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INSTALLATION, COMMISSIONING AND OPERATION OF AN INJECTABLE IN SITU PERMEABLE REACTIVE BARRIER TO PREVENT THE ADVECTION OF PER-AND POLYFLUOROALKYL SUBSTANCES AT A EUROPEAN AIRPORT

Marcello Carboni, Jack Shore

PlumeStop and PFAS

PlumeStop

What is it?

- Liquid 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





PlumeStop and PFAS

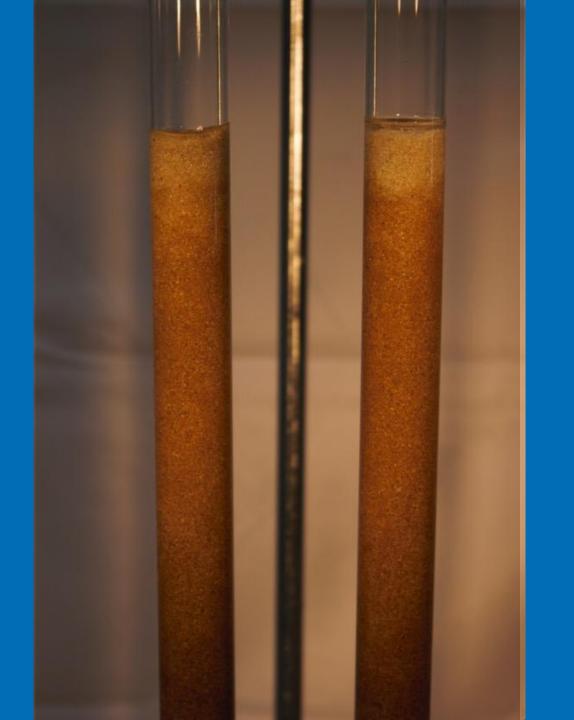
Column Study

CAC vs. PAC

Colloidal Activated Carbon

PLUME STOP

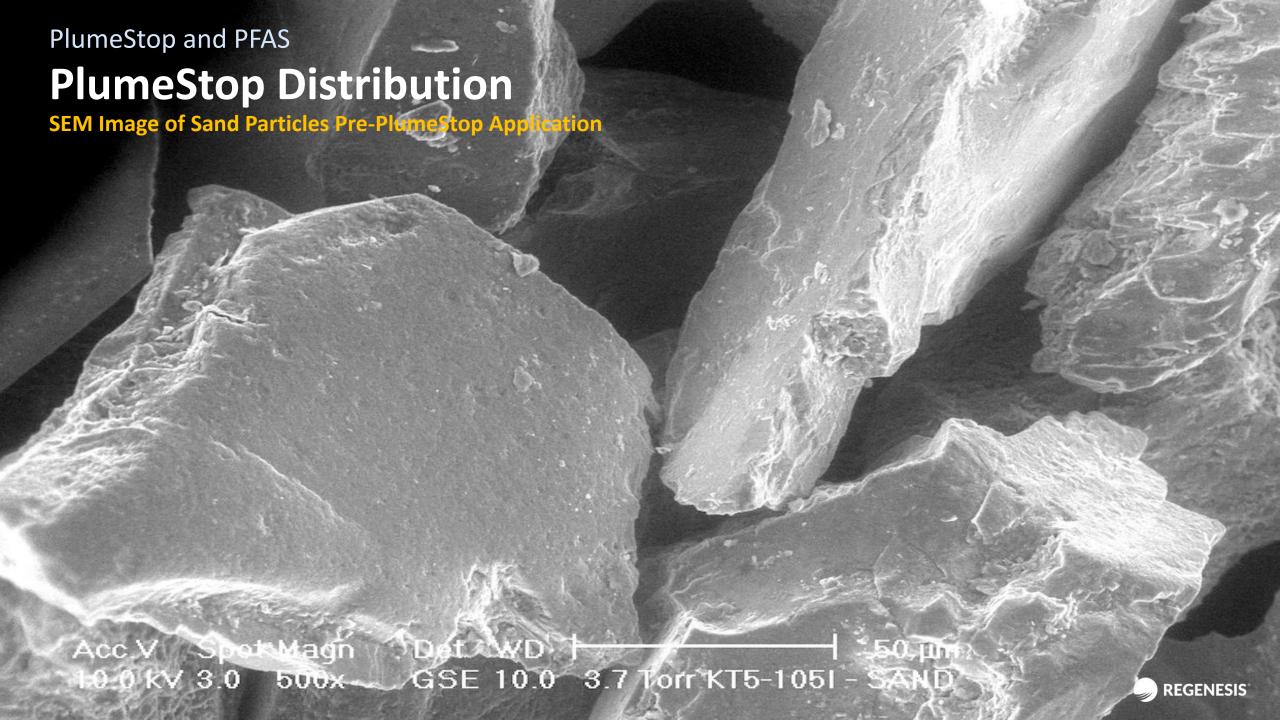
Liquid Activated Carbon

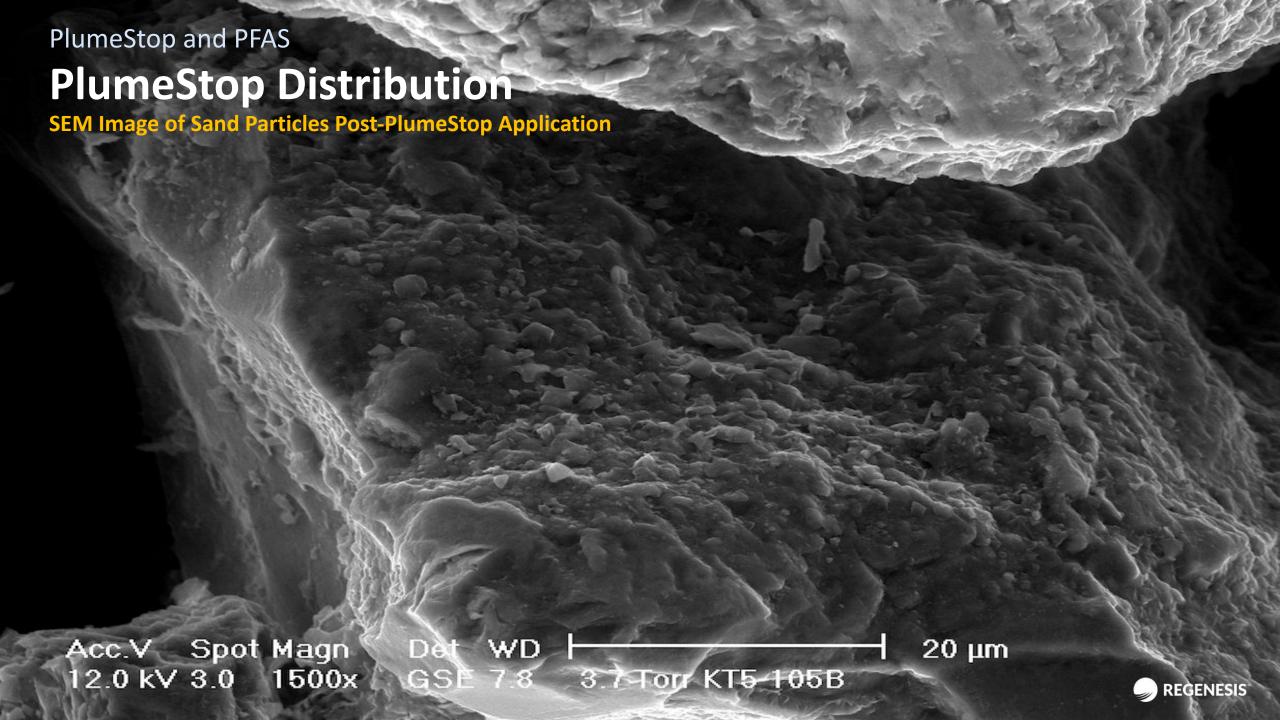


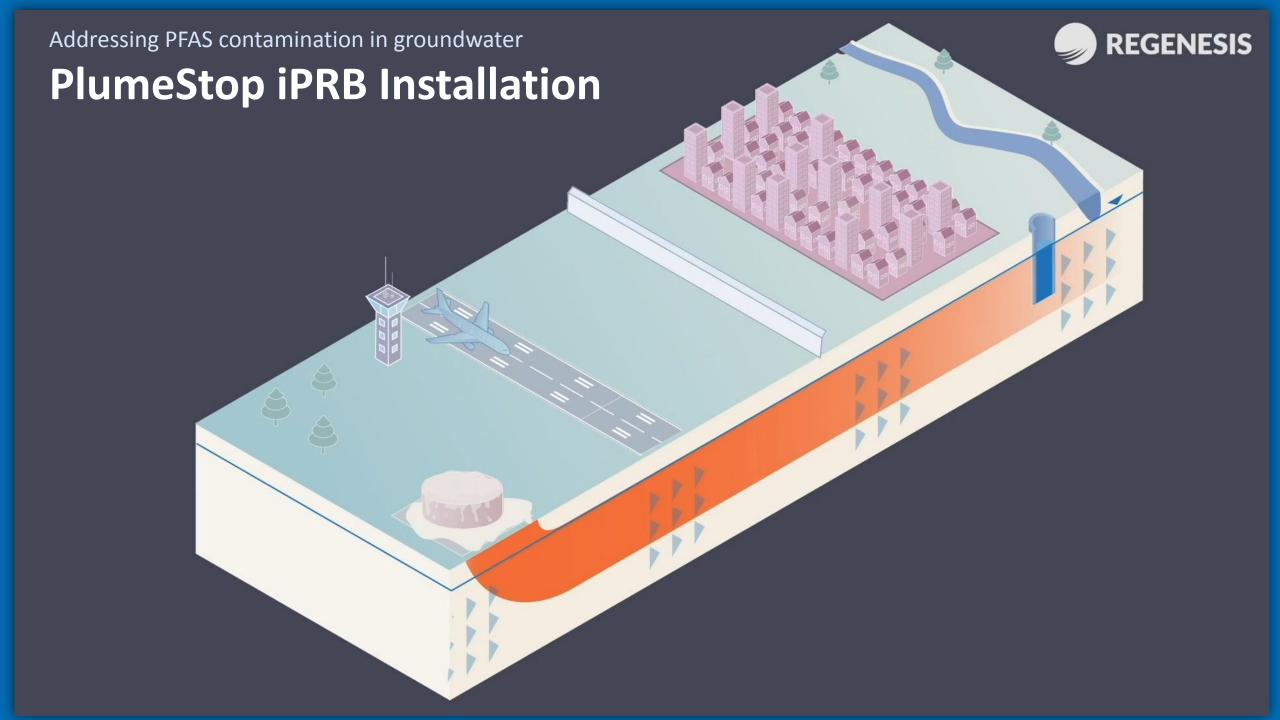


Powdered Activated Carbon (PAC)

Time Lapse = 12 minutes







Addressing PFAS contamination in groundwater

PlumeStop: Eliminates Risk of PFAS

- Hazard x Experience
- PlumeStop binds up PFAS in situ
- Eliminates potential for down gradient exposure
- Eliminates the risk





Capture Efficiency

What happens over time

Won't the barrier eventually fill up and break through?

- This is an *in situ* stabilisation/sequestration approach
- PFAS do not degrade, so the potential for breakthrough must be part of the design process
- The approach includes: how to predict, avoid, and prevent breakthrough



• Which we can do!

Addressing PFAS contamination in groundwater



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RESEARCH ARTICLE

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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 NaHCO₃ ($K_f = 142,800 \text{ mg}^{1-a} \text{ L}^a/\text{kg}$ and a = 0.59); and (2) a groundwater sample (pH = 7.4) containing PFOS among other PFAS from a former fire-training area in the United States ($K_e = 4,900 \text{ mg}^{1-a} \text{ L}^a/\text{kg}$ and a = 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 (Hatton, Holton, & DiGuiseppi, 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-Marianovic 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 (Hatton et al., 2018).

There are two classes of PFAAs: perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs). 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 (µg/L; USEPA, 2016a, 2016b). Health Canada drinking water screening values for PFOS and PFOA are 0.6 and 0.2 µg/L, respectively (Health Canada, 2018). These low cleanup levels and the persistent nature of PFAAs pose a significant challenge in remediating PFAS

Granular activated carbon (GAC) is effective for exsitutreatment of PFAS in groundwater in some cases (McCleaf 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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d groundwater using

ern within the environment. In recent years, regulatory authorir of health-based regulatory and evaluation criteria with groundpically being less than 50 nanograms per liter (ng/L). Subsurface spounds are recalcitrant and widespread in the environment. Trater is extracted and treated on the surface using media such as e resins. These treatment technologies are generally expensive, les to reach treatment objectives. The application of in situ remeor a wide variety of contaminants of concern such as petroleum anic compounds; however, for PFASs, the technology is currently the application of colloidal activated carbon at a site in Canada tanoate (PFOA) and perfluorooctane sulfonic acid (PFOS) were oncentrations up to 3,260 ng/L and 1,450 ng/L, respectively. The anaerobic with an average linear groundwater velocity of approxne colloidal activated carbon was applied using direct push techconcentrations below 30 ng/L were subsequently measured in month period, With the exception of perfluoroundecanoic acid. /L and perfluorooctanesulfonate which was detected at 40 ng/L ere below their respective method detection limits in all postinvated carbon was successfully distributed within the target zone the activated carbon being measured in cores up to 5 meters case study suggests that colloidal activated carbon can be sucow to moderate concentrations of PFASs within similar shallow

tances (PFASs) have been identified by many regulatory agen-

CCC, 2017b), but can be imported from China as of 2003 (Butt. erger, Bossi, & Tomy, 2010). Canada has no current drinking water groundwater regulations for any PFAS; however, the Federal Soil uality Guidelines and Groundwater Quality Guidelines for PFOS dicate 0.21 milligrams per kilogram (mg/kg) for fine soil, 0.14 mg/kg r coarse soil, and 68 micrograms per liter (µg/L) for groundwater r the protection of freshwater life (ECCC, 2017b). The EPA drinking ater health advisory level for the sum of perfluorooctanoate (PFOA) id perfluorooctanesulfonate (PFOS) concentrations is 70 nanograms er liter (ng/L), while other jurisdictions pose stricter regulations IGWA, 2017).

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

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ting the in situ treatment of PFAS

soroalkyl substances (PFAS) have been identified by many regulatory nerging contaminants of concern in a variety of media including currently, there are limited technologies available to treat PFAS in ith the most frequently applied approach being extraction (i.e., pump le this approach can be effective in containing PFAS plumes, previous and treat programs have met with limited remedial success. In situ es of PFAS have been limited to laboratory and a few field studies. Six studies were conducted in an unconfined sand aguifer coimpacted by ocarbon along with PFAS to determine if a variety of reagents could be ite dissolved phase PFAS in the presence of petroleum hydrocarbons. s consisted of two chemical oxidants, hydrogen peroxide (H2O2) and ite (Na₂S₂O₈), and four adsorbents, powdered activated carbon (PAC), ed carbon (CAC), ion-exchange resin (IER), and biochar. The reagents using direct push technology in six permeable reactive zone (PRZ) Groundwater concentrations of various PFAS entering the PRZs ran-00 µg/L perfluoropentanoic acid, up to 6,200 µg/L pentafluorobenzoic 100 µg/L perfluorohexanoic acid, up to 6,080 µg/L perfluoroheptanoic Jug/L perfluorooctanoic acid, and up to 140 µg/L perfluorononanoic nce groundwater sampling within and downgradient of the PRZs oco 18 months using single and multilevel monitoring wells. Results of impling indicated that the PFAS were not treated by either the perperoxide and, in some cases, the PFAS increased in concentration llowing the injection of peroxide and persulfate. Concentrations of dwater sampled within the PAC, CAC, IER, and biochar PRZs imthe injection were determined to be less than the method detection of groundwater samples over the 18-month monitoring period, inthe PRZs exhibited partial or complete breakthrough of the PFAS over nonitoring period, except for the CAC PRZ which showed no PFAS Analysis of cores for the CAC, PAC, and biochar PRZs suggested that niformly distributed within the target injection zone, whereas the PAC owed preferential injection into a thin coarse-sand seam. Similarly,

sand packs of monitoring wells installed before the injection of the

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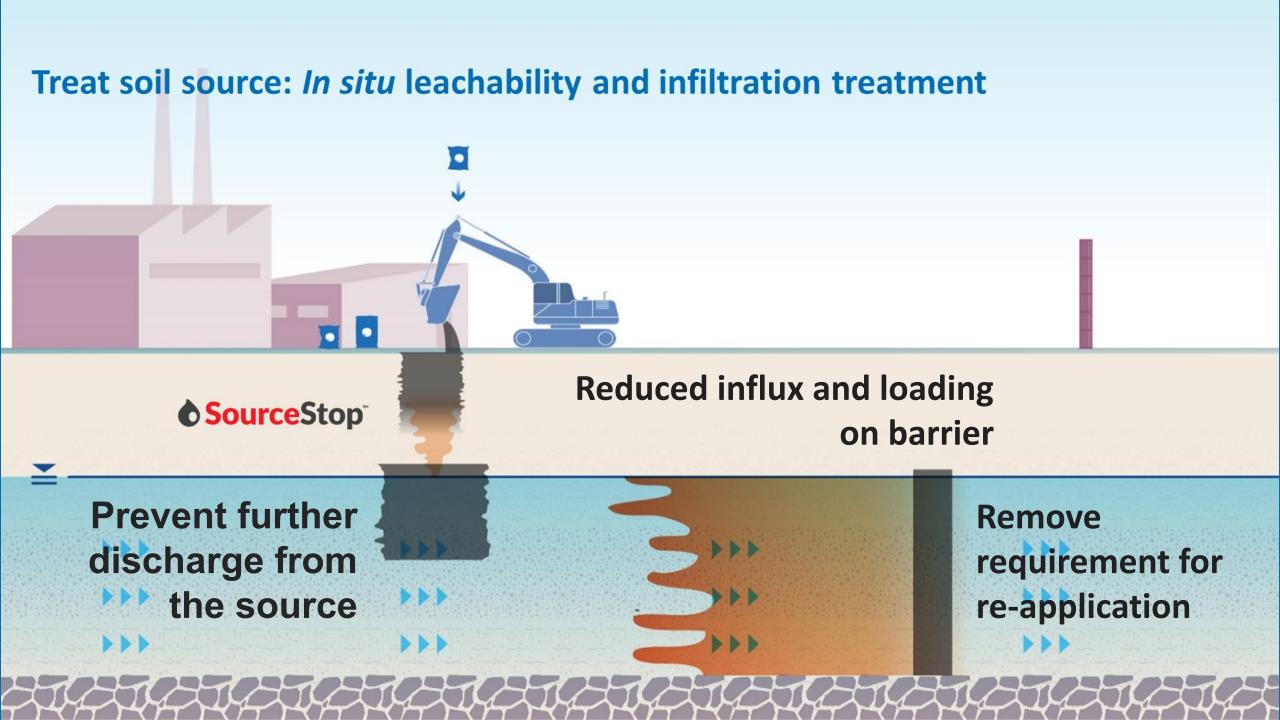
ts on regulatory policy, transport/fate, and Ikyl substances (PFAS)

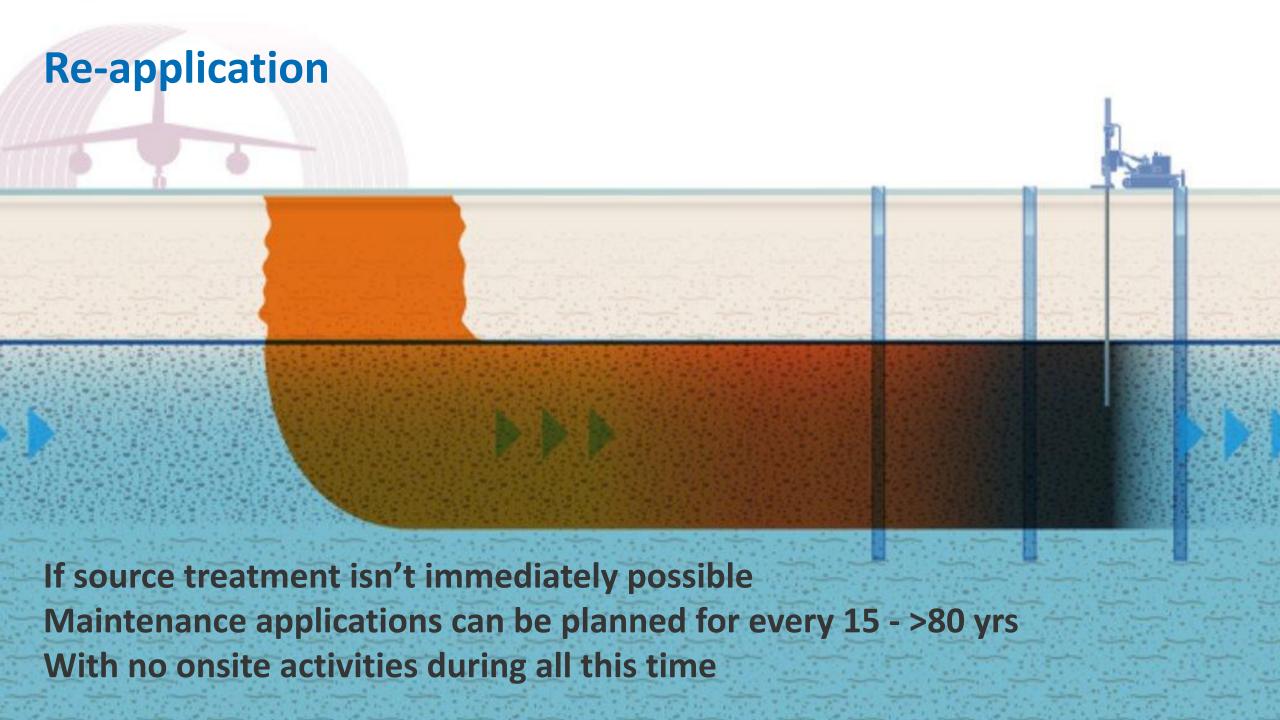
Dan Bryant⁴ | Matthew Burns⁵ | Chiang⁸ Douglas Cox⁹ ppi¹² Jim Fenstermacher¹³ an Hagelin¹⁶ | Linda Hall¹⁷ enigsberg²⁰ François Lauzon²¹ rath²⁴ Ravi Naidu²⁵ h²⁸ | Paul Tomiczek²⁹ | Rick Wice³⁰

ientific, engineering, regulatory, and legal commuxperts Symposium in Arlington, Virginia on May 20 lated to per- and polyfluoroalkyl substances (PFAS) developments of PFAS regulations, chemistry and epts, toxicology, and remediation technologies. The experts with various specialized skills to provide on existing and new approaches to PFAS assessment ons learned managing other contaminants encoun-The following summarizes several consensus points Symposium:

e response by many states and the US Environmental media exposure and public pressure related to PFAS uickly initiate programs to regulate PFAS sites. This relatively low lifetime health advisory levels for PFAS stringent guidance and standards in several states. In ed as hazardous substances at the federal level, as nal bills, there could be wide-reaching effects including lely for PFAS, application of stringent state standards. emediation at existing sites, reopening of closed sites.

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"Groundwater containment may be achieved through an injection of an amendment that causes the PFAS to attach onto materials in an aquifer"



PFAS Team



Case Study Private UK Airport

PFAS pilot trial leads to successful PlumeShield-guaranteed

full-scale installation



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Site Features

Site

- Fire fighting training area
- Land divestment

Contamination

- PFOS (320 ng/L)
- PFOA (6,320 ng/L)

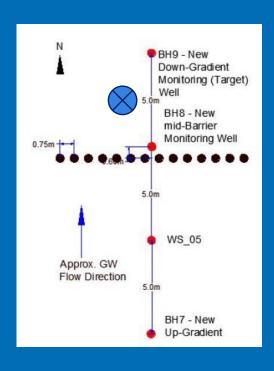
Formation

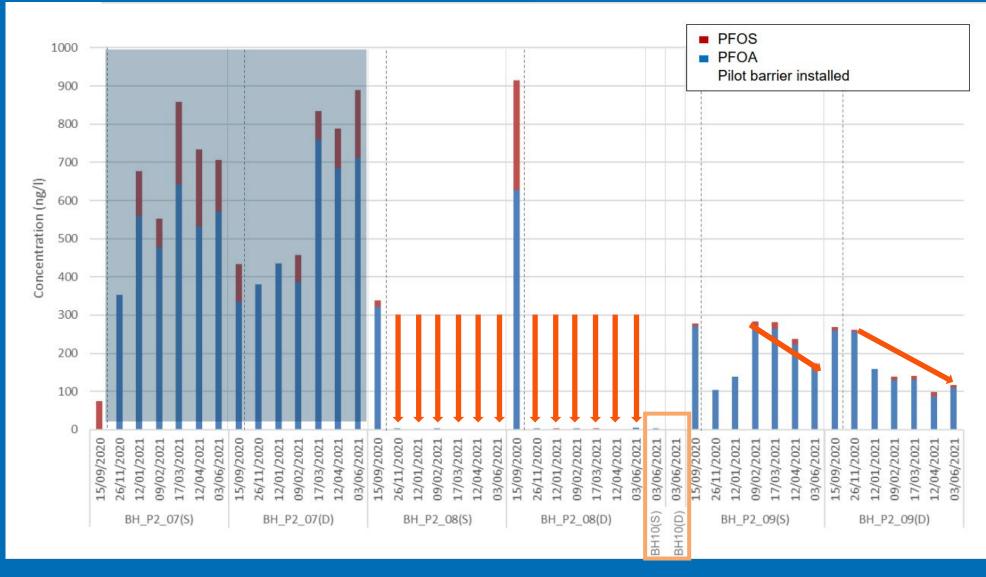
- Weathered Chalk
- Higher permeability layers
- Slow and fast-flowing flux zones
- Groundwater at 3m BGL





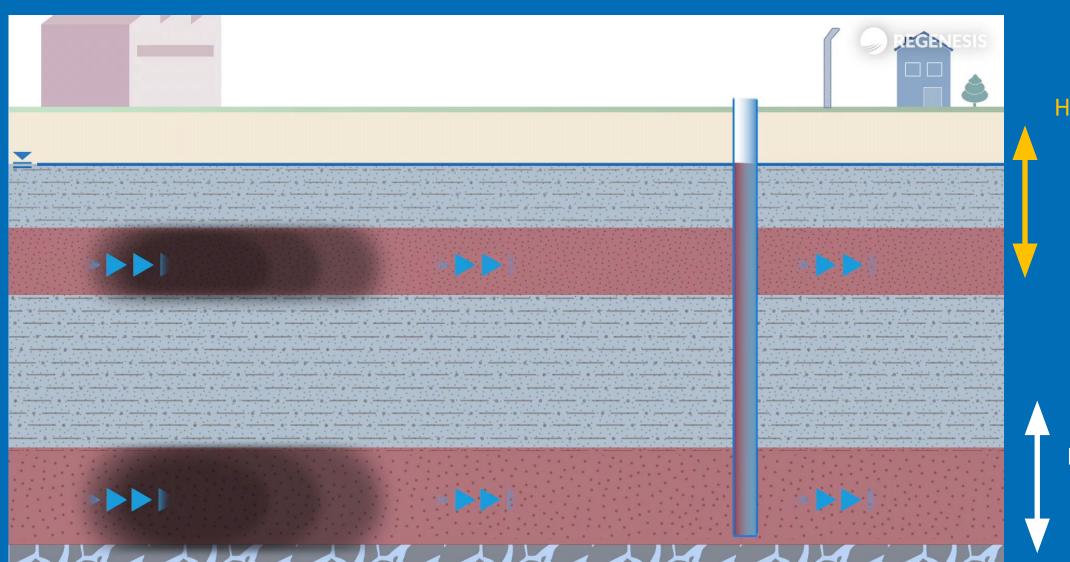
PlumeStop Pilot Installation – Summary





Case Study – Private UK Airport Updated CSM





Higher contaminant loading (WS5)
Greater back diffusion
Slow Flux
Greater noise

Lower concentrations
Less back diffusion
Faster flux
Down gradient
effect clearer



PlumeStop Pilot Installation – Concluded

- 0.5m and 2.5m down gradient of the barrier we are seeing a >99% reduction in PFOA/PFOS (<0.1ug/L)
 - Barrier is working
- Clear evidence of reducing concentrations
 5m downgradient in deeper well (BH09 (D))
 - Faster flowing flux zone
 - Wave of cleaner water arriving sooner

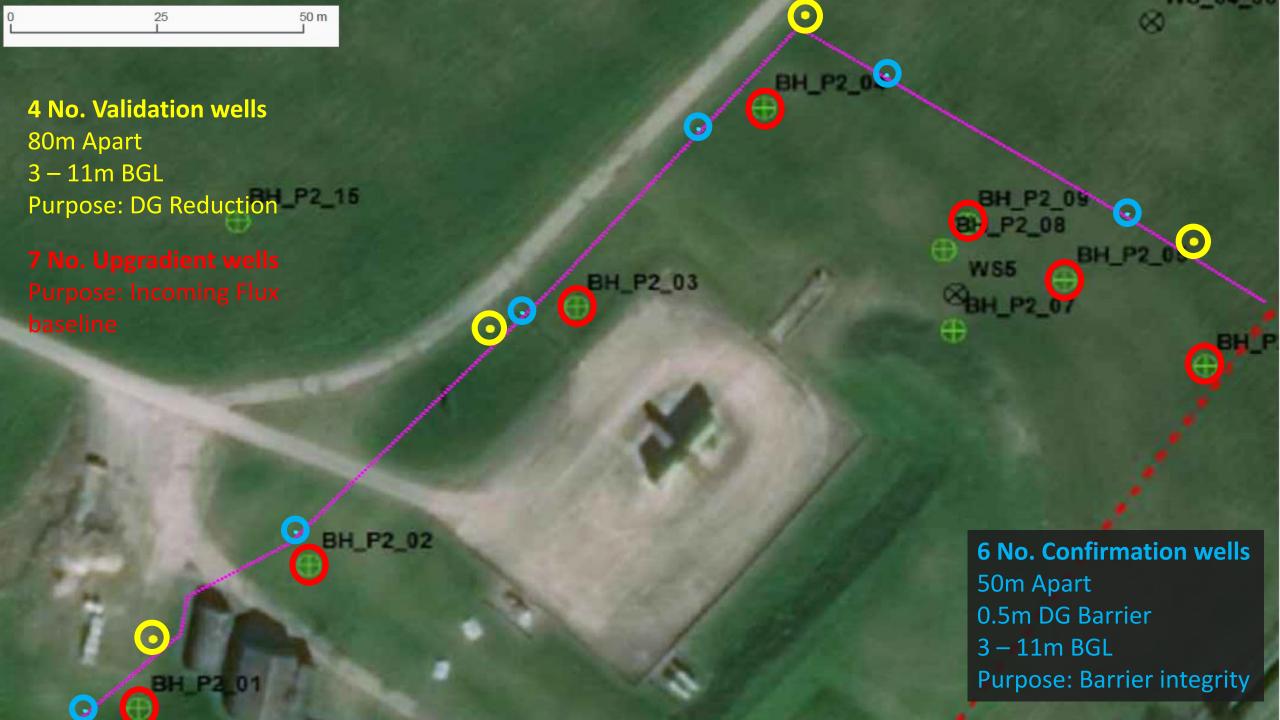


- Robust results that allow to:
 - Move to Full-Scale Installation

Case Study - Private UK Airport Full Scale Implementation

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- 277 meters long
- 3 to 11m BGL
- Installation works: 4 months (March-June 2022)
- Commissioning works: August 2022 to Feb 2023
- Placement validation
- Performance validation
- 3rd Party Validation and Verification
- Warrantied solution



REGENESIS*

Installation activities





Installation confirmation methods





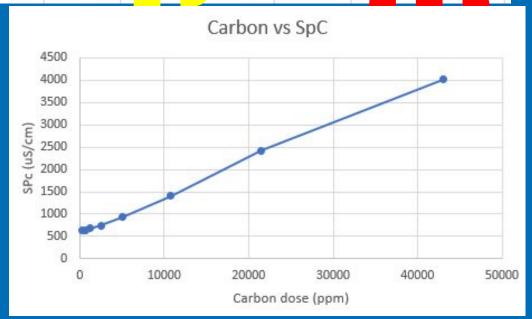


Placement Validation: Secondary lines of evidence

- Turbidity
- Electrical conductivity

Carbon concentration	Temp	Do	SPc	μH	ORP	FNU	NTU
PPM	С	%	uS/cm	-	mV	-	-
0 (clean water)	14.3	57.3	579	8.04	199	48.25	48.25
43000	15.4	12	4018	9.81	139.8	-2.99	-2.99
21500	15.1	20.2	2423	9.67	13	-3.11	-3.11
10750	14.9	49.3	1408	9.34	150	-3.12	-3.12
5000	15.1	64	924	8.81	17	-298	-298
2500	15.1	82	745	8.34	189	-2.38	-2.38
1250	15.8	88	674	7.98	199	1.92	1.92
625	16.1	93.2	638	7.74	205	15.5	15.5
312.5	16.2	95.7	626	7.61	208	22	22
						T	





Case Study – Private UK Airport



Performance Validation: Early results

- All wells = ND
- MDL > STL
- Centrifugation

MR2 (Installation #2)

Sampled Date: 31/05/2022

Concentration: (<Detection limit) ng/L

compound	BH_VH_C1	BH_VH_C2	BH_VH_C4
PFOA	<65	<113	<350
Linear PFOS	<65	<6 ₅	<6ɔ
Branched PFOS	<65	<65	<65
Total PFOS	<65	<65	<65

STL = 100



PlumeShield

PlumeShield guarantees our advanced PFAS remediation system eliminates the environmental risk of PFAS in groundwater

- Guaranteed price:
 - Time, product and injections included
- Guaranteed effectiveness:
 - Balance of payment due when barrier meets performance criteria
- Guaranteed performance:
 - Minimum 10-year PlumeShield warranty







- REGENESIS offers a suite of remediation technologies for soil and groundwater
- Colloidal Activated Carbon is a proven technology
- PlumeStop eliminates the risk of PFAS in groundwater
- Cost-effective strategies
- Guaranteed approach







THANK YOU FOR YOUR ATTENTION

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