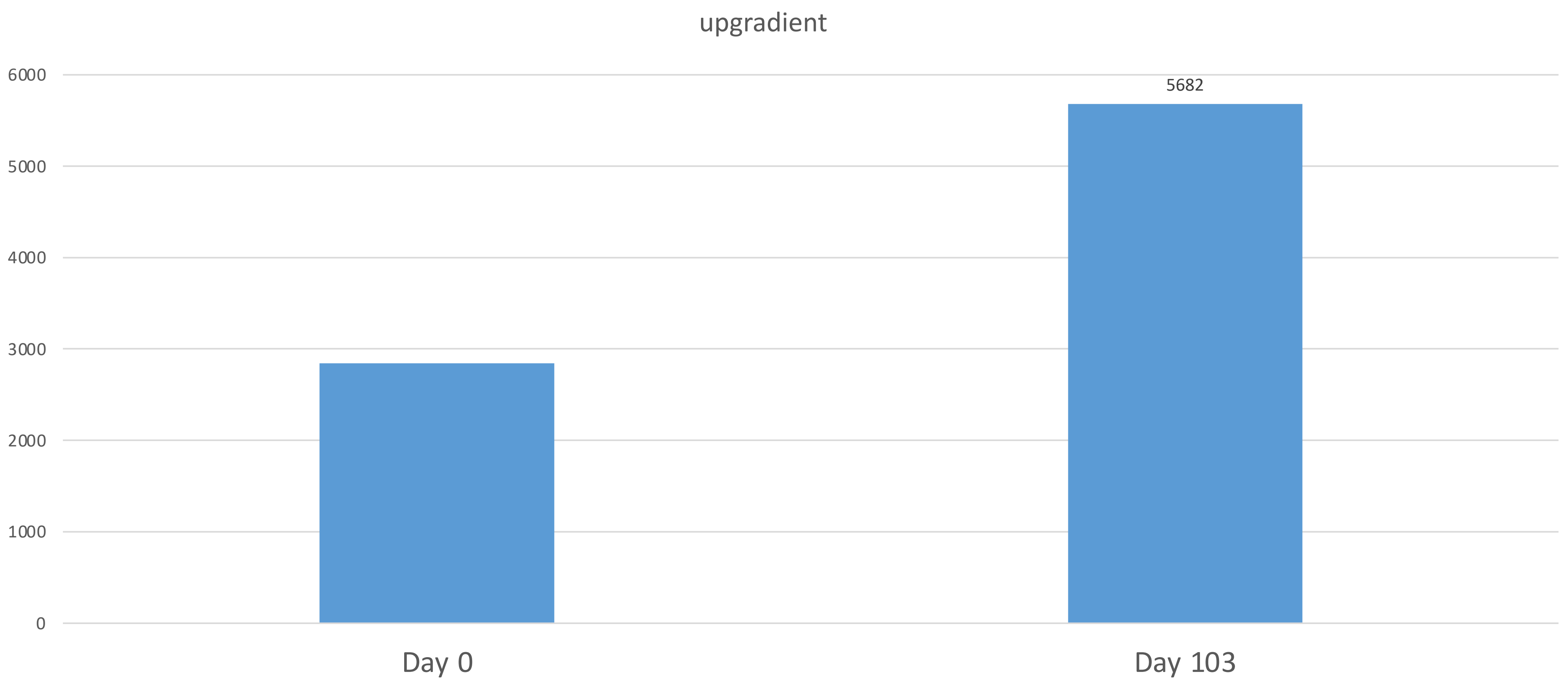
Upgradient Barrier: MA 6 PFAS



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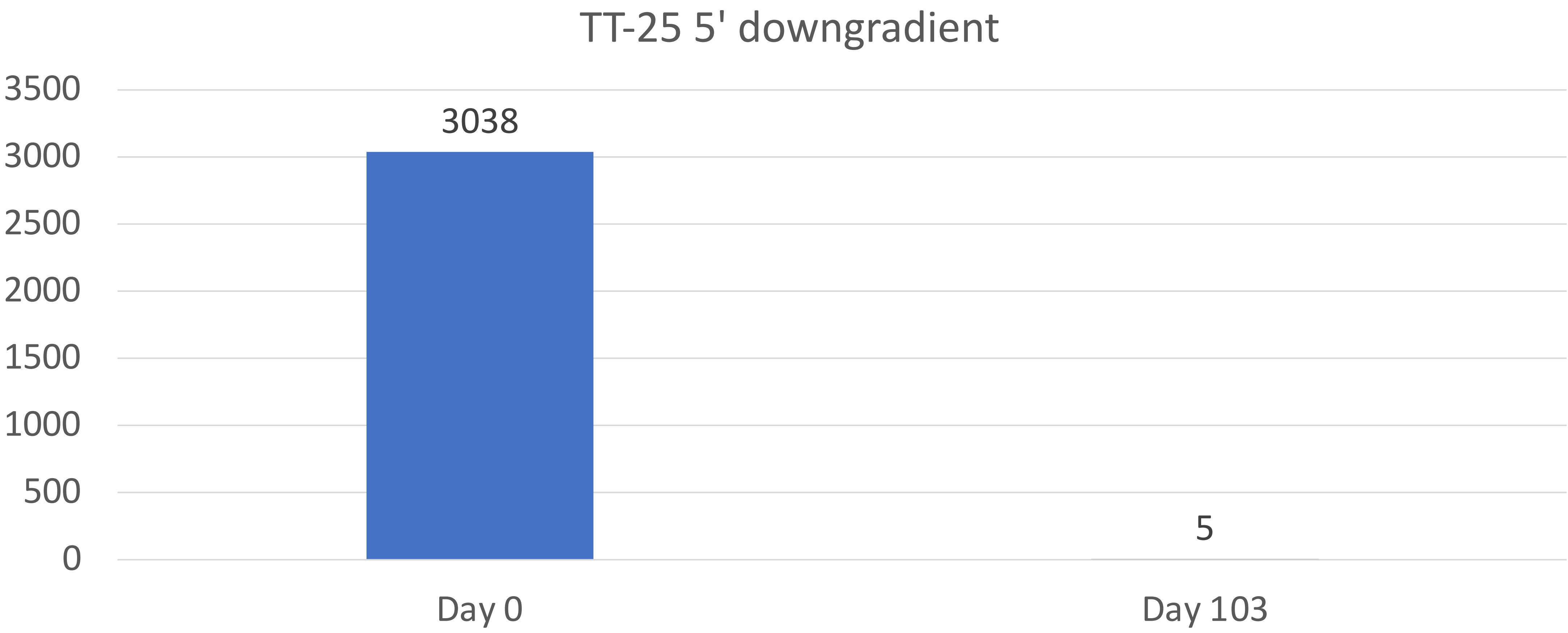
TT-25 5' Downgradient: PFAS 6



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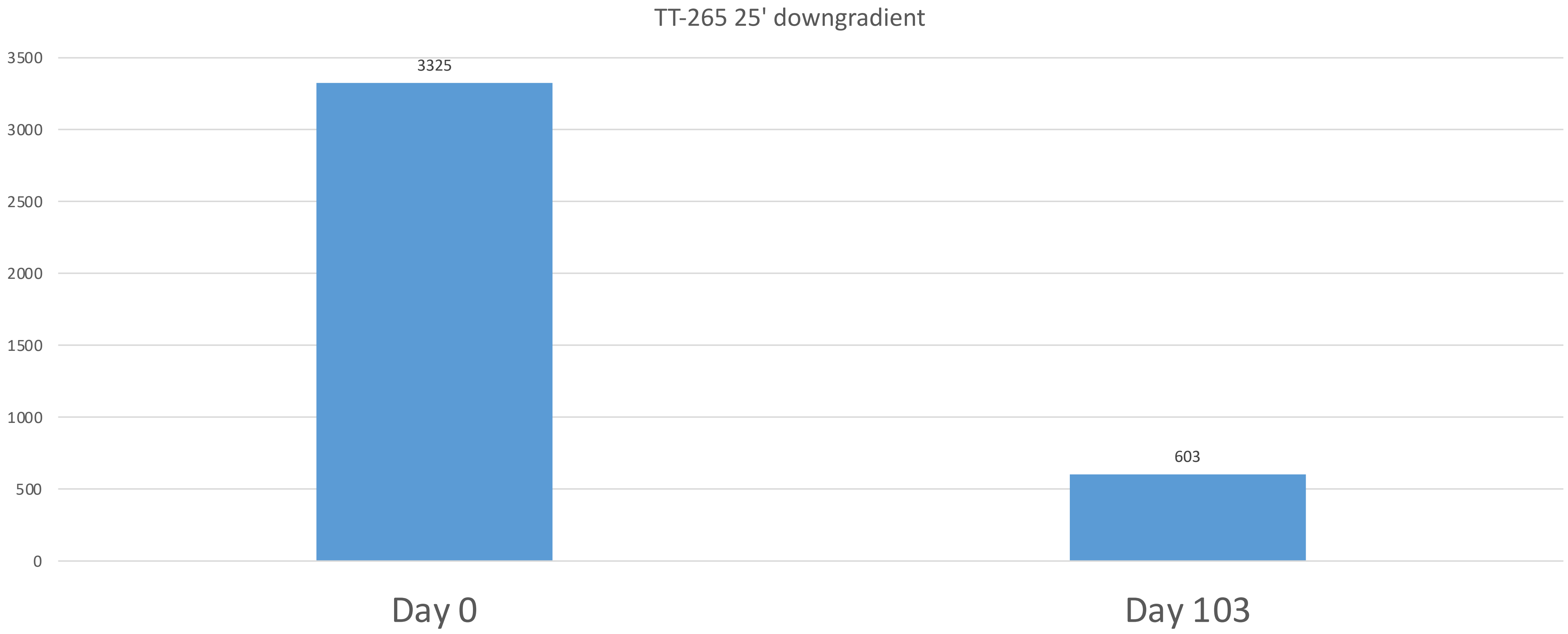
TT-26S 25’ Downgradient PFAS 6



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Summary

- **CAC is an effective, *in situ* option to address PFAS Risk**
  - Nearly 40 sites to date
  - Third-Party Evaluations
  - Strict regulatory standards have been met
  - Source treatment will further enhance effectiveness of barrier by reducing mass flux
  - NO waste is generated using this in situ approach
  - Treatment Expected to last for Decades

Questions?

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