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Virtual
remediationtechnologiessymposium2020
Together Apart

Technology Update & Review – Activated Carbon for Contaminant Control & Site Remediation

Presented by Jean Paré, P. Eng.
October 2020

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Presentation Summary

Virtual
remediationtechnologiessymposium2020
Together Apart

- *Activated Carbon Form, Capture & Treatment Mechanisms*
- *Back Diffusion and How it affect your site*
- *Activated Carbon Treatment Capabilities*
- *Case Studies*

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Typical site remediation technique

- ✓ Dig & Haul
- ✓ Pump & Treat
- ✓ Soil Vapour Extraction under vacuum with or without air/steam injection
- ✓ Chemical Oxidation In Situ/Ex Situ
- ✓ Chemical Reduction In Situ/Ex Situ
- ✓ Monitored Natural Attenuation
- ✓ Activated Carbon Sorption & Treatment Technology
- ✓ Enhanced Bioremediation
- ✓ Risk Analysis
- ✓ Stabilization/Solidification
- ✓ Soil Washing
- ✓ Phytoremediation
- ✓ Reactive Barriers
- ✓ Thermal degradation/desorption

Reference Literature

NAVFAC
Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

TECHNICAL REPORT

IN SITU ACTIVATED CARBON CASE STUDY REVIEW

Clemson University
TigerPrints

All Theses | Theses

8-2018

The Influence of In-Situ Activated Carbon on Biodegradation of Chlorinated Solvents

Kameryn McGee
Clemson University, ksmcgee@g.clemson.edu

Activated Carbon-Based Technology for In Situ Remediation

EPA 542-F-18-001 | April 2018

EPA
United States
Environmental Protection
Agency

Remedial Technology Fact Sheet – Activated Carbon-Based Technology for In Situ Remediation

Introduction

At a Glance

- An emerging remedial technology combining adsorption by activated carbon (AC) and degradation by reactive amendments.

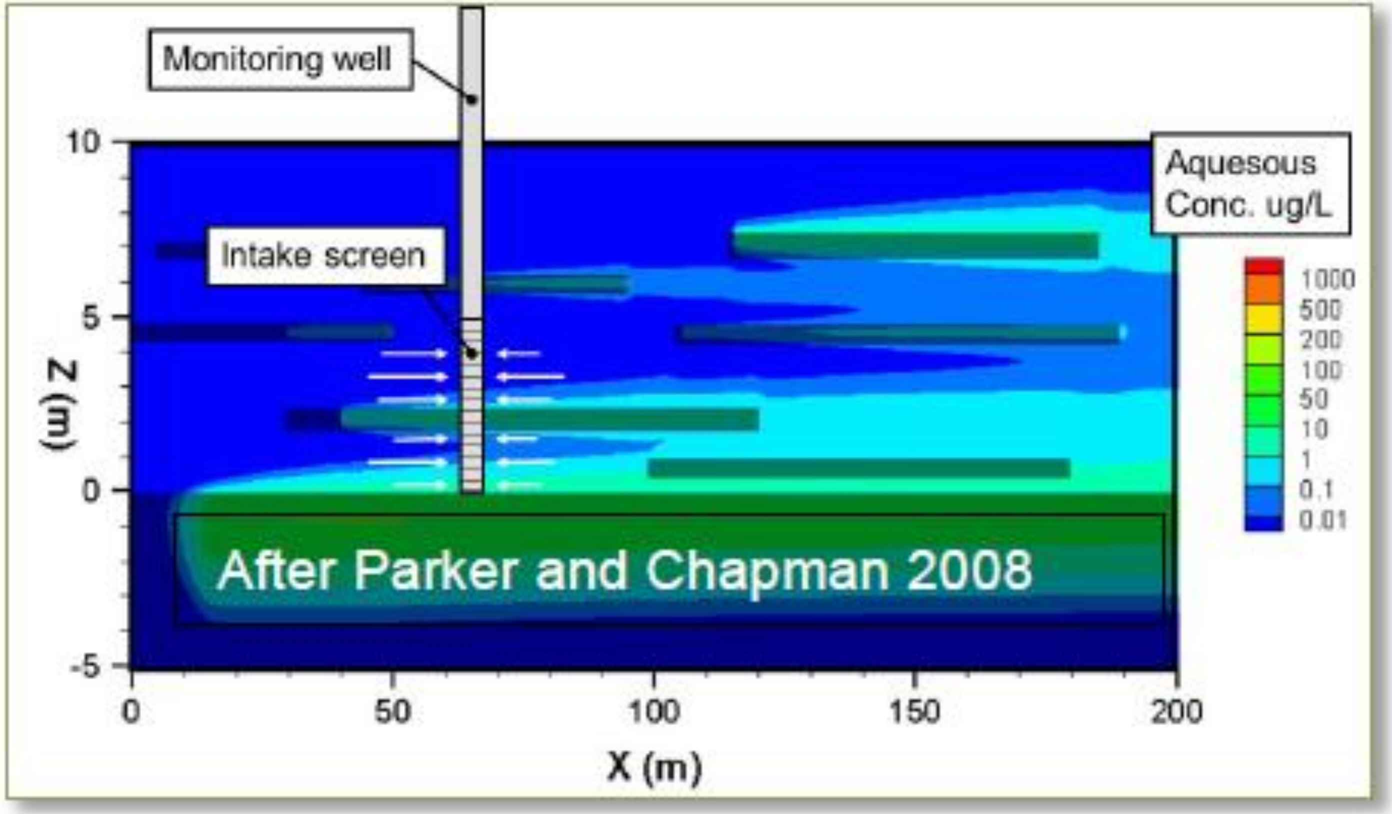
This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Office of Superfund Remediation and Technology Innovation, concerns an emerging remedial technology that applies a combination of activated carbon (AC) and chemical and/or biological amendments for in situ remediation of soil and groundwater contaminated by organic contaminants, primarily petroleum hydrocarbons and chlorinated solvents. The technology typically is designed to carry out two contaminant removal

& Others

The Back Diffusion Issue

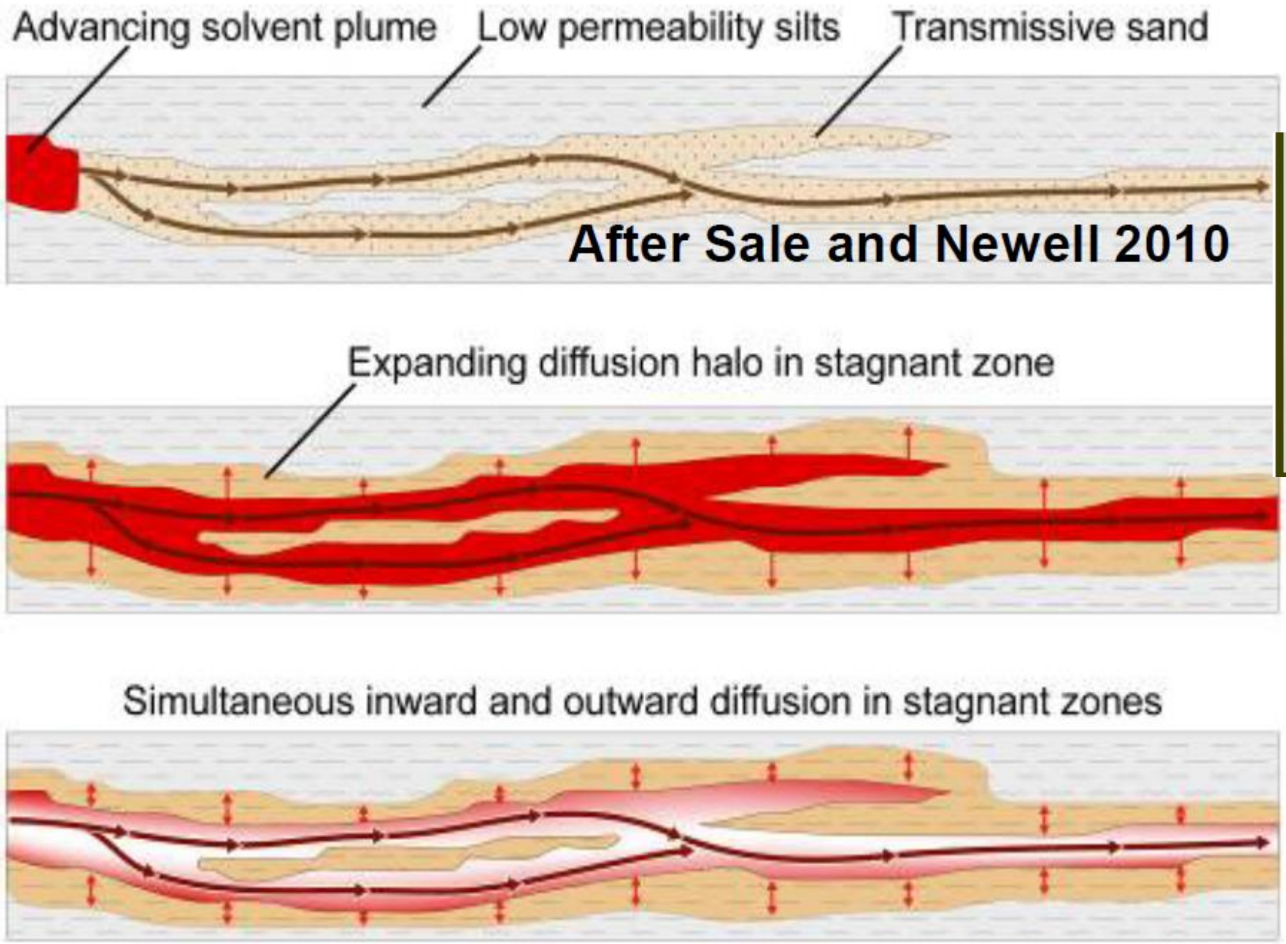
Back Diffusion Visualation

Multilayer Flow Systems



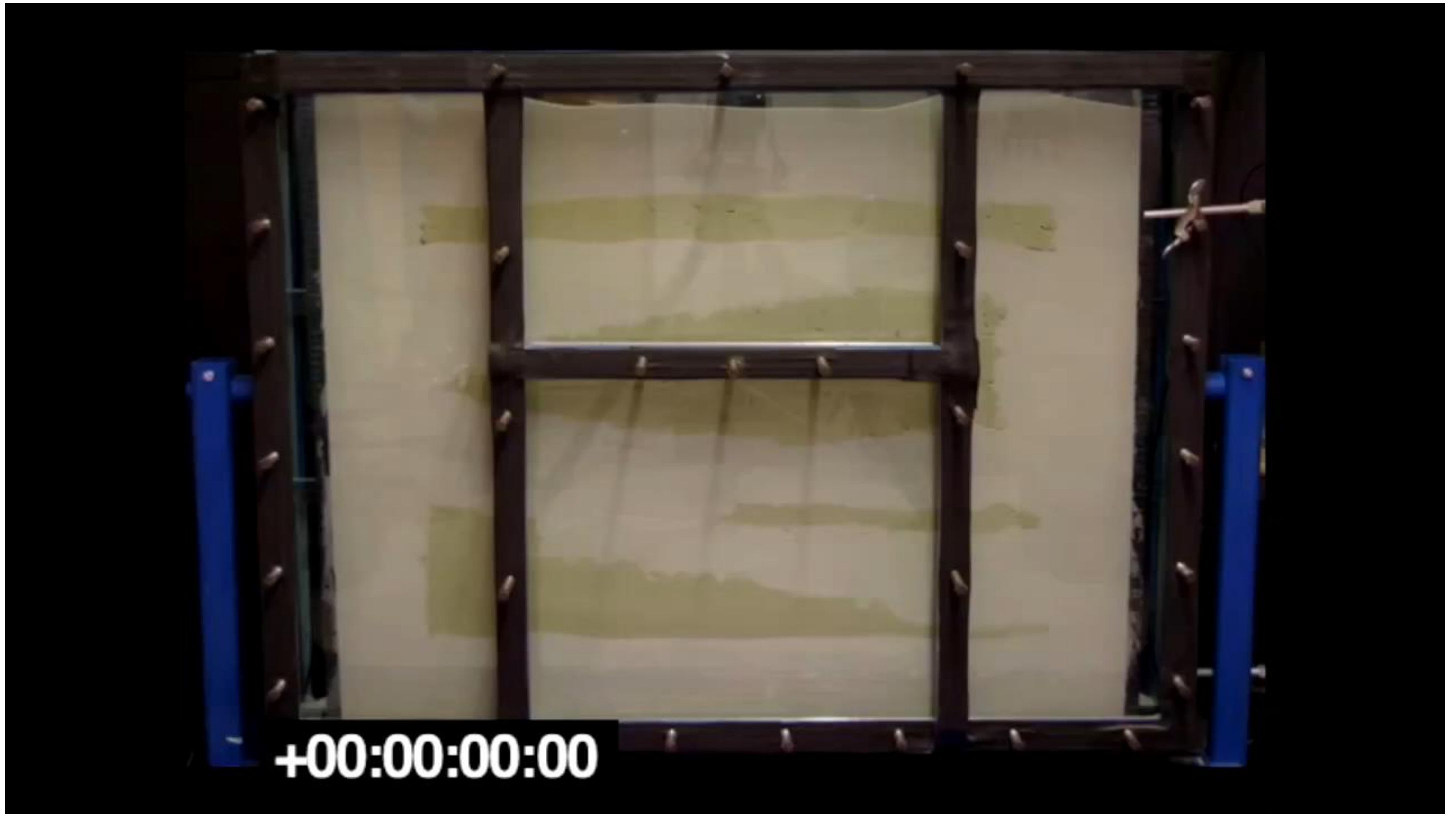
Source: SERDP – Project ERP 1740

Back Diffusion Visualation



Source: SERDP – Project ERP 1740

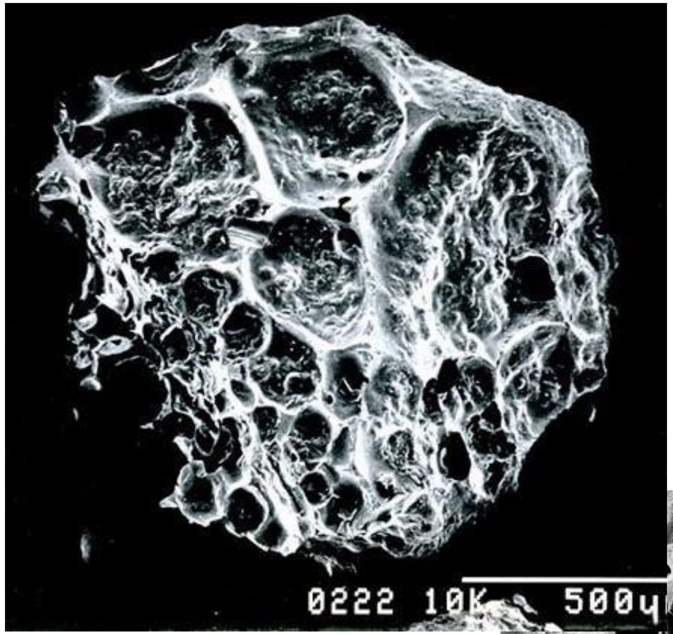
Back Diffusion Visualation

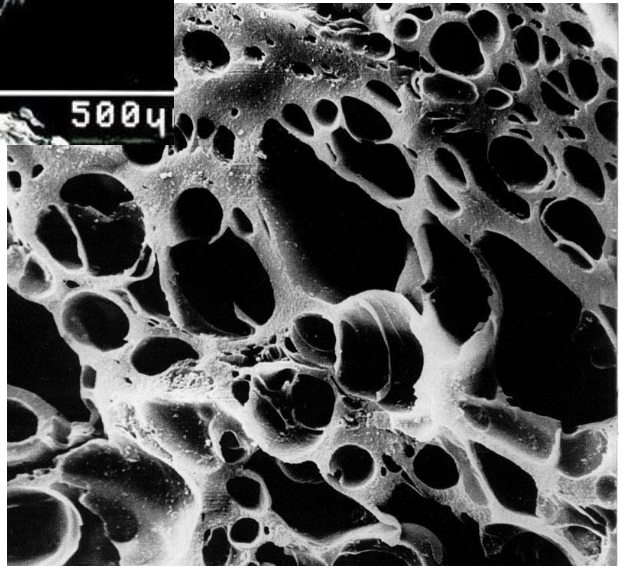


Source – Colorado State University

Activated Carbon Form, Capture & Treatment Mechanisms

Adsorptive





Granular Activated Carbon

Activated Carbon Form, Capture & Treatment Mechanisms

Pore Sizes

•**Transport pores** are >5 molecular diameters to visible cracks and crevices.

Transport pores are too large to adsorb and act simply as diffusion paths to transport the adsorbate to the adsorption sites.

–Macropores (>50 nm diameter) (=.05 µ)

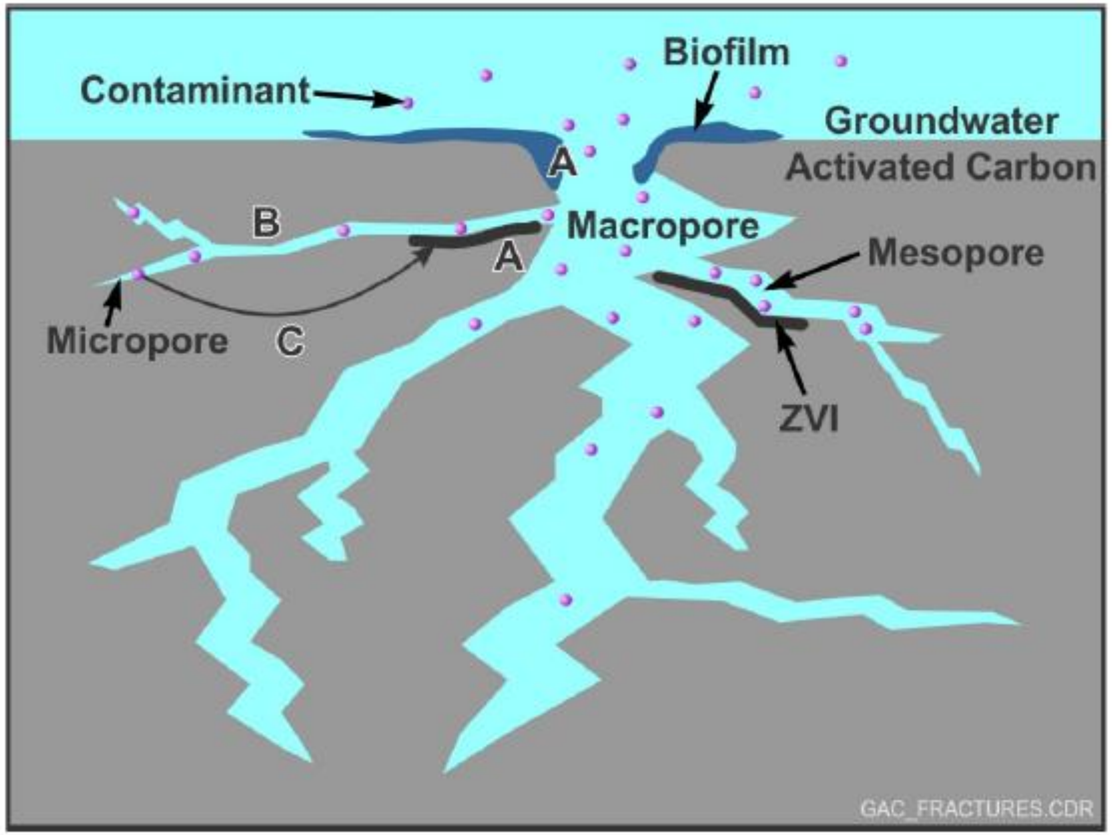
–Mesopores (2-50 nm diameter)

•**Adsorption pores** are the smallest pores within the particle, consisting of gaps between the graphite plates.

40% of the carbon particle/granule volume

–Micropores (< 2 nm diameter) (=.002 µ)

Macro and mesopores are the highways into the carbon particle while micropores are the parking lots.



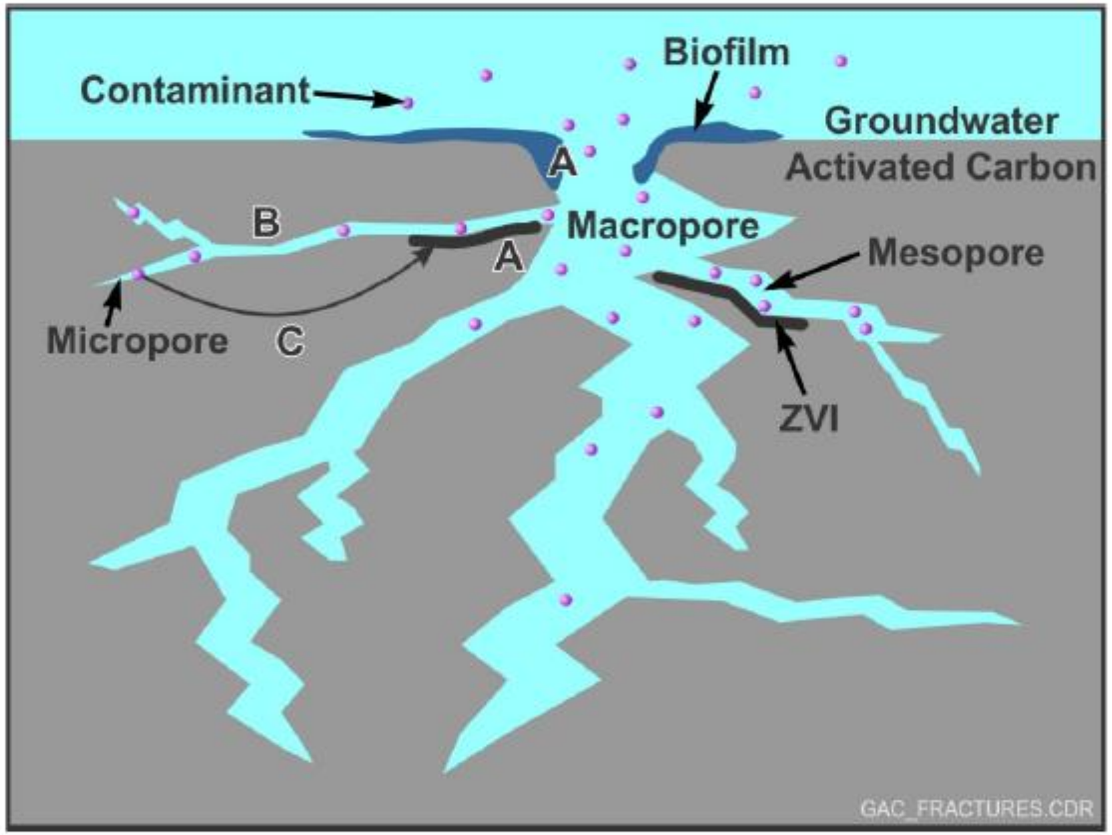
Source – Modified from Fan et al., 2017 and reproduced with permission from Journal of Environmental Management

Activated Carbon Form, Capture & Treatment Mechanisms

- **Granular Activated Carbon Particle size** >90% retained by an 80-mesh sieve (177 µ) [ASTM D2862] *> 4x larger than PAC*

- **Powder Activated Carbon Particle size <40 microns (µ)**

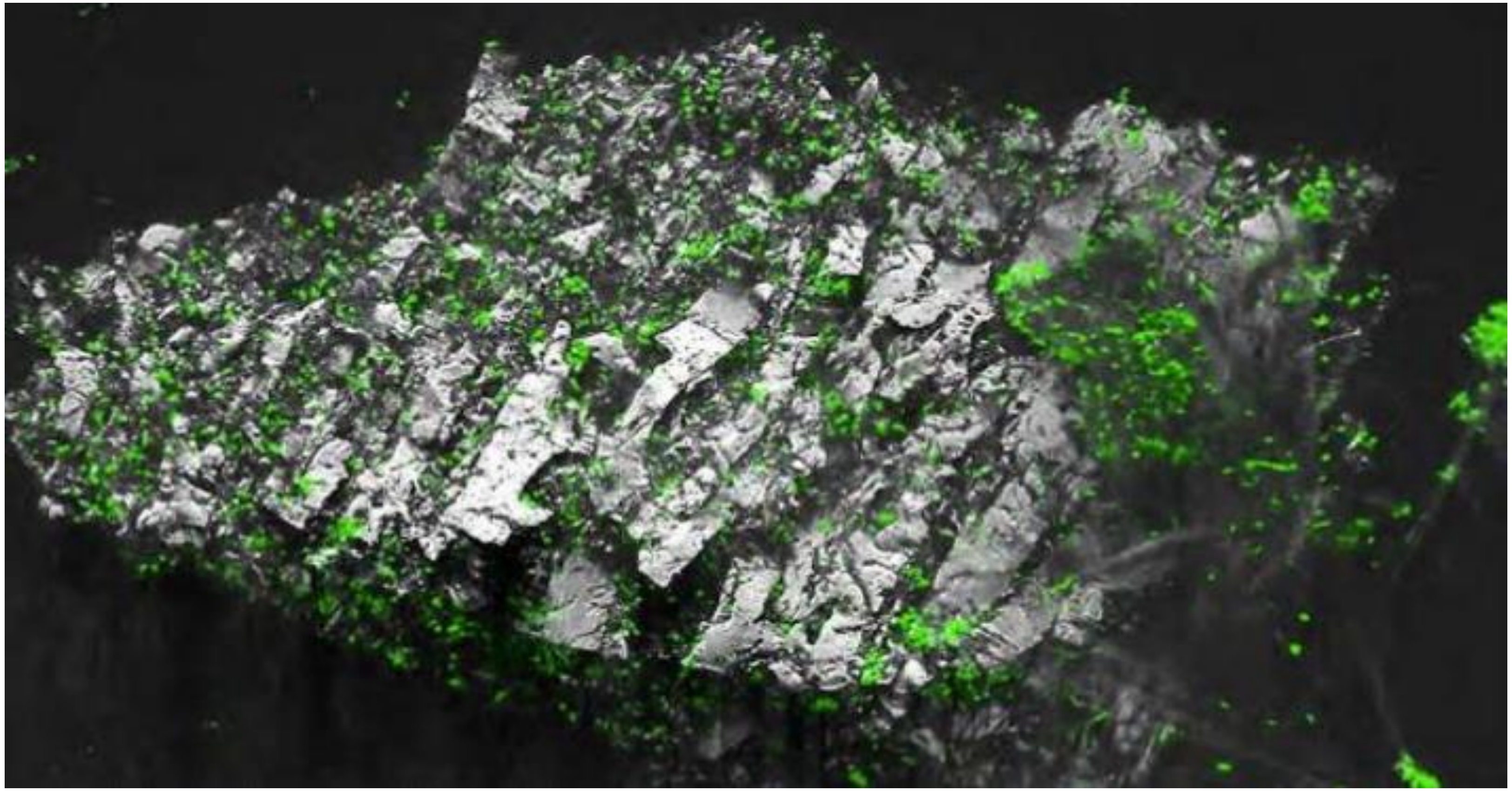
- **Colloidal Activated Carbon Particle size 1-2 microns (µ)**



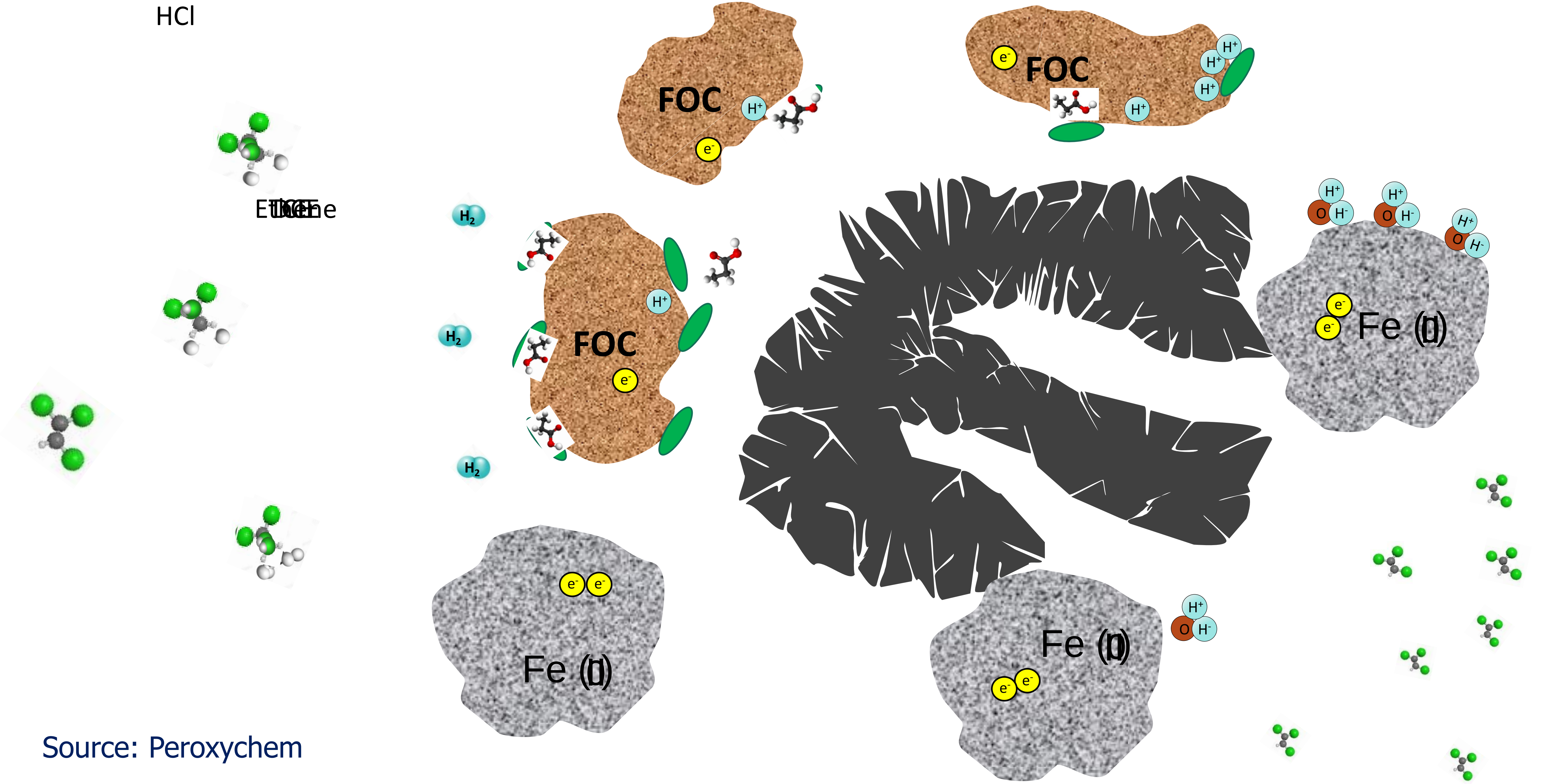
Source – Modified from Fan et al., 2017 and reproduced with permission from Journal of Environmental Management

- ✓ 10-slot screen = 256 µ
- ✓ 200-mesh sieve (clay) = 75 µ
- ✓ Bacteria = 0.5 - 2 µ
- ✓ Pore throats (*Nelson, AAPG Bull., 3/09*):
  sand >2 µ *silt* 0.03 – 2 µ *clay* 0.005 – 0.1 µ
- ✓ Mesopore = 0.05 µ; Micropore = 0.002 µ
- ✓ BTEX molecules = 7 Angstroms (Å) = 0.0007 µ
- ✓ ➢Water molecule = 3 Angstroms (Å) = 0.0003 µ

Activated Carbon Surface Biotic Treatment Mechanism



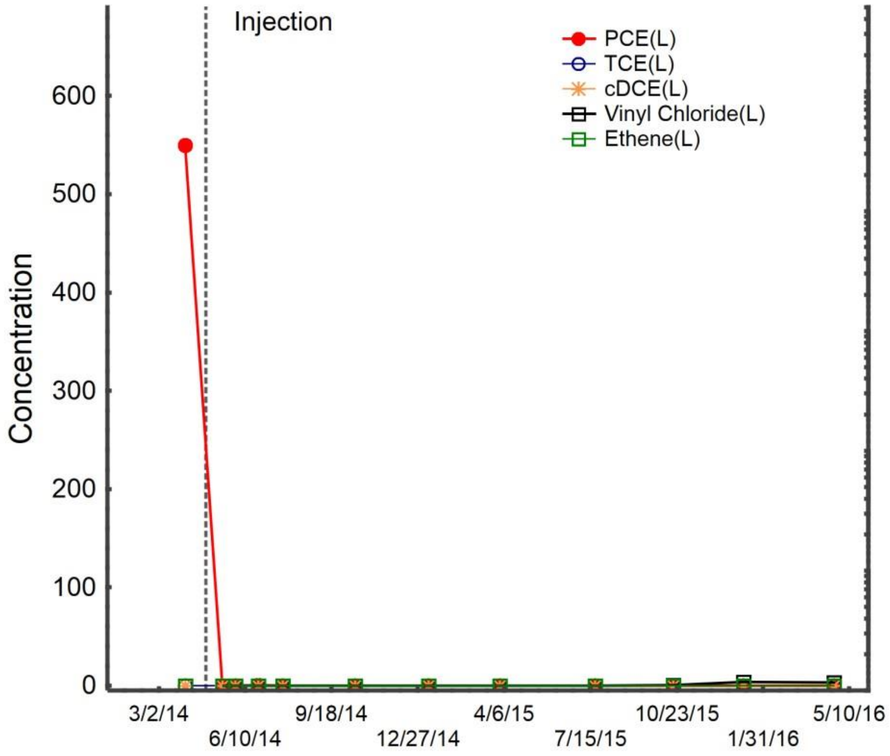
Application of Biofilm Covered Activated Carbon Particles as a Microbial Inoculum Delivery System for Enhanced Bioaugmentation of PCBs in Contaminated Sediments, Birthe Kjellerup and Sarah Edwards, SERDP Project ER-2135



Source: Peroxychem

Capture in Action

Typical GW Contaminant Concentration Curves



But what about the soil and the contaminant sorbed ?!?

Activated Carbon Form, Capture & Treatment Mechanisms

- ✓ Activated carbon (AC) based amendments are being applied for the in situ remediation of a wide range of organic contaminants in groundwater.
- ✓ Amendments combine AC for enhanced contaminant sequestration, along with chemical or biological additives to facilitate in situ contaminant destruction.
- ✓ Physical adsorption is the dominant removal mechanism under typical subsurface conditions.
- ✓ Decreases groundwater mass immediately
- ✓ Disrupts groundwater/soil mass equilibrium to help drive desorption
- ✓ Concentrated mass accelerates degradation rates
- ✓ Various degradation mechanisms are used to treat
  - ➢ Bioremediation (aerobic/anaerobic)
  - ➢ Chemical reduction/oxidation

Source: AST / NavFac 2019

Activated Carbon Form, Capture & Treatment Mechanisms

- ✓ Contaminants sorbed deeper into the micropores of the AC are not directly degraded but may back diffuse over time in to the mesopores and/or macropores. The contaminant then comes into contact with the reactive component of the AC amendment and is further degraded.
- ✓ Long term treatment amendment needed to cope with the desorption process when they will occur
- ✓ Degradation reaction products including dissolved hydrocarbon gases (i.e., methane, ethane, and ethene) mignt be difficult to observe
- ✓ Need to be careful with Benzene & Vinyl Chloride as competitive adsorption may affect long-term effectiveness when the strongly sorbed compounds may displace weakly sorbed compounds resulting in release of the latter
- ✓ NAPL need to be removed BEFORE amendment application as it could be cost-prohibitive and potentially result in adverse impacts to the aquifer (e.g., reduced hydraulic conductivity)

Source: AST / NavFac 2019

Compounds Targeted by AC Technology

Example Contaminants Treated by Activated Carbon

(not all Ac Technology treat all compounds listed)

Chlorinated Solvents
PCE, TCE, DCE
TCA, DCA
Vinyl chloride
Carbon tetrachloride
Chloroform
Chloroethane
Chloromethane
Dichloropropane
Trichloropropane
Methylene chloride

Others
Carbon disulfide
Aniline
1,4-Dioxane

TPH
BTEX
GRO
DRO
ORO
creosote

Oxygenates
MTBE
TBA

Perfluorinated
Freon
PFOA, PFBA

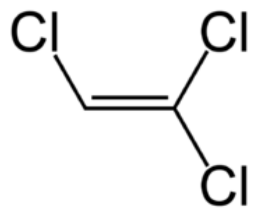
Chlorobenzenes
Chlorobenzene
Dichlorobenzene
Trichlorobenzene

Phenols
Phenol
Chlorophenols
Nitrophenols

PAHs
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
Trimethylbenzene

Pesticides
DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil

Energetics
Trinitrotoluene (TNT)
Dinitrotoluene (DNT)
RDX



Commercial AC-based Amendments for In Situ Remediation

Product	Property	Target Contaminant	Reactive Mechanism
BOS-100®	Granular AC (GAC) impregnated by ZVI	Chlorinated Solvents	Abiotic reductive dechlorination
BOS-200®	Powder AC (PAC) mixed with nutrients, electron acceptors, and facultative bacteria mix	Petroleum Hydrocarbons	Aerobic and anaerobic bioaugmentation
CAT-100®	BOS-100® and reductive dechlorination bacterial strains	Chlorinated Solvents	Abiotic and biotic reductive dechlorination
COGAC®	GAC or PAC mixed with calcium peroxide, and sodium persulfate	Chlorinated solvents or petroleum hydrocarbons	Chemical oxidation, aerobic and anaerobic biostimulation
PlumeStop® & PetroFix®	Colloidal AC suspension with an organic stabilizer, co-applied with hydrogen or oxygen release compounds, nutrients and/or corresponding bacterial strains	Chlorinated solvents or petroleum hydrocarbons	Enhanced biotic reductive dechlorination for chlorinated solvents and aerobic biodegradation for petroleum hydrocarbons
Carbo-Iron®	Colloidal AC impregnated with ZVI	Chlorinated Solvents	Abiotic reductive dechlorination
EHC Plus®	Micrometric ZVI and fermentable carbon substrate mixed with Powder AC (PAC) and facultative bacteria mix	Chlorinated Solvents	Abiotic & Biotic reductive dechlorination
Chemcarb H®	Powder AC (PAC) mixed with nutrients, electron acceptors, and facultative bacteria mix	Petroleum Hydrocarbons	Aerobic & Anaerobic biodegradatio n
Daramend Plus®	Macro ZVI and fermentable carbon substrate mixed with Powder AC (PAC) and facultative bacteria mix	Chlorinated Solvents	Abiotic & Biotic reductive dechlorination
Bioavailable Absorbent Media (BAM)	Pyrolyzed, cellulosic biomass product (>80% fixed carbon) derived from a proprietary blend of recycled organic materials	Chlorinated solvents or petroleum hydrocarbons	Aerobic and anaerobic biodegradatio n enhanced via biostimulation

AC-based Amendments In Situ Application

- **Permeable Reactive Barriers (PRBs) for Plume Control**

- **Hot Spot Applications**
  - Adsorptive capability and longevity allows for continued treatment of contaminants as they slowly back diffuse from the solid matrix to groundwater (typically observed at sites with high concentrations of sorbed mass or clays).

- **Plume Treatment**
  - Designs with multiple reactive zones along the plume for cost effective treatment of large dilute plumes.

AC-based Amendments Installation Methods

- Injection of slurry via direct push technology (DPT)
- Hydraulic or Pneumatic Emplacement (applied to fine-grain formations including clay, weathered and fractured bedrock)
- Direct placement into open excavations or trench PRBs
- Deep soil mixing

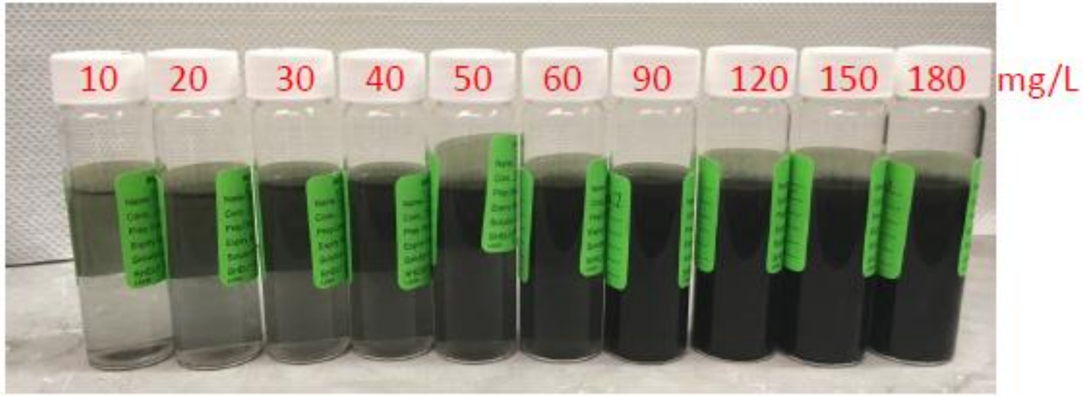
Chemical Assessment of Remedial Performance

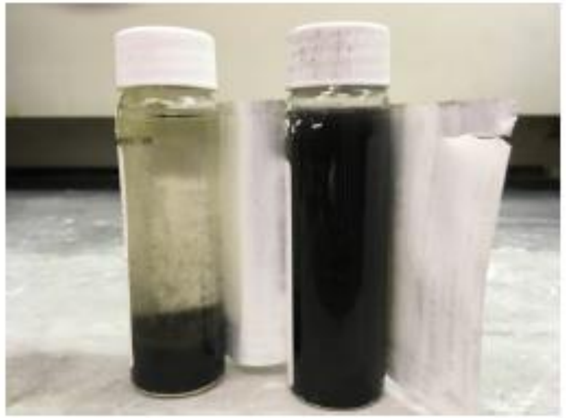
Field

- ✓ Monitor contaminant concentrations in separate monitoring wells.
- ✓ Amendment may appear in monitoring wells.

Lab

- ✓ Allow carbon to settle prior toanalysis.
- ✓ Complete settling not always possible within required hold times.
- ✓ If material does not settle, analytical complications are possible.
- ✓ High suspended carbon in monitoring wells interferes with lab analysis starting around 100 mg/L





Right vial did not settle

Source: BV Veritas

Case study 1

BOS 200®
Former Underground Storage Tank (UST)

Case Study 1 : Former UST with BOS 200®

Site Background

- **Tenant occupied** light industrial site for over 25 years
- Former diesel fuel UST for truck fleet removed and soil / groundwater remediated in 1998
- **Lease expiring** and tenant vacating property

Contaminant Situation

- PHC impacts in soil and groundwater (vs current standards)
- Soils a mixture of granular fill, clayey silt, silty clay, silty sand, silt, sand

Remedial Objective

- Complete remediation of site prior to lease expiry
- **Generic regulatory standards**
- Allow for **"four quarters clean"** verification sampling (therefore prevent back diffusion or "rebound")

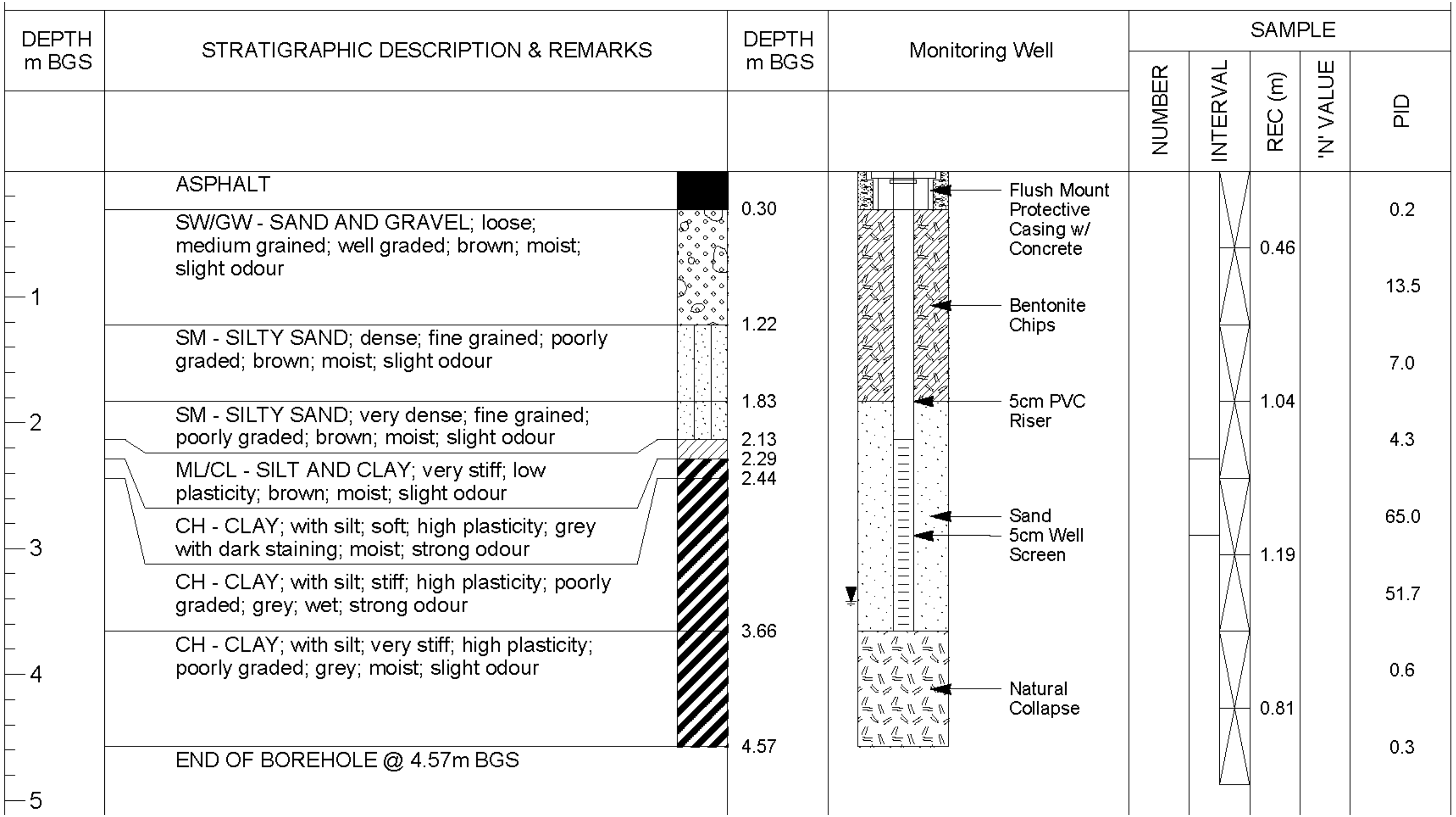
Source: Vertex Environmental

Case Study 1 : Former UST with BOS 200®

Source: Vertex Environmental

Case Study 1 : Former UST with BOS 200®

Mixed geology of sands, gravels, silts **and clays**



Source: Vertex Environmental

BOS 200® Case Study: Former UST

Locations	Date	Soil								
		Depth	B	T	E	X	F1	F2	F3	F4
MW07-2	07/2007	2.71-3.05	<0.02	<0.02	0.31	0.34	21	330	170	<10
		3.05-3.23	<0.02	<0.02	0.12	0.07	<10	220	89	<10
BH3	11/2012	2.5-3.6	<0.02	<0.05	0.45	<0.05	61	800	350	<50
BH4	11/2012	3.7-4.8	<0.02	<0.05	1.9	<0.05	72	530	160	<50
MW01-16	10/2016	2.29-2.90	<0.0068	<0.08	0.040	<0.05	6.9	1120	454	<50
MW02-16	10/2016	3.66-4.27	<0.0068	<0.08	0.203	0.297	101	66	56	<50
MOECC Standards (Table 3)		**-**	**0.32**	**68**	**9.5**	**26**	**55**	**230**	**1700**	**3300**

Locations	Date	Groundwater							
		B	T	E	X	F1	F2	F3	F4
MW07-2	08/2007	83	4.5	90	51	550	530	<100	<100
	11/2012	-	-	-	-	190	<100	<100	<100
	12/2016	5.49	<0.50	2.20	2.90	98	310	<250	<250
MW01-16	12/2016	1.39	<0.50	2.76	4.36	83	210	<250	<250
MW02-16	12/2016	1.60	<0.50	3.33	5.71	97	180	<250	<250
MOECC Standards (Table 3)		**44**	**18000**	**2300**	**4200**	**750**	**150**	**500**	**500**

Main Concern

Source: Vertex Environmental

BOS 200® Case Study: Former UST

Obstacles

- **Excavation** approach ("cut & fill") would require **shoring & dewatering**
- Relatively small work area with **lots of truck traffic**
- Limited disruption allowed = **no multiple injection events**
    - ISCO or bio alone would have required at least 2 to 3 injection events
- Client anxious to ensure site is remediated before end of lease
    - Therefore, **certainty in approach was a priority**

Remedial Approach

- Full-scale **BOS 200® injection** program
    - Combined carbon adsorption and anaerobic biodegradation for PHCs

Source: Vertex Environmental

BOS 200® Case Study: Former UST

Source: Vertex Environmental

BOS 200® Case Study: Former UST

Work Completed

- Impacted area 100 m^2 by 2 m thick with soil and groundwater impacts
- Approx. 40 temporary injection points advanced via Geoprobe
    - 1.5 m lateral spacing for points
    - Vertical injection intervals from 2.1 to 4.5 mbgs
- 2,000 kg of BOS 200® , 800 kg gypsum & microbes in 10,000 L of slurry injected
- Completed over 3 working days on-Site

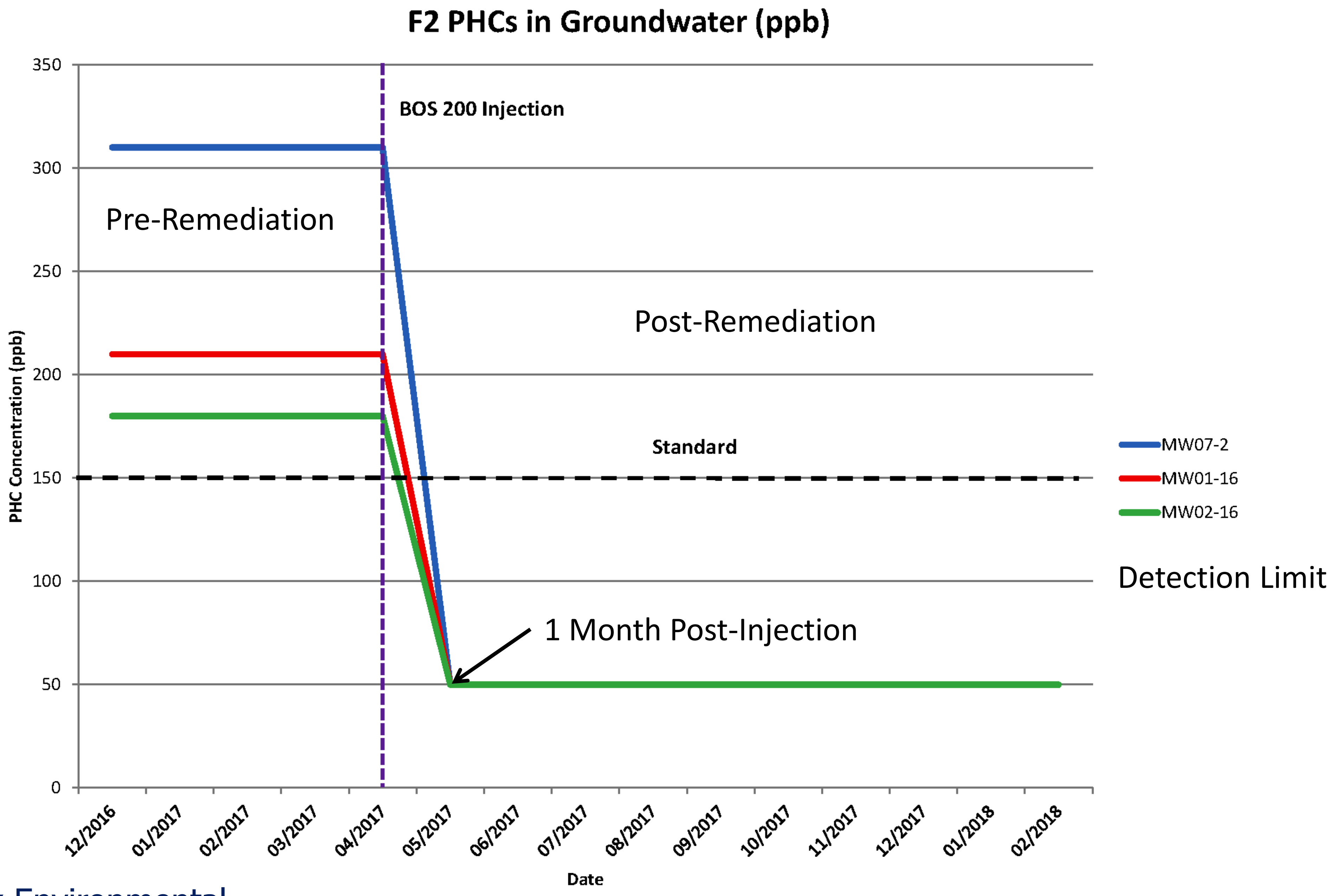
Source: Vertex Environmental

BOS 200® Case Study: Former UST

Locations	Date	Groundwater							
		B	T	E	X	F1	F2	F3	F4
MW07-2	08/2007	**83**	4.5	90	51	550	**530**	<100	<100
	11/2012	-	-	-	-	190	<100	<100	<100
	12/2016	5.49	<0.50	2.20	2.90	98	**310**	<250	<250
MW01-16	12/2016	1.39	<0.50	2.76	4.36	83	**210**	<250	<250
MW02-16	12/2016	1.60	<0.50	3.33	5.71	97	**180**	<250	<250
N/A	04/2017	BOS 200® Injection Event							
MW07-2	05/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	08/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	11/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	02/2018	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
MW01-16	05/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	08/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	11/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	02/2018	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
MW02-16	05/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	08/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	11/2017	<0.50	<0.50	<0.50	<0.50	44	<100	<250	<250
	02/2018	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
MW03-17	05/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	08/2017	1.13	<0.50	<0.50	<0.50	<25	<100	<250	<250
	11/2017	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
	02/2018	<0.50	<0.50	<0.50	<0.50	<25	<100	<250	<250
MOECC Standards (Table 3)		**44**	**18000**	**2300**	**4200**	**750**	**150**	**500**	**500**

Pre-injection groundwater analytical data

Four rounds of post-remediation groundwater analytical data



Source: Vertex Environmental

BOS 200® Case Study: Former UST

Project Summary:

- Client **required certainty** prior to end of lease
- Trap & Treat® BOS 200® approach selected
- **Design work was essential**
  - Calculation of carbon and sulphate demand
  - Designed lateral and vertical injection spacing to ensure uniform distribution in the subsurface
- Full-scale application completed as planned
- Remedial objective achieved – **below Generic Standard**
- **PHCs remain low (mostly ND) one year after injection event!**

Source: Vertex Environmental

Case study 2

Former manufacturing facility, USA

Sand & gravel deposits with till lenses and aquitards

EHC® Plus and EHC® Liquid Case Study – Confidential Site USA

- **Site Background**
  - Former manufacturing facility where operations ceased in 1990s.
  - TCE distributed via sub-grade piping to pits used for degreasing.

- **Site Hydrogeology**
  - 7.5 m of fill placed above former canal.
  - >60 m of sand and gravel deposits with till lenses and aquitards.
  - GW seepage velocity is 0.2 m/day.

EHC® Plus and EHC® Liquid Case Study – Confidential Site USA

- **Key Findings**
  - TCE in soil gas at property boundary as high as 176,000 µg/m^3
  - TCE in source area soils up to 280 mg/Kg in the fill material.
  - Highly aerobic aquifer; no degradation products present
  - Maximum TCE in groundwater up to 5.5 mg/L in source area.
  - Groundwater plume migrating E/SE away from the river, across road, and into residential area.

Remediation Objectives

- Prevent off-site migration of CVOCs
- Treat portion of the off-site plume and eliminate exposure to down-gradient receptors.

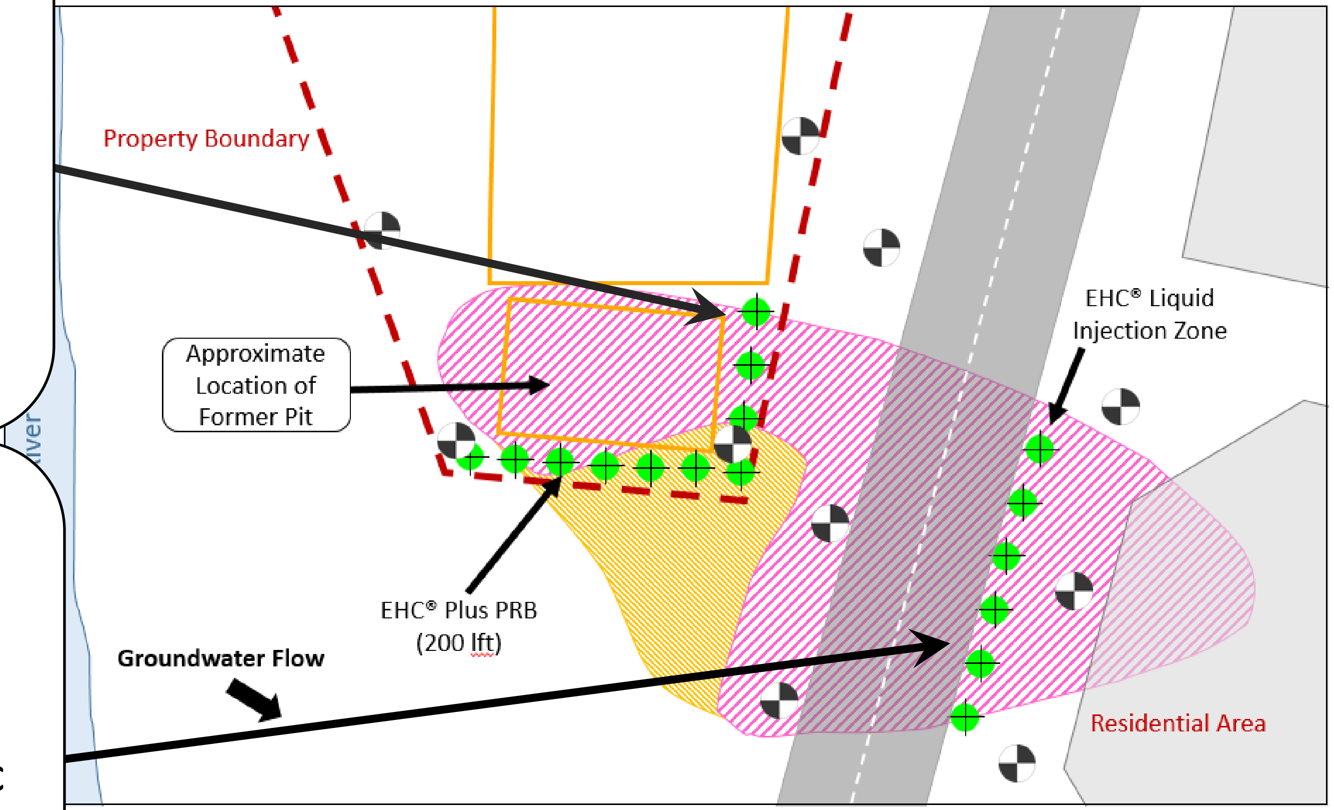
Remedial Approach

EHC Plus Permeable Reactive Barrier

- 10,000 Kg of EHC Plus in 10 injection points
- 40 L of SDC-9 DHC culture
- Treatment of CVOCs is via physical, chemical and biological pathways

EHC Liquid Reactive Zone

- 10,000 Kg of EHC Liquid in 6 injection points
- 18 L of SDC-9 DHC culture
- Treatment of CVOCs is via biological and abiotic pathways

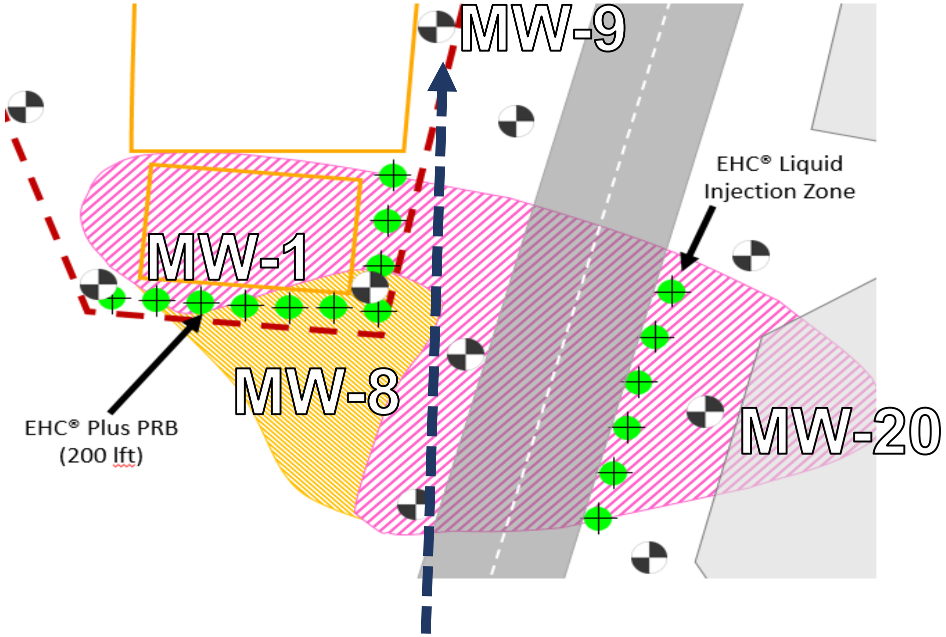


Environmental Molecular Diagnostics (EMDs) Used

- Molecular Biological Tools (MBTs)
- Compound Specific Isotope Analysis (CSIA)

One Year Performance Monitoring Results

- Pre-Injection Feb 2017
- Post-Injection in Feb 2018



	In the EHC Plus PRB		Downgradient of the EHC Plus PRB		Downgradient of the EHC Liquid Reactive Zone	
	MW-1		MW-8		MW-20	
	Pre	Post	Pre	Post	Pre	Post
ORP, mV	126	-399	125	-344	132	-362
Sulfate, mg/L	99.8	16.4	133	<10	78	21
VFAs, mg/L	<0.10	103.2	<0.10	59.9	<0.10	0.26
DHC, cells/ml	5.7E+02	1.6E+05	<5.0+01	3.9E+06	<5.0+01	3.0E+04
TCE, mg/L	0.13	<0.005	0.038	<0.005	0.26	<0.005
Cis-DCE, mg/L	<0.005	0.04	0.004	0.072	0.0037	<0.005
VC, mg/L	ND	0.019	<0.002	0.022	<0.002	0.042
Ethene, mg/L	<0.0001	0.016	<0.0001	0.032	<0.001	0.002

MW-9 Cross-Gradient of EHC Plus PRB

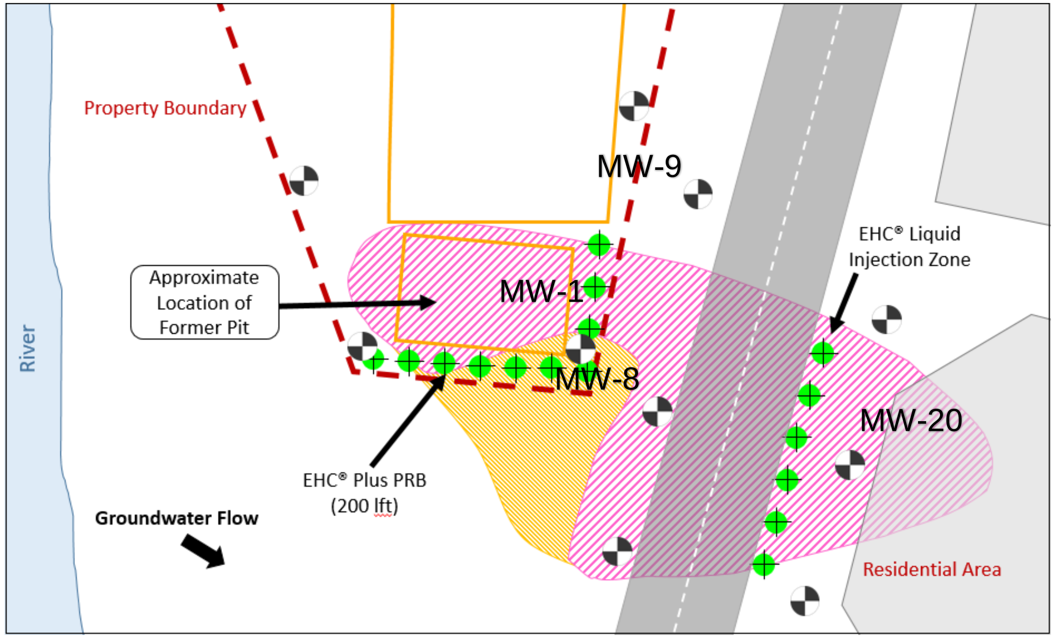
- Well not under the influence of treatment
- Rise in water level due to seasonal change
- Concentration of TCE increased from <0.005 to 0.034 mg/L

Confirmation of Degradation Occurring

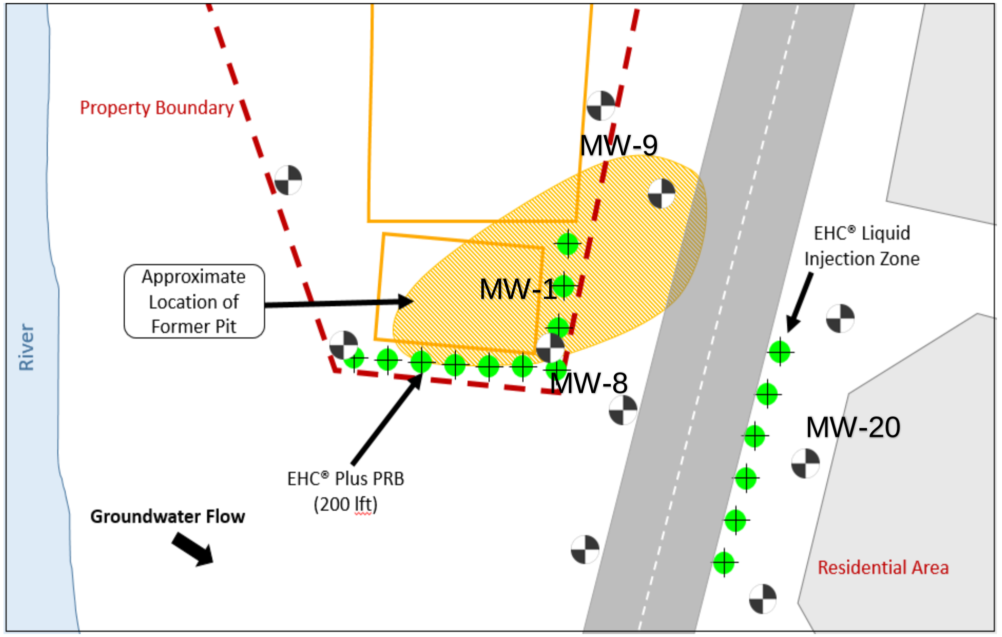
- CSIA confirmation
- MBT's: Increase in DHC populations
- Formation of daughter products

Plume Response to EHC® Plus and EHC® Liquid Injections

February 2017



February 2018



Expected Continued Site Treatment

- EHC® Plus PRB: 5-10 years expected
- EHC® Liquid Reactive zone 2-5 years expected

✓ **Prevent off-site migration of CVOCs**
✓ **Treat portion of the off-site plume and eliminate exposure to down-gradient receptors**
✓ **72% Mass Removal from combined remedy after one year of treatment**

Case Study 2 - Summary & Conclusions

- Highly aerobic aquifer turned anaerobic and reducing in 12 months
- Plume pulled back from the property line and off-site migration of TCE was prevented
- Post injection changes in geochemical parameters, MBTs, and CSIA indicate that chemical and microbiological treatment of TCE and daughter products has occurred in wells MW-1 and MW-8 which were under the influence of EHC Plus.
- Concentration of DHC increased by several orders of magnitude in key wells under the influence of EHC Plus and EHC Liquid.
- EHC Plus and EHC Liquid combined remedy met the site-specific remedial objectives.

Reagent Mixing Station

Conclusions & Lessons learned

Conclusion & Lessons learned

- ✓ Perform bench-scale treatability studies to test one or more amendments using site-specific soils and groundwater BEFORE getting to the field
- ✓ AC-based amendments have been demonstrated to be an effective technology to address a range of dissolved-phase COCs in groundwater and possibly treat source areas containing residual NAPL.
- ✓ Competitive adsorption may affect long-term effectiveness when the strongly sorbed compounds may displace weakly sorbed compounds, resulting in release of the latter and performance assessment
- ✓ Post injection monitoring is performed to evaluate the long-term effectiveness of the remedy, identify the need for additional application of amendments, assess progress toward achieving remedial goals and remedial action objectives, and determine if rebound is occurring

Source: NavFac 2019

Conclusion & Lessons learned

- ✓ Fast groundwater flow velocity might limit the effectiveness of soluble amendments due to dilution, non colloidal AC-based amendments may be considered since they more likely to adsorb to aquifer contaminants and remain in the target treatment area
- ✓ Additional research is needed to better understand the implications of long-term & hydraulics effects from emplacement of the AC-based amendments.
- ✓ Long term & extended release TREATMENT amendments (years rather than months) combined with the AC must be favored to deal with sorption-desorption processes for the contaminant trap in the micropore structure.

About us

Canadian Company founded in 1988

- **Production and warehouses throughout Canada**
  - Quebec
  - Ontario
  - Manitoba
  - Alberta
  - British Columbia

- **Sectors of activity:**
  - Industrial and Municipal Potable & Waste Water
  - Contaminated Soil and Groundwater
  - Air, Odours and Atmospheric Emissions (Activated Carbon, filtering medias)
  - Process Water & Thermal Exchange Fluids (Glycols)
  - Drilling Fluids (Oil and Gas & Diamond exploration)
  - Aircraft De-icing Fluids

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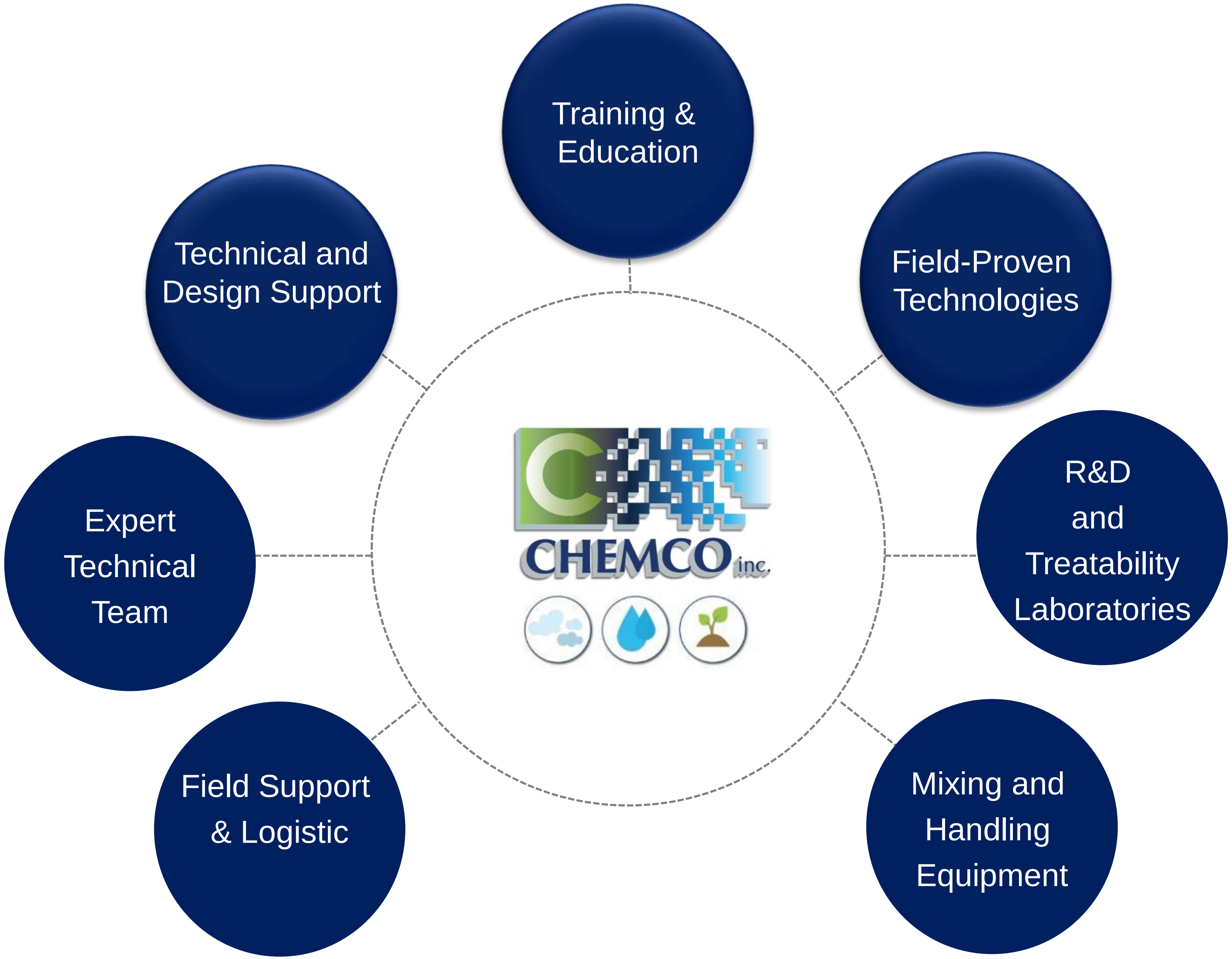

Our product and services

Acknowledgements

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- *Regenesis*
- *Remediation Product Inc.*
- *Vertex Environmental Inc.*

Thank you for your attention !
Have a good day !!!

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