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Colloidal Activated Carbon Used to Reduce PFAS and PCE Concentrations in Groundwater to Below Michigan's Drinking Water Limits for Over Four Years

Ryan E. Moore
Senior District Manager and PFAS Program Manager
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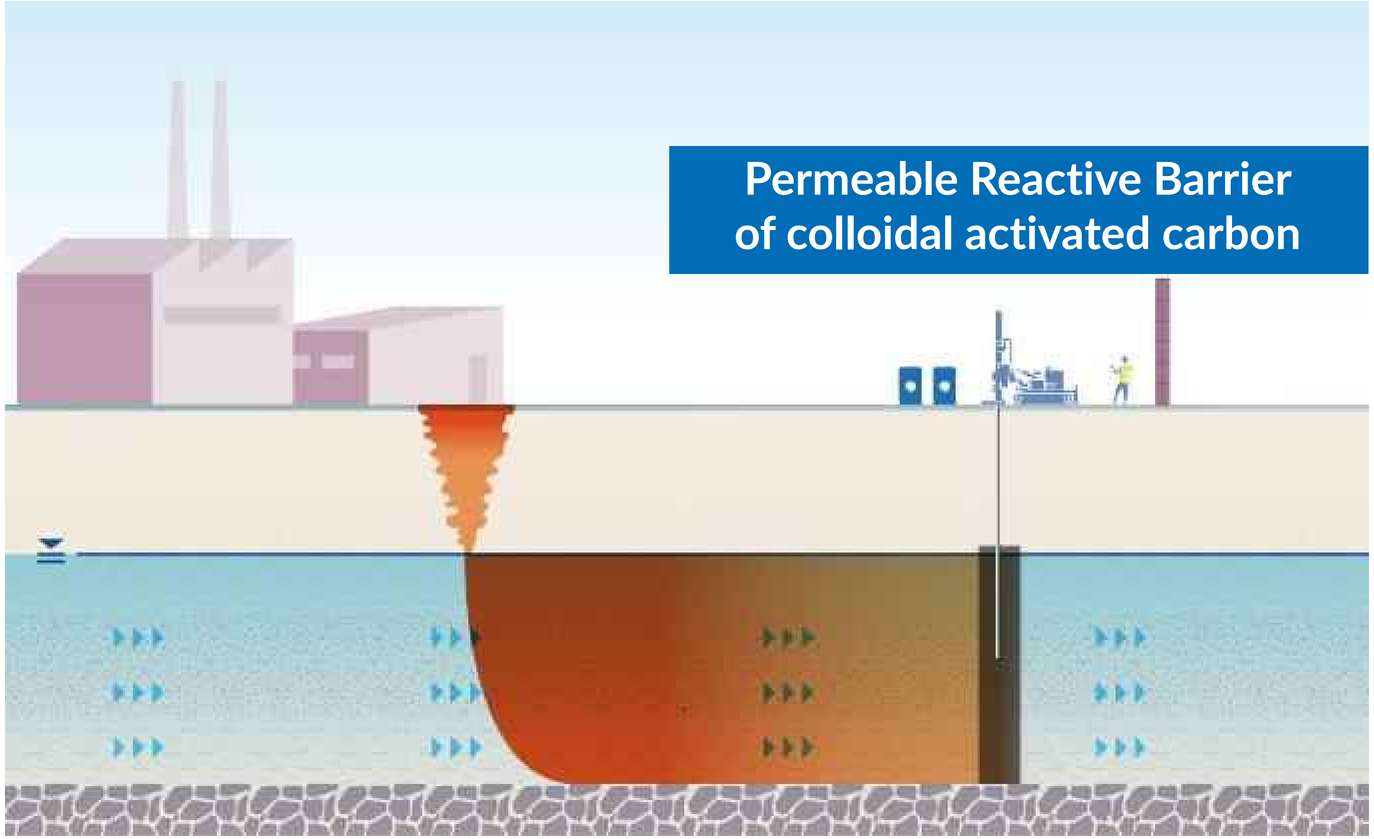
Presentation Overview

- Effectiveness of CAC Treatment for PFAS
- Ever-changing Remediation Goals
- Design & Implementation Process
- Long-term Data

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."

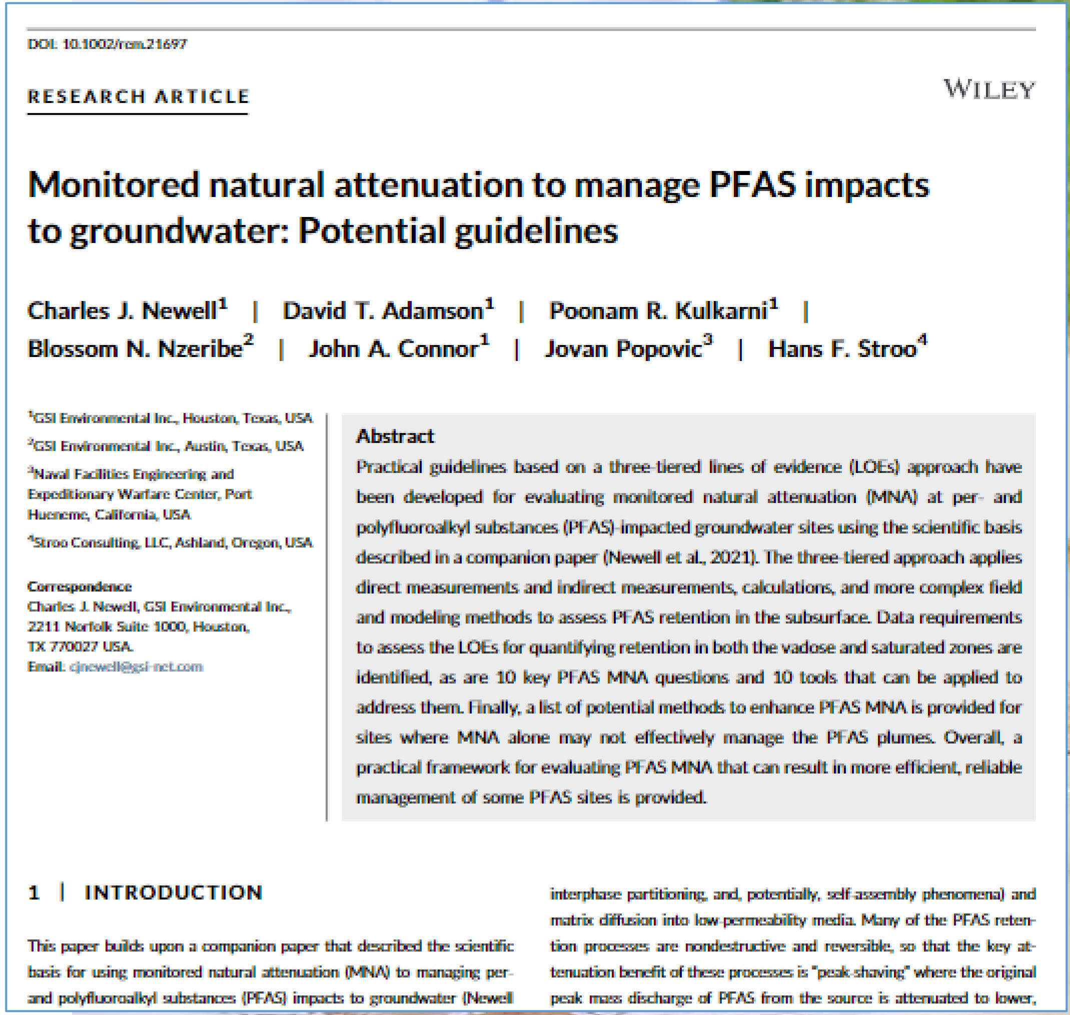
Eliminating Risk

~~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,

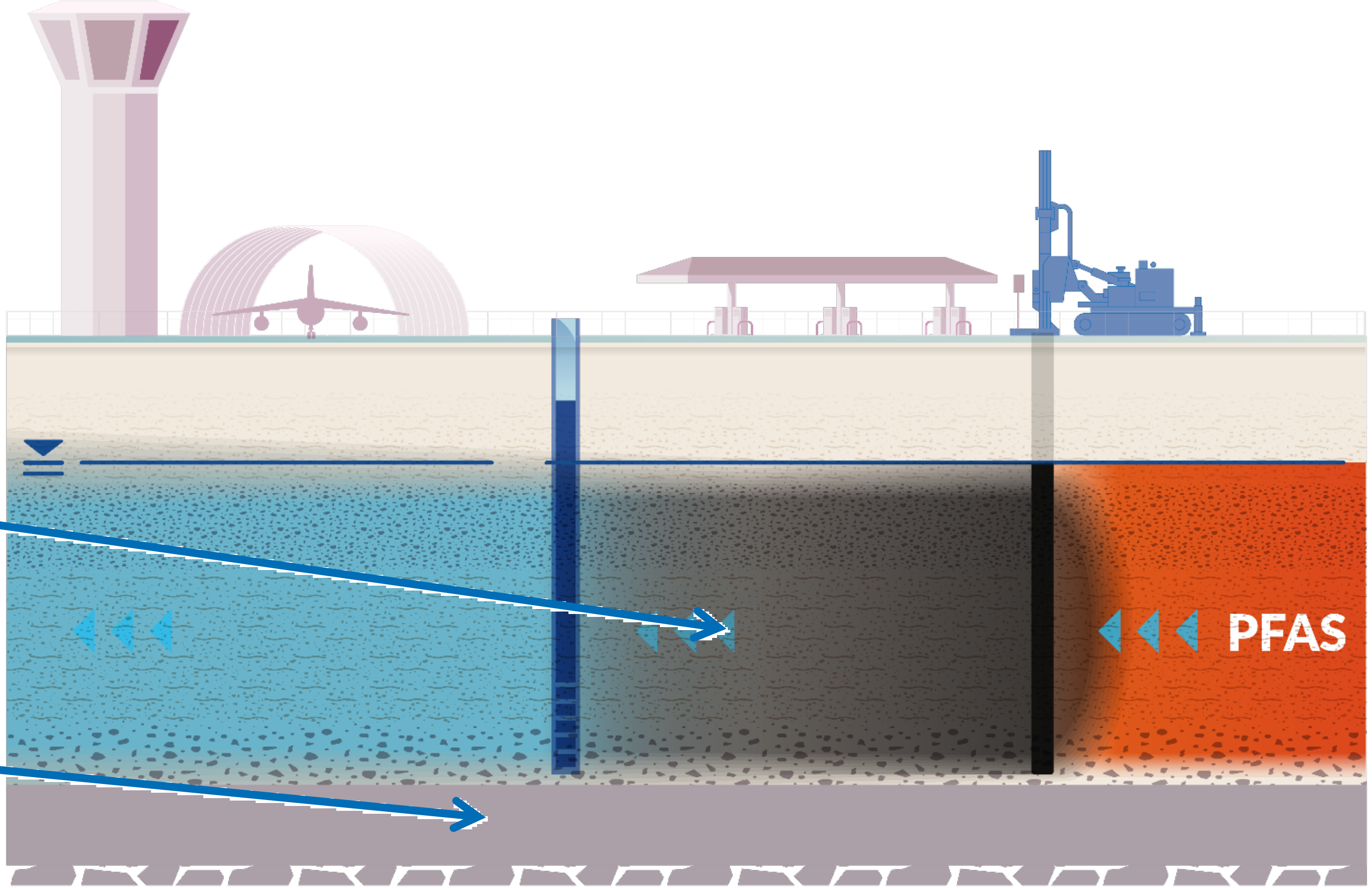
U.S. EPA. Use of Monitored Natural Attenuation for Inorganic Contaminants at Superfund Sites, Directive 9283.1-36. Published online 2015.
Newell CJ, et al. Monitored Natural Attenuation to Manage PFAS Impacts to Groundwater: Scientific Basis. Groundwater Monitoring & Remediation. 2021;41(4):76-89.
Newell 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



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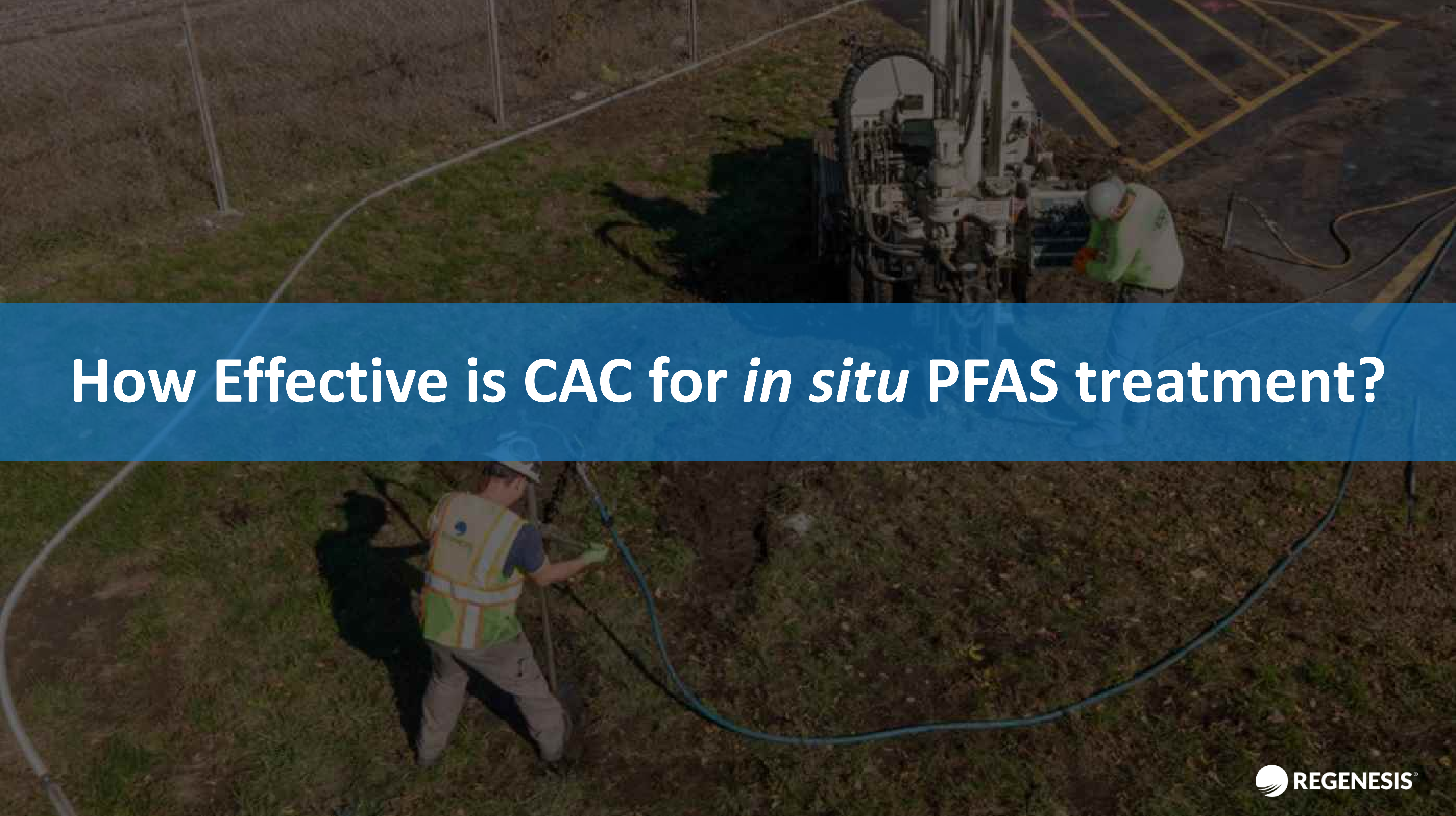
How Effective is CAC for *in situ* PFAS treatment?



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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


Grant Carey

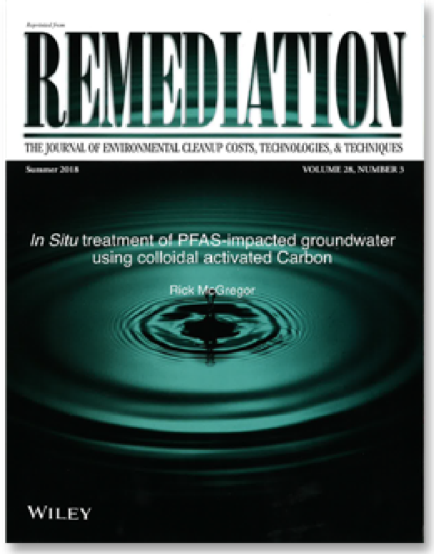
Abstract

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.

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})

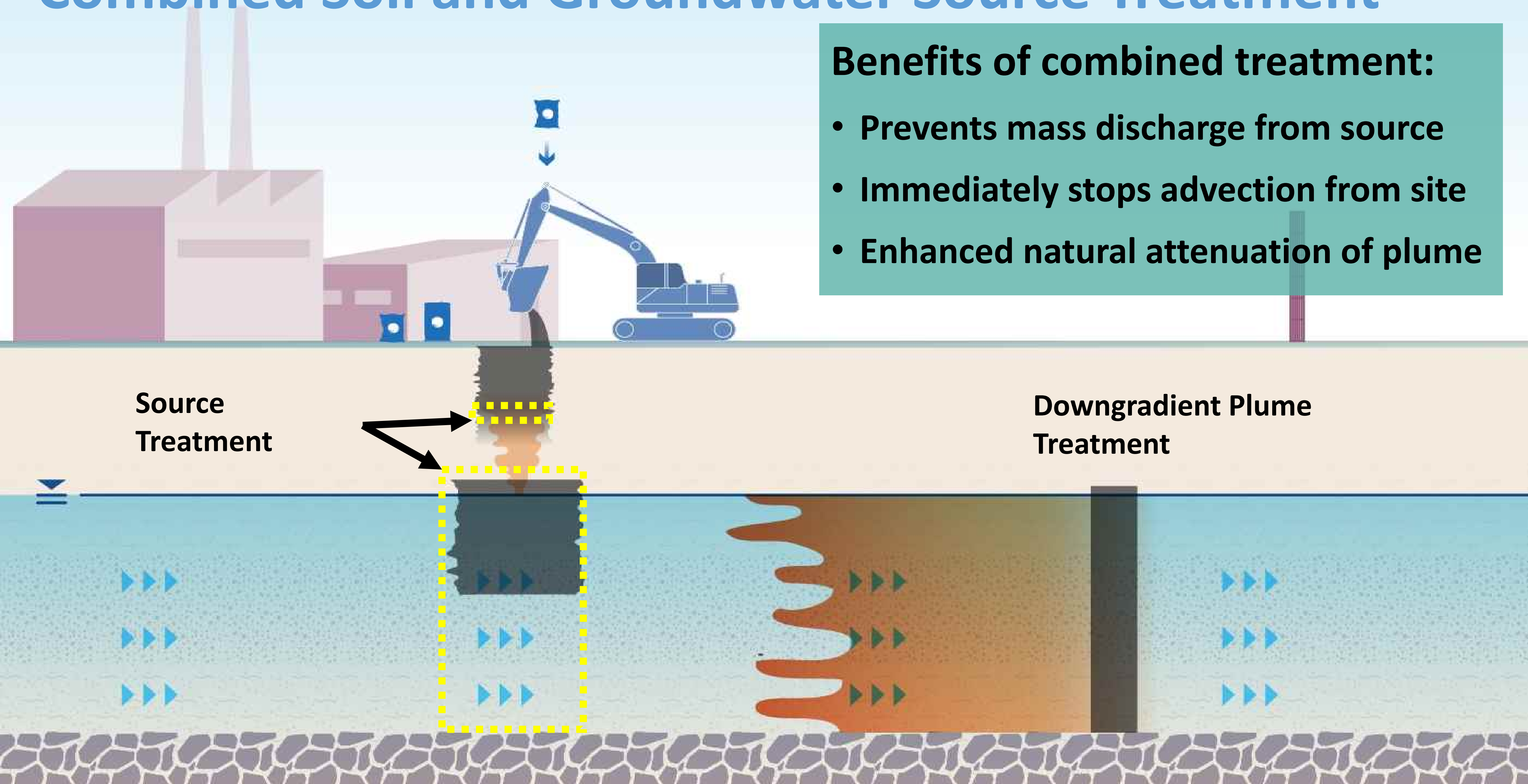
Field site ID	Reference	Maximum detected PFAS groundwater concentrations before CAC injection(µg/L)	Maximum concentrations of co-contaminants before CAC injection (µg/L)	Soil type	Measuredf_{cac}	Description of monitoring network within the CAC adsorption zone	No. of postinjection monitoring events	Postinjectionmonitoring 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 Benevenuto (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.

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



Grayling Army Airfield

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

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

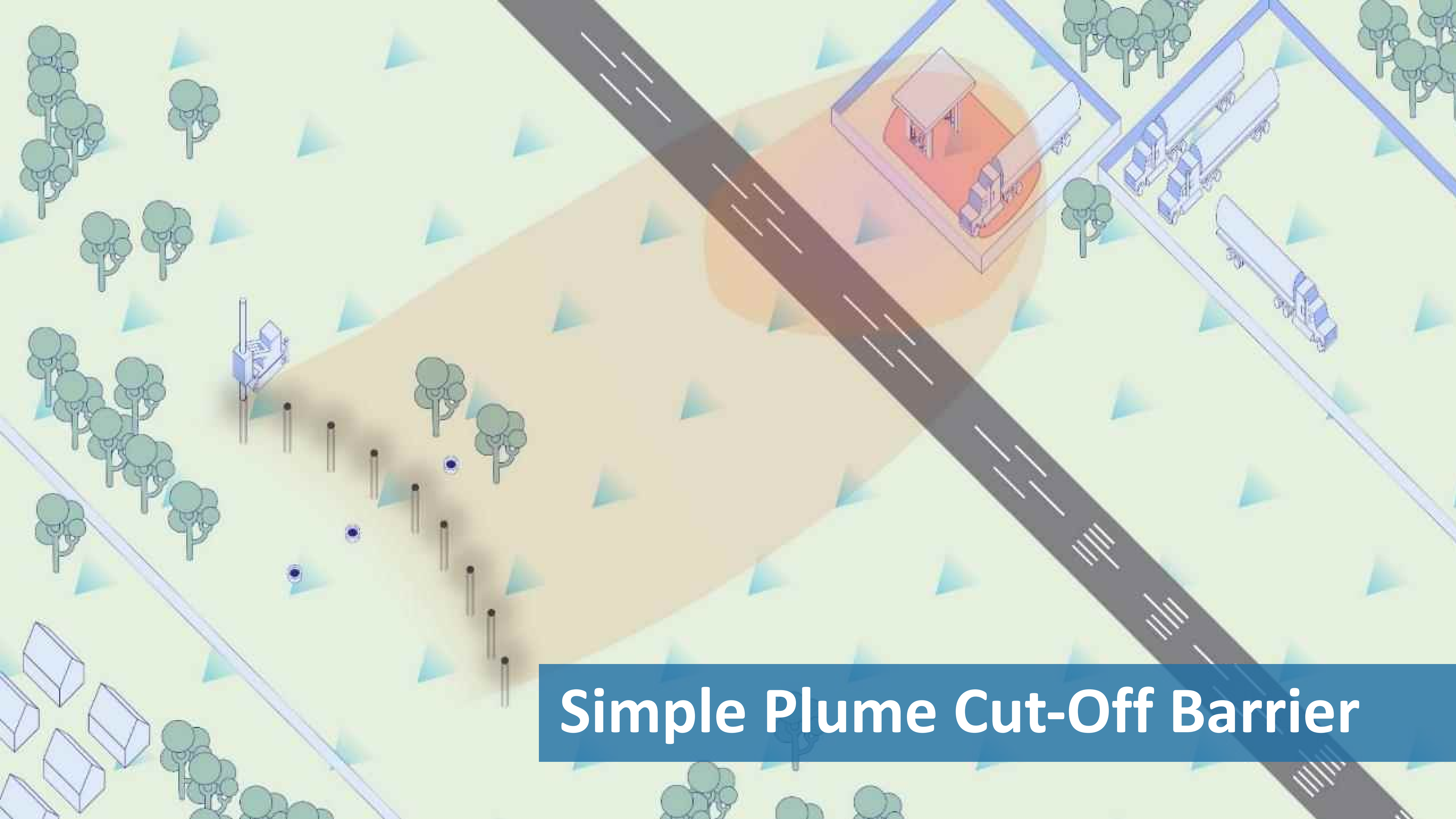
- **Fall 2018: 70ppt Total PFOS/PFOA USEPA Health Advisory Level**
- **August 2020: Michigan MCLs**
- **March 2023: Proposed USEPA MCLs**

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

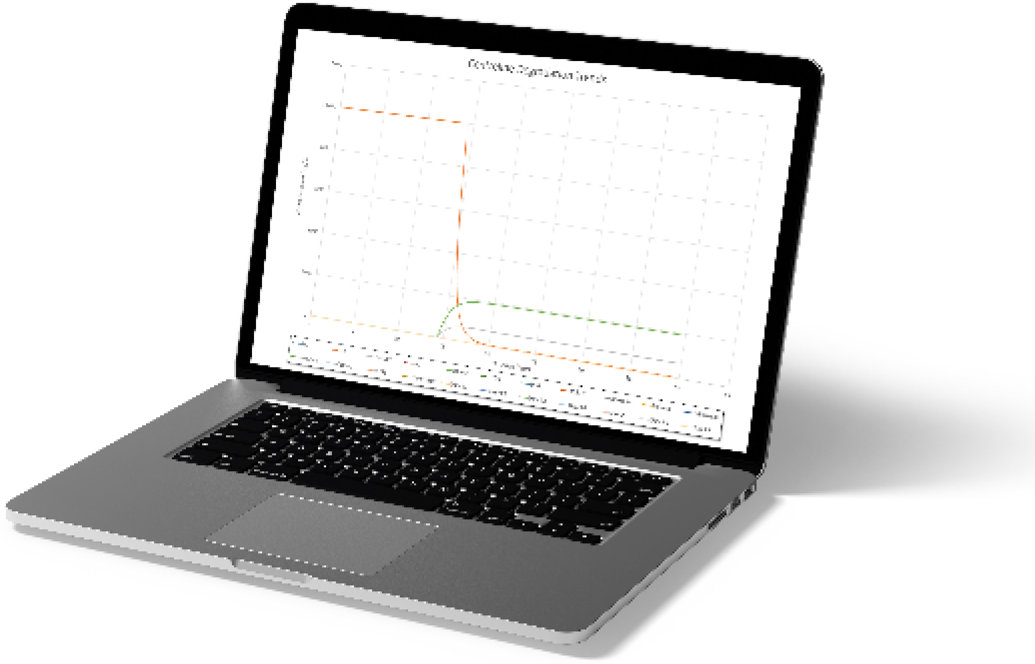


Simple Plume Cut-Off Barrier

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

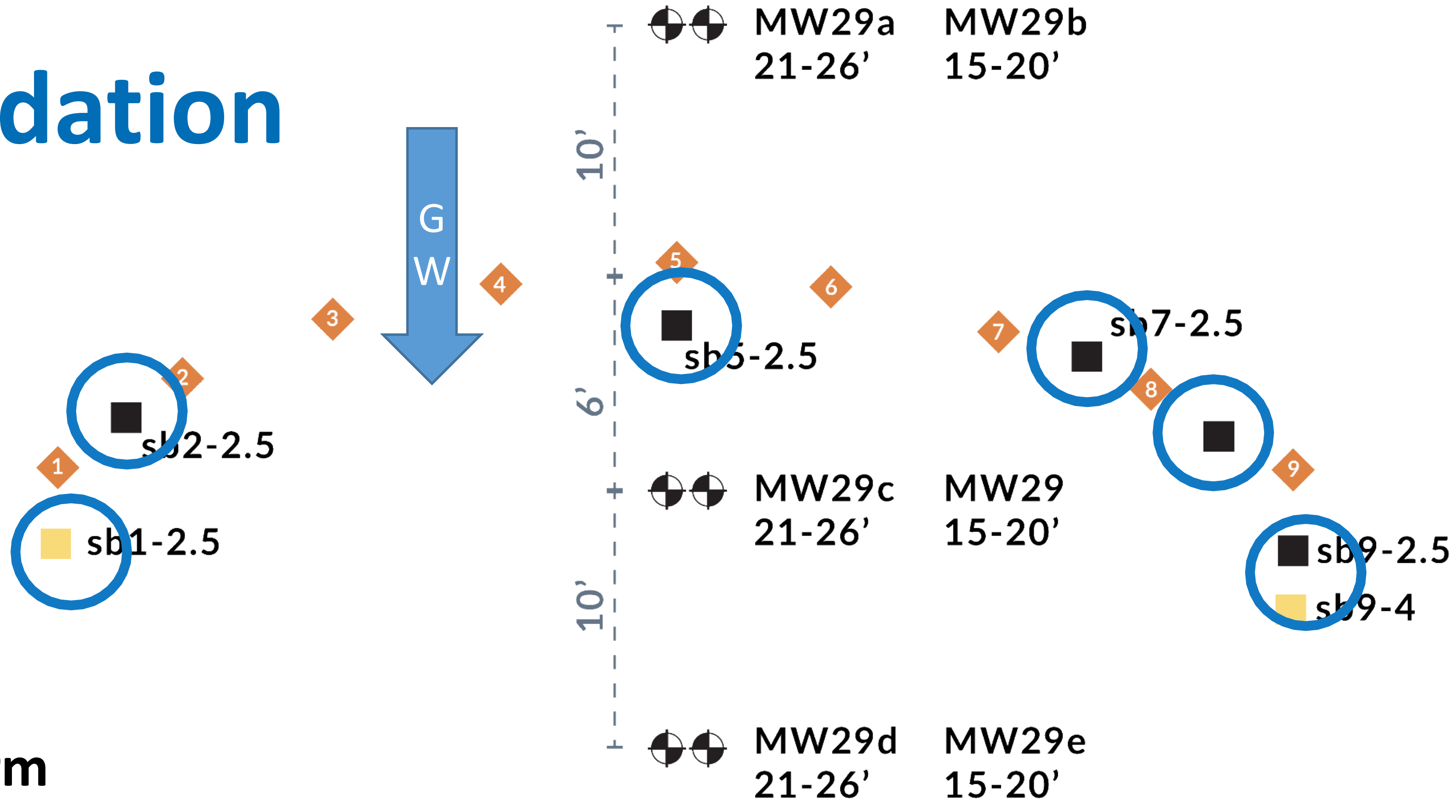
PlumeForce™
Modeling Tool



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

CAC-Distribution Confirmation

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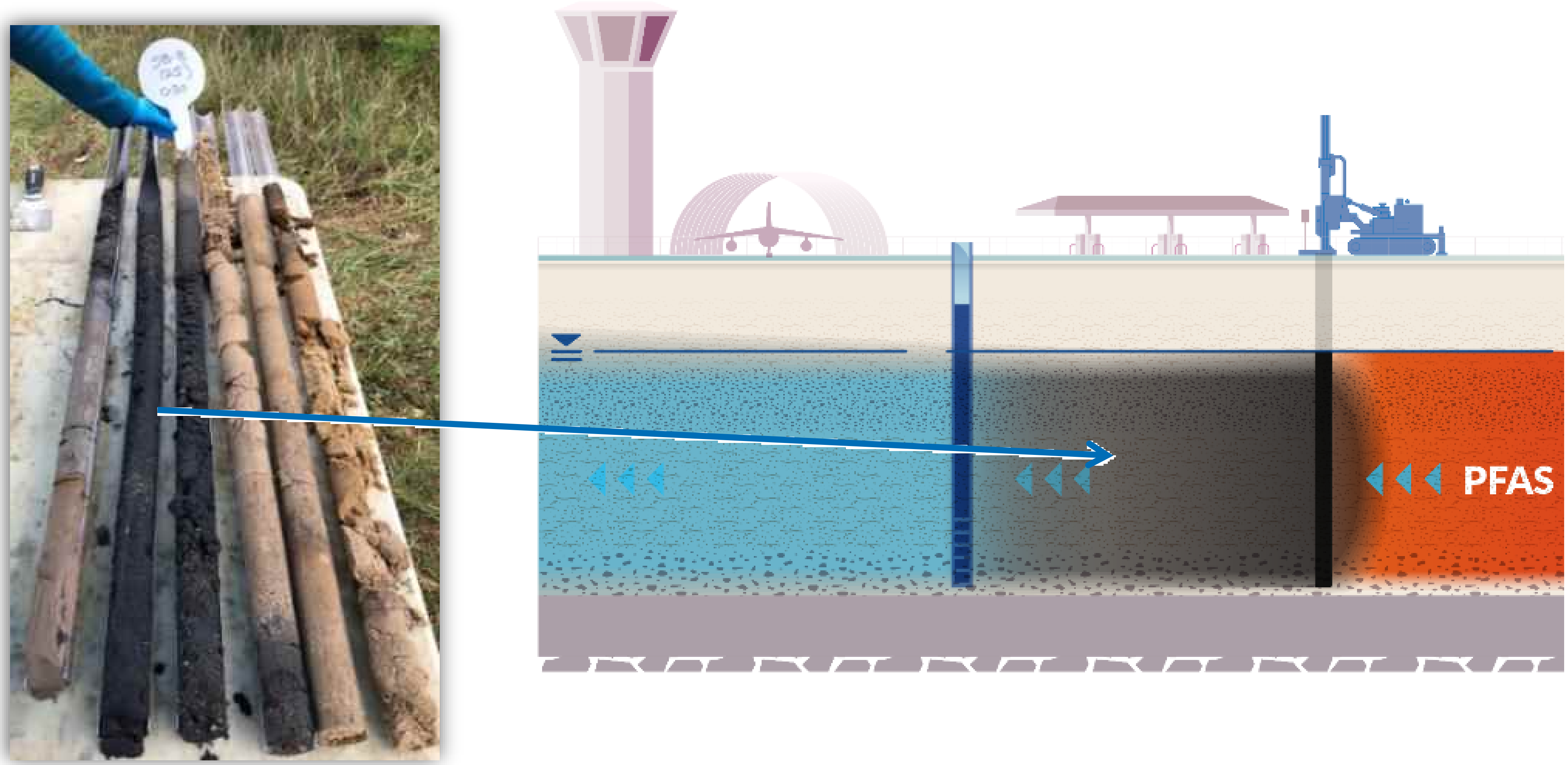
CAC-Distribution Confirmation



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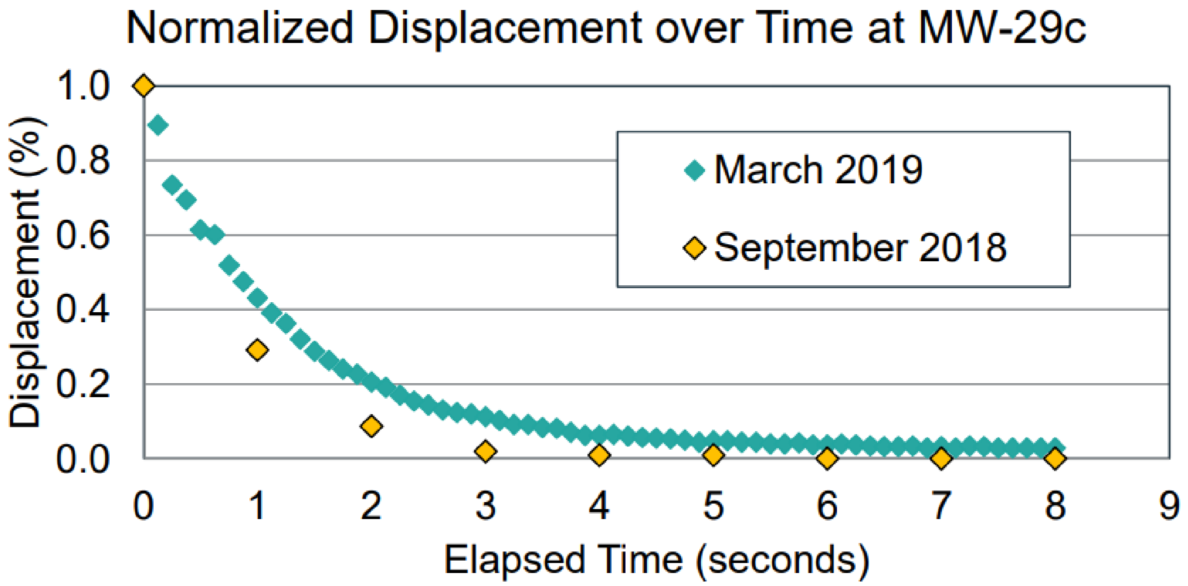
Did the CAC Application change the Characteristics of the Site?

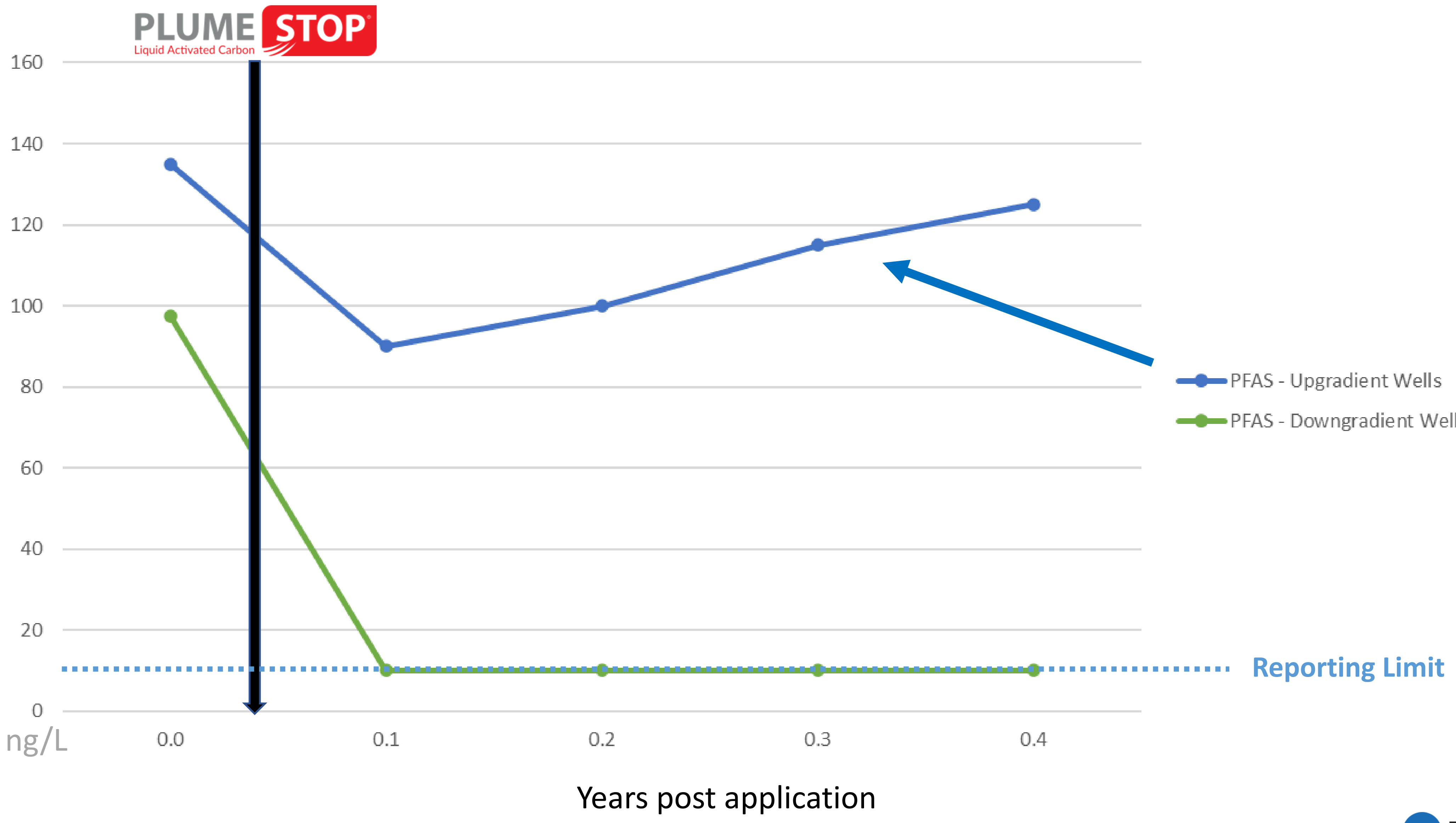
Pre-/Post-Injection Slug Test Results Relatively Unchanged



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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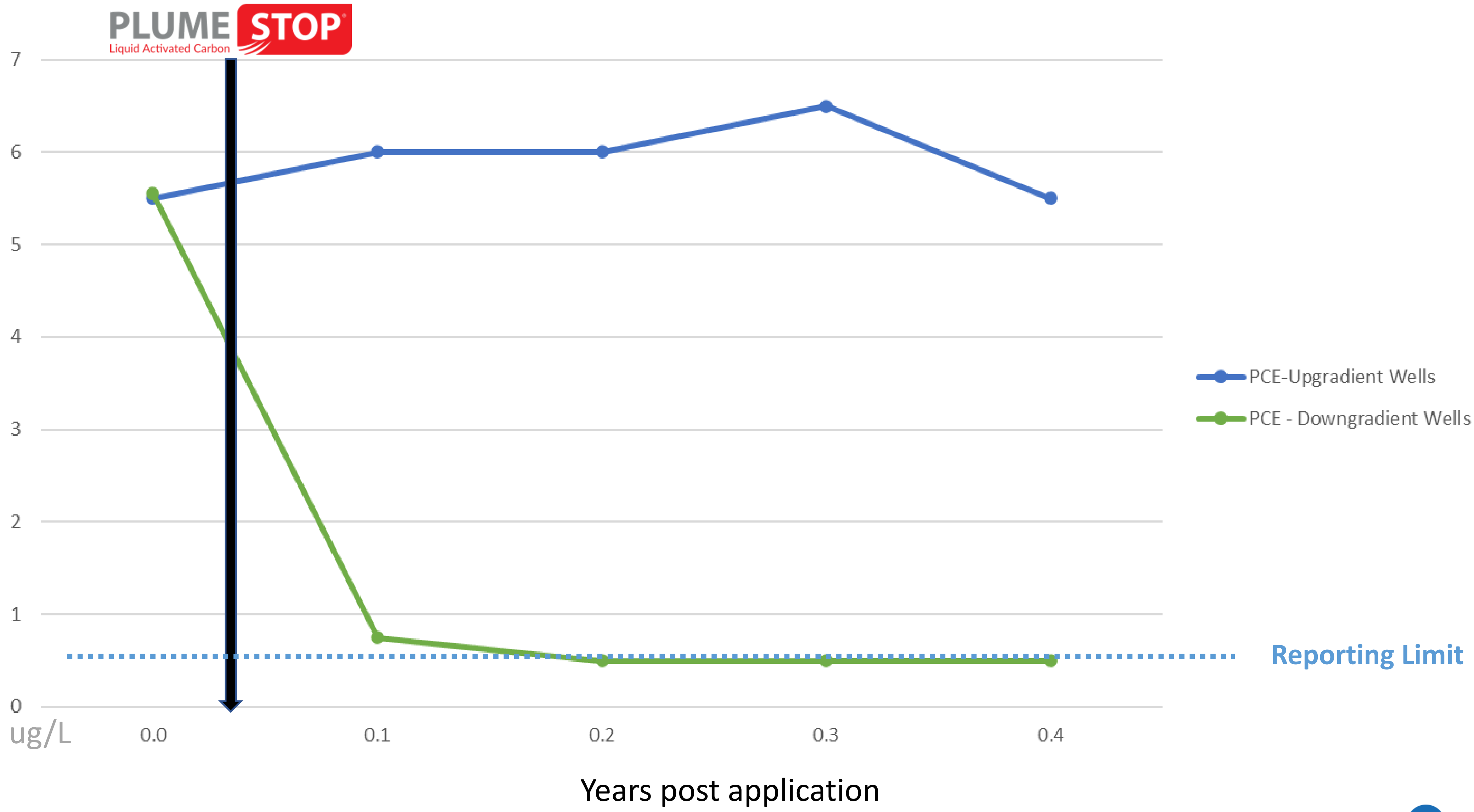
Average PCE Concentrations in Upgradient and Downgradient Well Pairs



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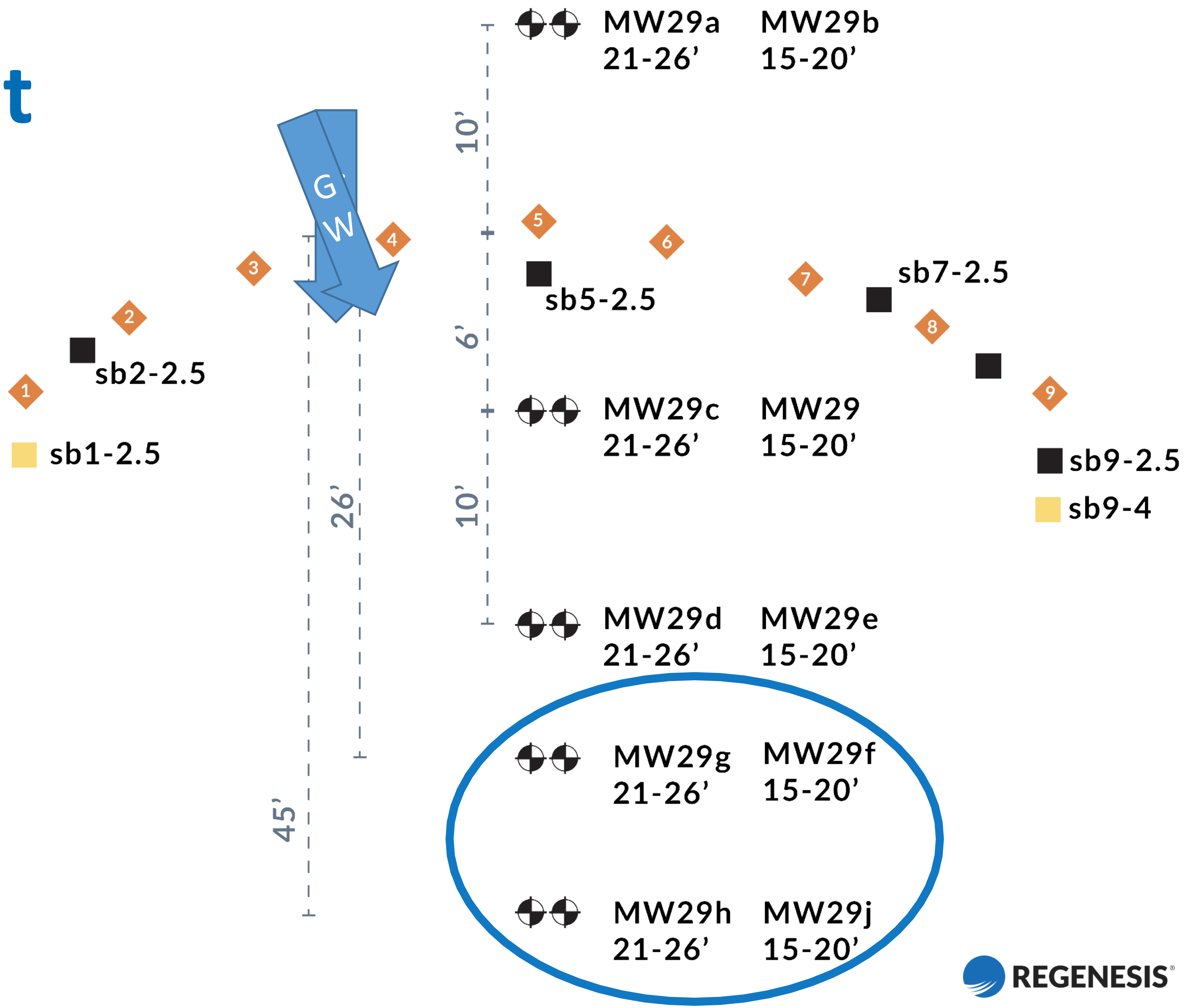
Pilot Test Layout

- At 6 Months we Added Four Downgradient Wells



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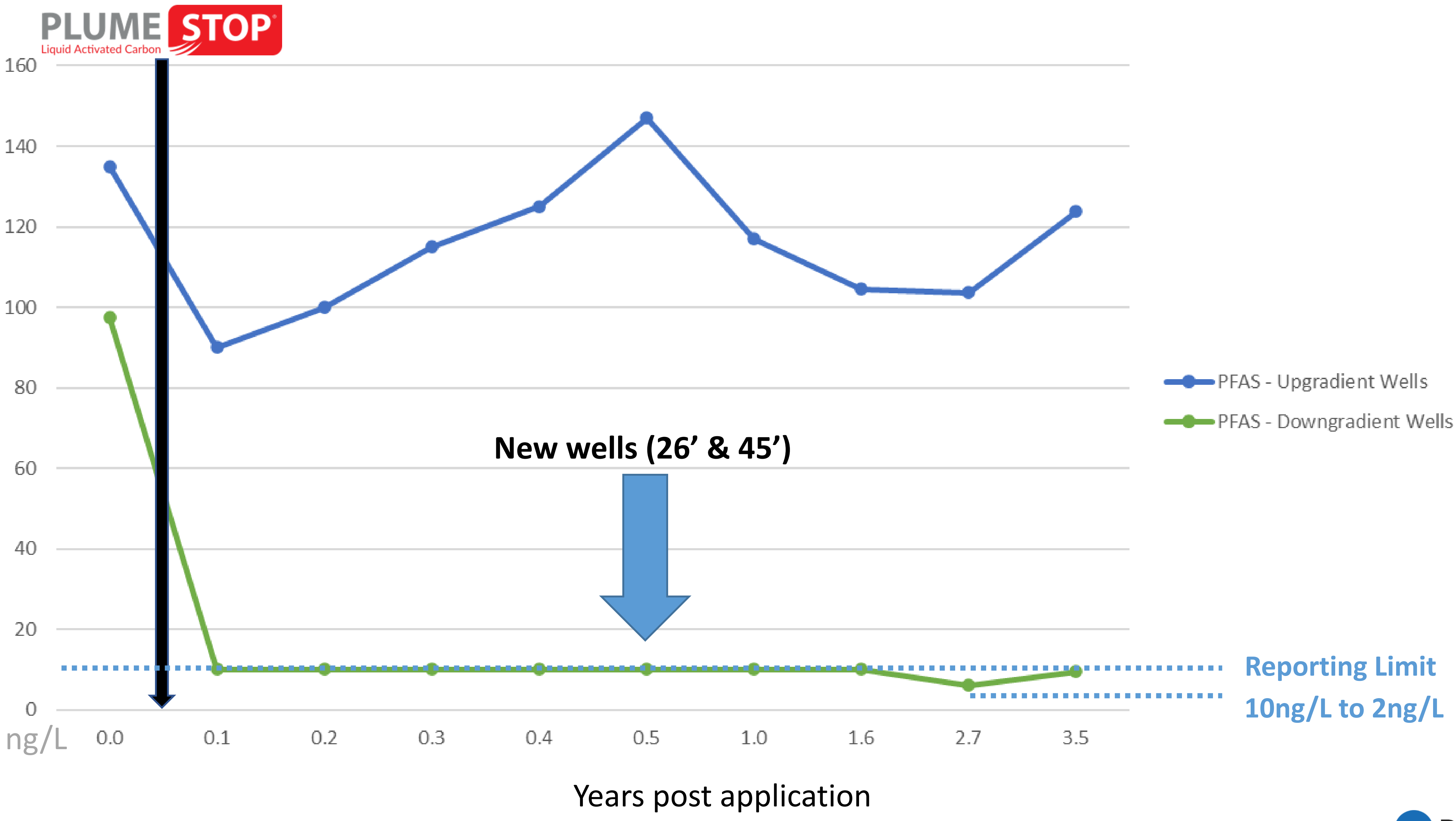
Average Total PFAS Concentrations in Upgradient and Downgradient Well Pairs



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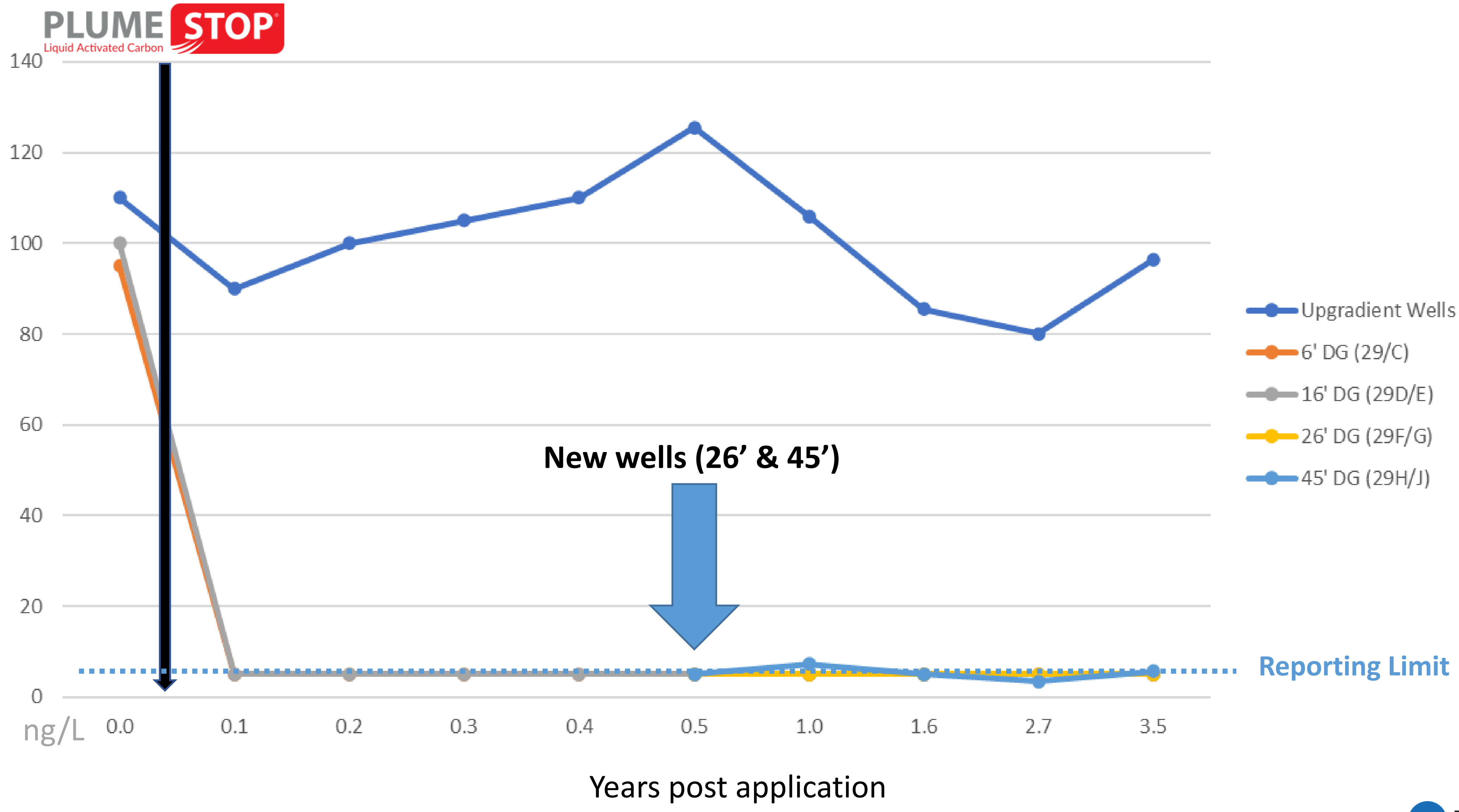
Average Total PFHxS/PFOS Concentrations in Upgradient & Downgradient Wells Pairs



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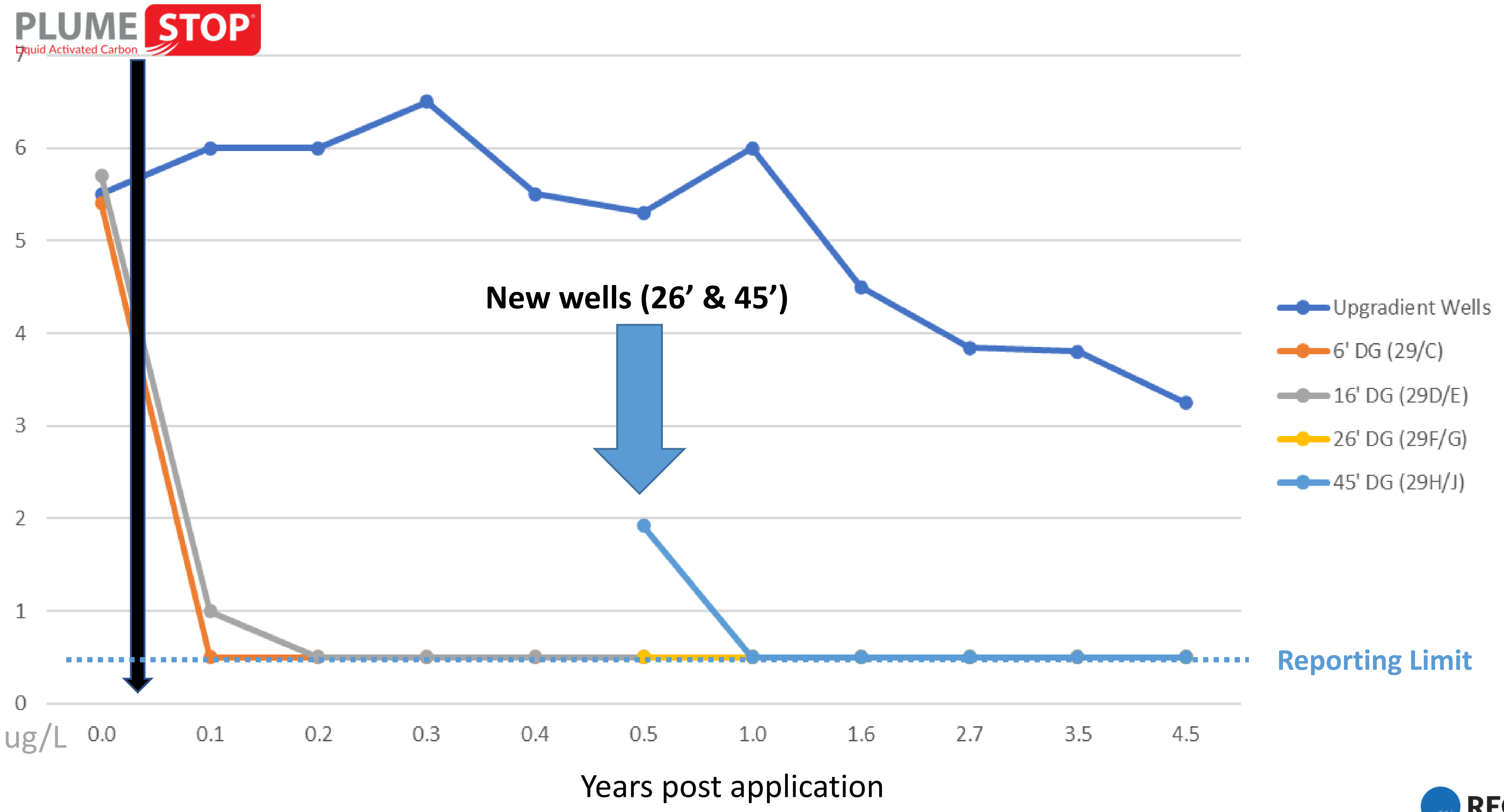
Average PCE Concentrations in Upgradient and Downgradient Wells Pairs



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Summary

- **Very Successful Test**
  - Verified distribution of CAC
  - Sustained reductions of PFAS and PCE over time
  - Treatment Below Proposed USEPA MCL

- **CAC is an effective, *in situ* option to address PFAS Risk**
  - Nearly 40 sites to date
  - Third-Party Evaluations
  - Treatment Expected to last for Decades

Questions?

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