In Situ Activated Carbon-Based Technology for Groundwater Remediation: **Overview**, Best Practice and Case Studies

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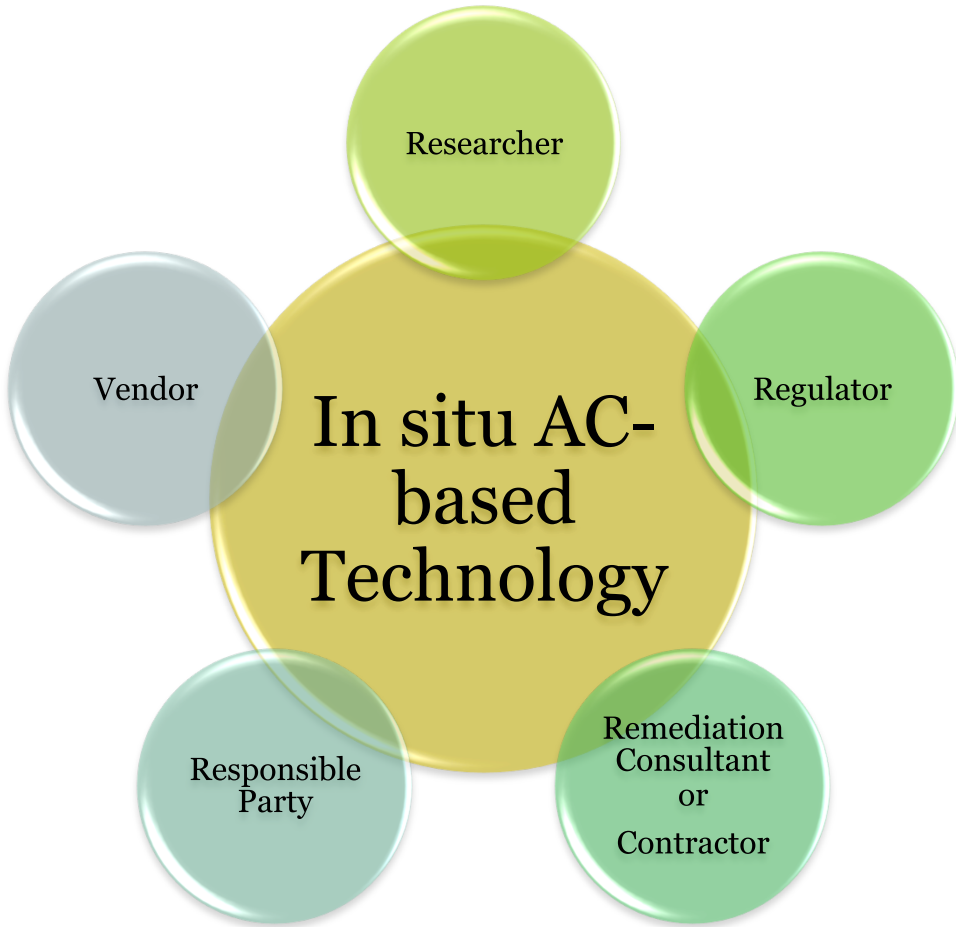
Different Perspectives from Different Stakeholders



What is this Webinar about?

To provide the State-of-the-Art of the *scientific knowledge*, *engineering experiences*, and *field applications* of AC based remedial technology for in situ subsurface remediation.

- Overview of Science, Engineering, and Applications
- *Best practice* for applying AC-based technology for in-situ treatment
- A long-term pilot study of applying AC-based technology for in situ treatment of chlorinated solvent in Germany

What is In Situ AC-based Technology?

Activated Carbon-Based Technology for In Situ Remediation

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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.
- Several commercial products of various AC particle size and different amendments.
- Synergy between adsorption and degradation for treating chlorinated solvents and petroleum hydrocarbons.
- Applied to treat plumes but also residual source in low-permeability zones.
- Primarily uses direct push injection, including high-pressure in low-permeability zones for granular AC- and powdered AC-based products and low pressure for colloidal AC-based products in high-permeability zones. Injection well has also been used for delivering colloidal AC-based products.
- Requires adequate characterization (i.e., a high-resolution conceptual site model (CSM)) for effective remedial design.
- Adsorption to AC results in rapid concentration reduction in aqueous phase after injection.
- Rebound may occur due to greater contaminant influx than the rate of adsorption and degradation, poor site characterization, or lack of effective distribution.
- Performance assessment may be subject to bias if AC is present in monitoring wells. Other lines of evidence are important.
- Field evidence of degradation is limited but promising. However, persistence and contribution of degradation need further validation.

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 processes: adsorption by AC and destruction by chemical and/or biological amendments.

With the development of several commercially available AC-based products, this remedial technology has been applied with increasing frequency at contaminated sites across the country, including numerous leaking underground storage tank (LUST) and dry cleaner sites (Simon 2015). It also has been recently applied at several Superfund sites, and federal facility sites that are not on the National Priorities List.

This fact sheet provides information to practitioners and regulators for a better understanding of the science and current practice of AC-based remedial technologies for in situ applications. The uncertainties associated with the applications and performance of the technology also are discussed.

What is AC-based technology?

- AC-based technology applies a composite or mixture of AC and chemical and/or biological amendments that commonly are used in a range of in situ treatment technologies.
- Presently, five commercial AC-based products have been applied for in situ subsurface remediation in the U.S.: BOS-100® & 200® (RPI), COGAC® (Remington Technologies), and PlumeStop® (Regenesis) are the four most commonly used commercial products. CAT-100® from RPI is the most recent product, developed based on BOS-100®. One research group in Germany also developed a product called Carbo-Iron®. Detailed properties and compositions of these products are shown in Exhibit 1.
- The AC components of these products typically are acquired from specialized AC manufacturers. These types of AC have desired adsorption properties for chlorinated solvents and petroleum hydrocarbons. Different products also have different AC particle sizes, which determine the suitable injection approach and the applicable range of geological settings.

https://semspub.epa.gov/work/HQ/100001159.pdf

AC-based technology applies a composite or mixture of AC and chemical and/or biological amendments that commonly are used in a range of in situ treatment technologies.

- 6 commercial and 1 research products
- 2 composites and 5 mixtures
- 5 for chlorinated solvents and 3 for petroleum hydrocarbons
- AC size: granular, powder, colloidal

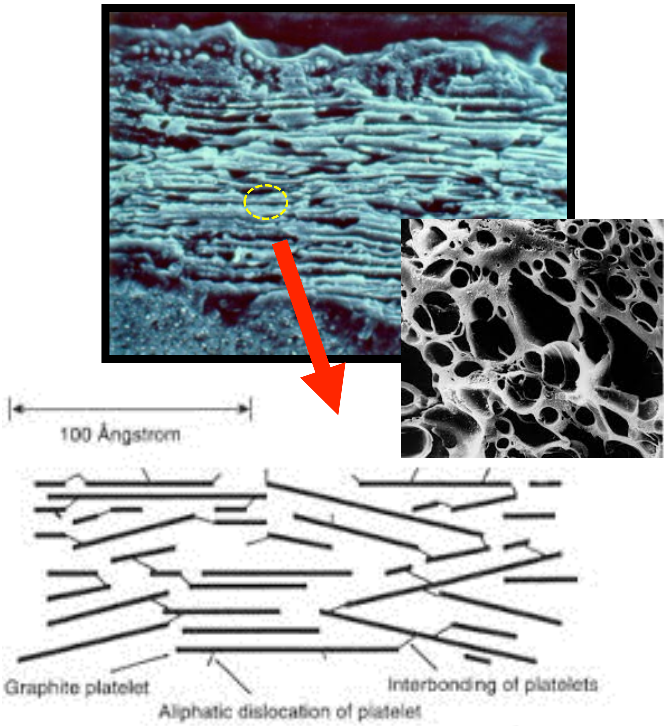
Product List

Product	Property	Target Contaminant	Degradation Pathway
BOS-100® (2004)	Granular AC (GAC) impregnated by ZVI	Chlorinated solvents	Abiotic reductive dechlorination
BOS-200® (2002)	Powder AC (PAC) mixed with nutrients, electron acceptors, and facultative bacteria mix	Petroleum hydrocarbons	Aerobic and anaerobic bioaugmentation
CAT-100® (2016)	BOS-100® and reductive dechlorination bacterial strains	Chlorinated solvents	Abiotic and biotic reductive dechlorination
COGAC® (2011)	GAC or PAC mixed with calcium peroxide, and sodium persulfate	Chlorinated solvents or petroleum hydrocarbons	Chemical oxidation, aerobic and anaerobic biostimulation
PlumeStop® (2014)	Colloidal AC (1–2 μm) suspension with an organic stabilizer, co-applied with hydrogen or oxygen release compounds, 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 (1–2 μm) impregnated with ZVI	Chlorinated solvents	Abiotic reductive dechlorination
EHC® Plus (2018)	PAC + Microscale ZVI + Organic C + Nutrients	Chlorinated solvents	Abiotic and biotic dechlorination

Fundamental Processes involving AC-based Technology

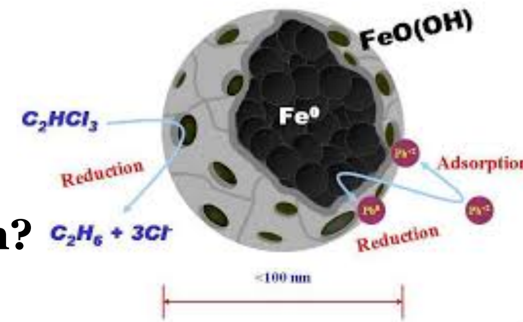
Adsorption
- Large adsorption capacity
- Reversible process

Degradation
- Mechanistically well characterized
- Aqueous phase reaction

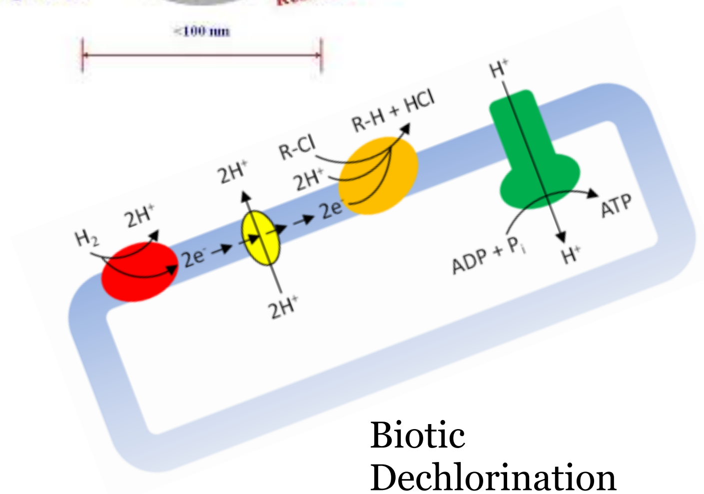


Desportion

Regeneration?



Abiotic Dechlorination



Biotic Dechlorination

Synergy Between Adsorption and Degradation

Removal of Trace Chlorinated Organic Compounds by Activated Carbon and Fixed-Film Bacteria

Edward J. Bouwer* and Perry L. McCarty

1982

Environmental Engineering and Science, Department of Civil Engineering, Stanford University, Stanford, California 94305

INOCULATION OF CONTAMINATED SUBSURFACE SOILS WITH ENRICHED INDIGENOUS MICROBES TO ENHANCE BIOREMEDIATION RATES

1994

W. J. WEBER JR[1] and H. X. CORSEUIL[2]

[1]Department of Civil and Environmental Engineering, The University of Michigan, Ann Arbor, MI 48109, U.S.A. and [2]Departamento de Engenharia Sanitária, Universidade Federal de Santa Catarina, Florianópolis, SC 88039, Brazil

Environ. Sci. Technol. **2009**, *43*, 4137–4142

Effects of Aging and Oxidation of Palladized Iron Embedded in Activated Carbon on the Dechlorination of 2-Chlorobiphenyl

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nanoscaling Pd and Fe particles (*6, 7*) and dispersing Pd particles uniformly to Fe surface without significant agglomeration (*8, 10*) can maximize the reactivity of Fe coupled with a small amount of Pd.

Recently, we addressed the integration of the physical adsorption of PCBs with their chemical dechlorination on reactive activated carbon (RAC), where Fe/Pd bimetallic nanoparticles were impregnated into the mesopores of granular activated carbon (GAC) (*8, 9*). For the full scale environmental applications of RAC (*11*), our research activities have been geared toward (i) aging and oxidation of RAC, (ii) treatment of positional and highly chlorinated PCBs, and (iii) practical application aspects to contaminated sites. In this study, we particularly focused on the first issue to predict the dechlorination capacity and longevity of RAC. In the RAC system, PCBs adsorption capacity is closely related to the properties of AC such as surface area. The content of Fe^0 (zerovalent iron, ZVI) as a primary electron donor determines

Activated carbon enhanced persistence of abiotic dechlorination by nZVI

WATER RESEARCH 42 (2008) 2839–2848

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WATER RESEARCH

Review

Biofilm processes in biologically active carbon water purification

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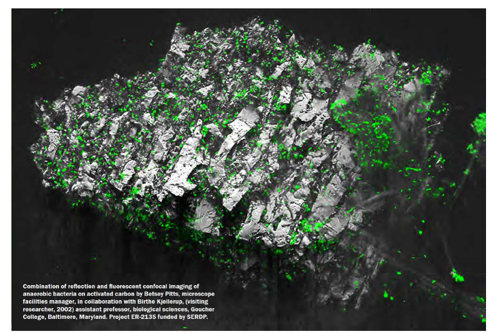
Process control

ABSTRACT

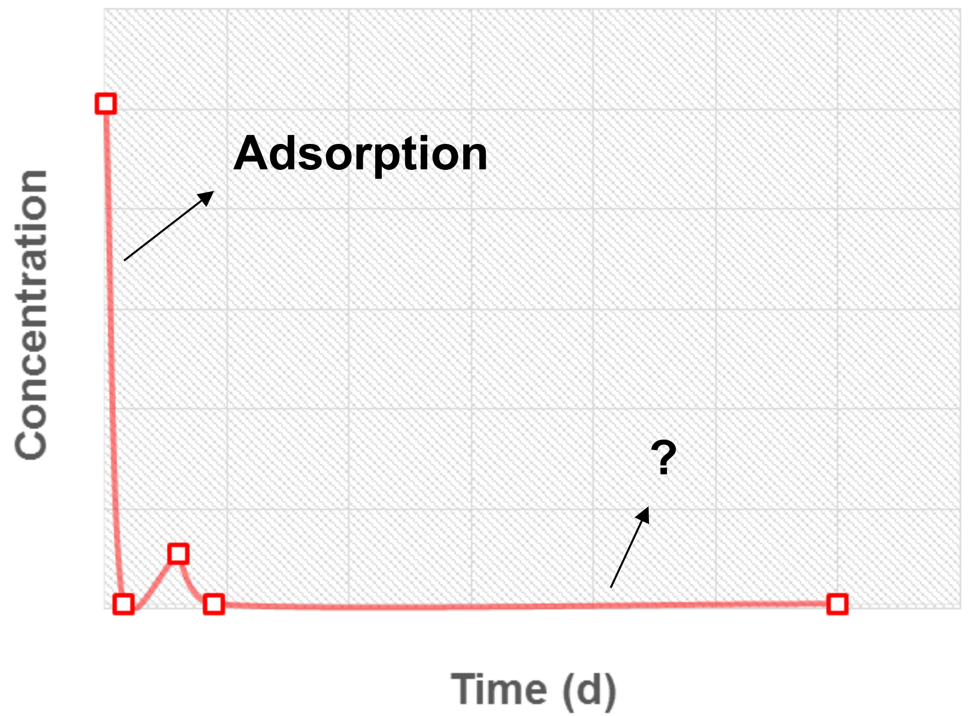
This review paper serves to describe the composition and activity of a biologically active carbon (BAC) biofilm used in water purification. An analysis of several physical-chemical, biochemical and microbiological methods (indicators) used to characterize the BAC biofilm's composition and activity is provided. As well, the ability of the biofilm to remove and biodegrade waterborne organic substances and pollutants will be reviewed, with context to other industrial processes such as pre-ozonation and post-membrane filtration. Strategies to control the growth of the BAC biofilm, such as varying the nutrient loading rate, manipulating influent DO and pH levels, altering the frequency of BAC filter backwashing and applying oxidative disinfection, will be described in detail along with their respective process control challenges.



Kjellerup et al., 2013

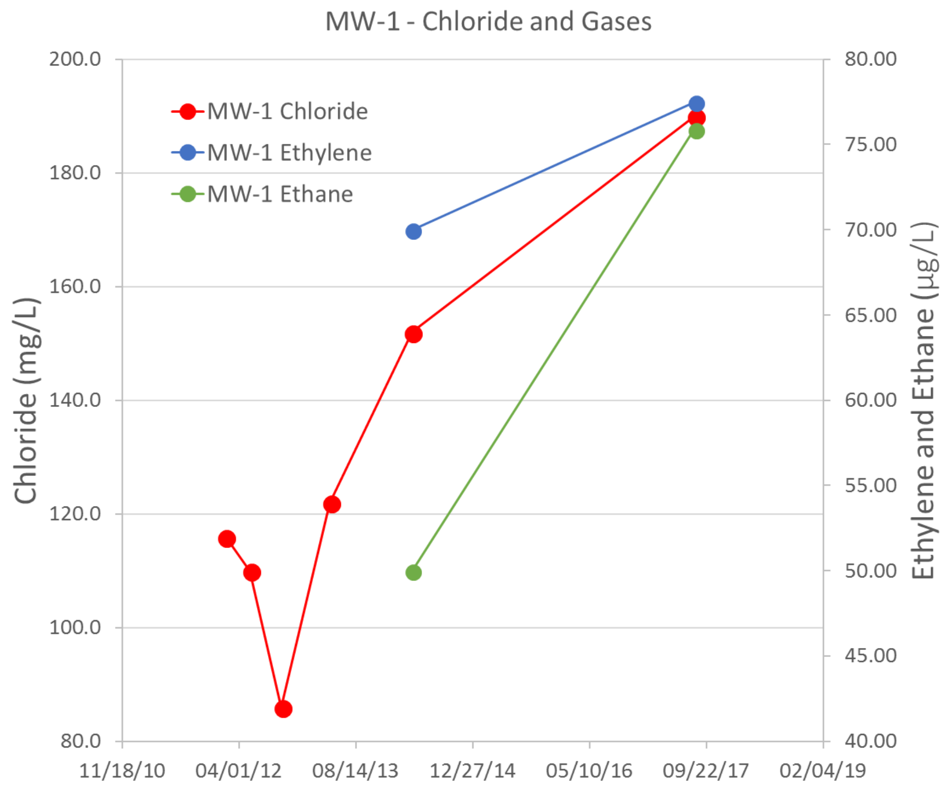
Evaluation of Degradation in the Field

- Adsorption removes aqueous contaminants rapidly and also may sorb daughter products, which creates challenges in evaluating the rate and extent of degradation processes.
- Progresses have been made in recent applications to look for definitive evidence of degradation:
  - Alternative indicators
  - Environmental Molecular Diagnostic Tools (EMDs)



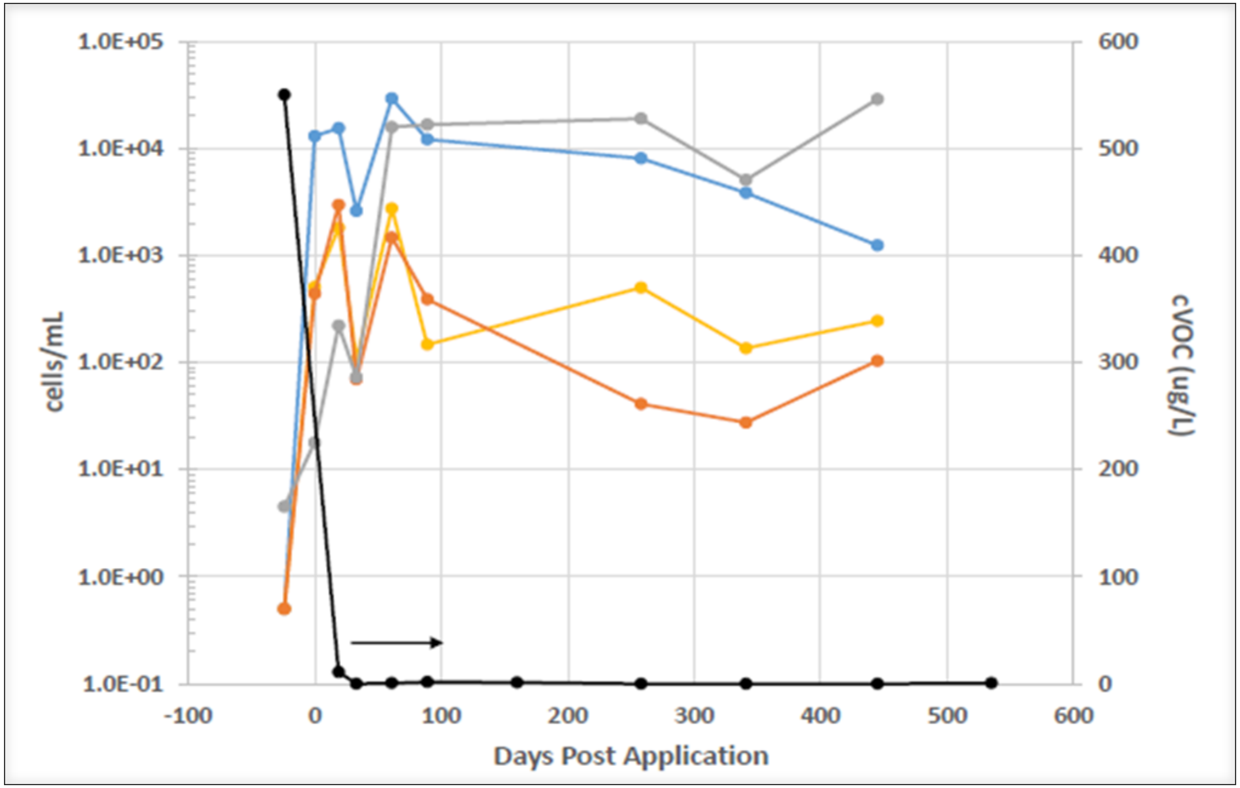
Examples of Degradation Evaluation

Abiotic reductive dechlorination with BOS-100®
at a dry cleaner site in fracture bedrock



Examples of Degradation Evaluation

Biotic reductive dechlorination with PlumeStop® + HRC® + *DHC* at a dry cleaner site



Vogel et al. 2018: Pilot Injection of Carbo-Iron to Treat PCE

Combined chemical and microbiological degradation of tetrachloroethene during the application of Carbo-Iron at a contaminated field site

Maria Vogel[a], Ivonne Nijenhuis[b], Jonathan Lloyd[c], Christopher Boothman[c], Marlén Pöritz[b], Katrin Mackenzie[a,*]

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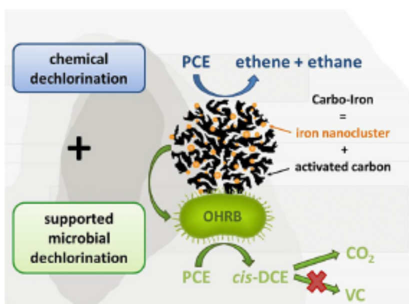
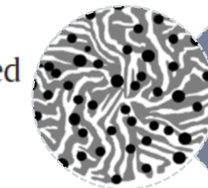
[c] School of Earth and Environmental Sciences, University of Manchester, Manchester M13 9PL, United Kingdom

HIGHLIGHTS

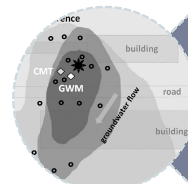
- Successful combination of chemical and microbial degradation of PCE at a field site
- Carbo-Iron improves the aquifer conditions for microbial dechlorination for months.
- No vinyl chloride formation due to sequential reduction and oxidation processes.

GRAPHICAL ABSTRACT

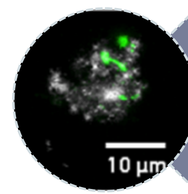




Colloidal AC impregnated by nZVI and stabilized by CMC



Injection in a source area with PCE concentration up to ~100 ppm



3 yr monitoring of contaminant and microbial community under different redox conditions

A 3-yr case study that documents detailed characterizations of chemical and biological reductive dechlorination of PCE over time

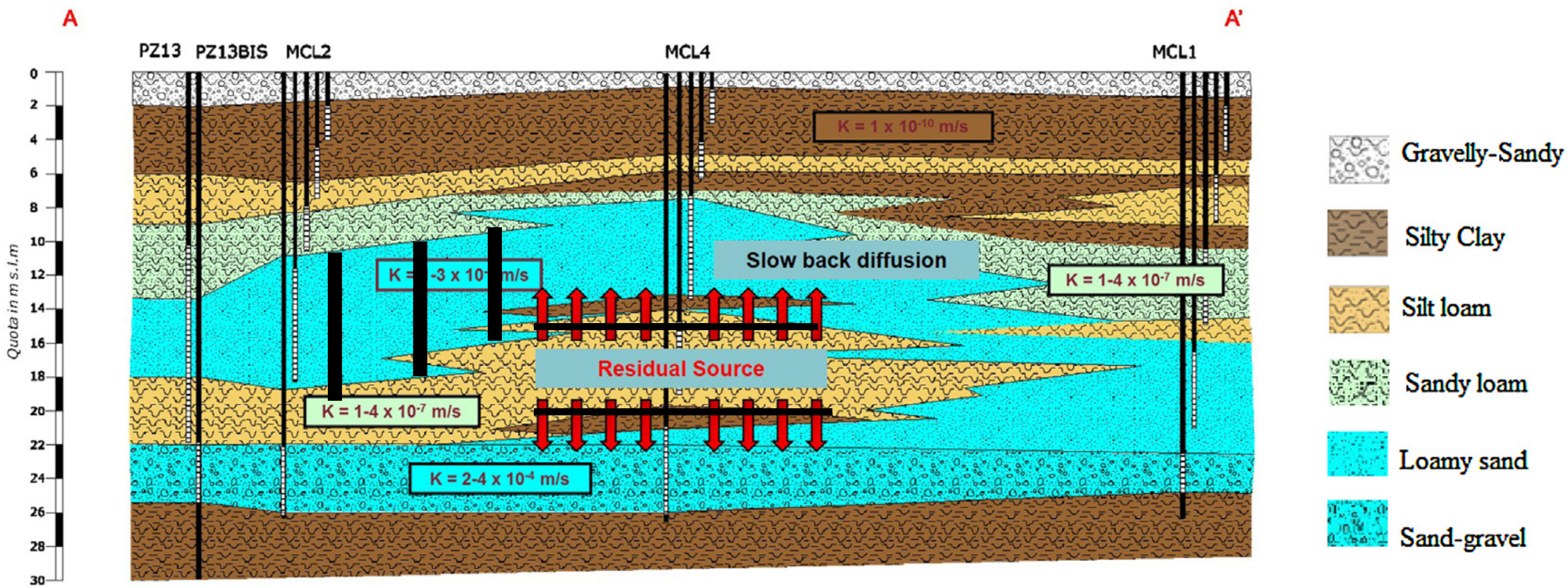
Two Major Science Questions to be Answered

- Long-term effectiveness
  - Many early UST applications do not require long-term monitoring data.
  - Recent cVOC sites yet have long-term data.
- Contributions of degradation vs. adsorption.
  - Important policy implications: leave waste in place or not?
  - If waste is left in place, how to maintain the degradation activity to counter continuous but slow desorption processes.

The Importance of Collaborative Research

- Vendor-University partnership
  - Regenesis and Colorado State University to study effects of PS + Bio on mitigating back diffusion
- Projects funded by industrial association
  - U of Waterloo funded by American Petroleum Institute to study biodegradation of BTEX involved in AC-based technology (ongoing)
- Projects funded by Federal programs
  - NIEHS grant to JHU, USGS, and Geosyntec to study AC + mixed biofilm for chlorobenzene degradation at a groundwater-surface water interface (ongoing)
  - SERDP grant to UMD on activated carbon supported biofilm for PCB dechlorination (completed)
- Project(s) to be funded by Air Force
  - Air Force is interested in investigating and validating applications of coupled sorption-degradation technologies to address chlorinated solvent sites with complex hydrogeology.
  - Proposal offers must provide for field-scale demonstration and/or validation of amendment delivery, *sorption/sequestration*, *biogeochemistry*, and *contaminant degradation*.

Application Scenario



The concept is to rely on the combination of adsorption and degradation as a long-term mechanism to combat back diffusion.

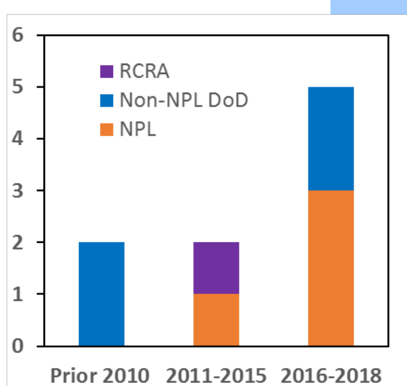
The State of Application

- As of 2015, RPI reported:
  - Over 100 sites with BOS-100®
  - Over 1000 sites with BOS-200®
- As of 2017, Regenesis reported:
  - Over 50 sites with PlumeStop®
  - Chlorinated vs. Petroleum: 1:1
- As of 2018, Federal program has
  - 1 RCRA sites
  - 4 NPL sites
  - 4 DoD sites

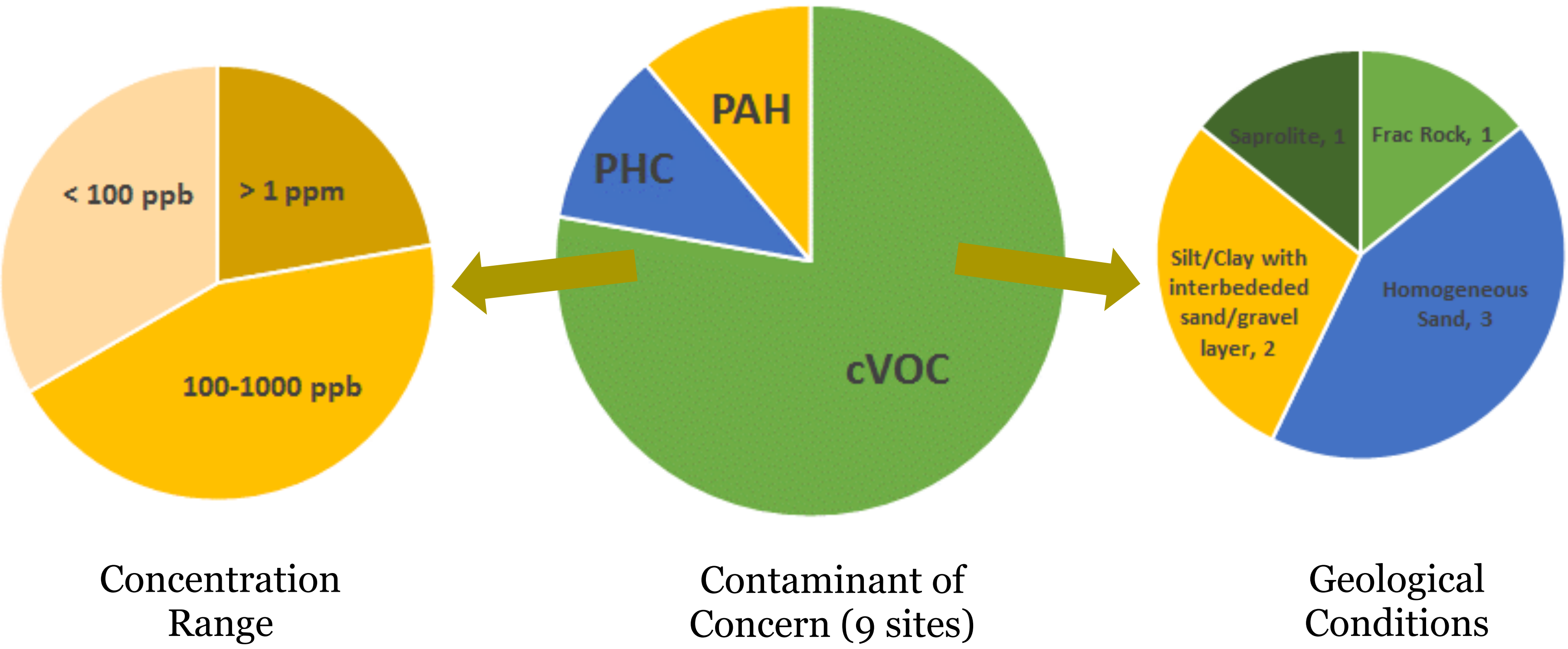
2015

Editor's Perspective—An *In Situ* Revelation: First Retard Migration, Then Treat

John A. Simon

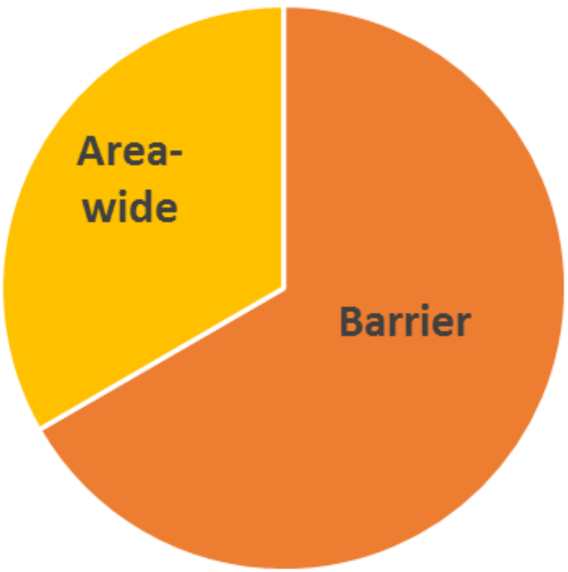


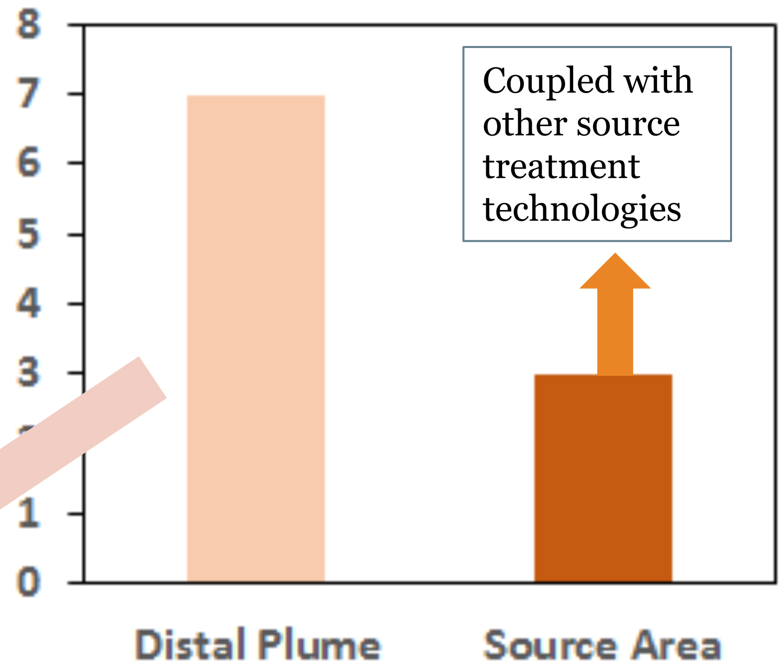
Overview of Site Conditions



Overview of Technology Applications

Treatment Configuration



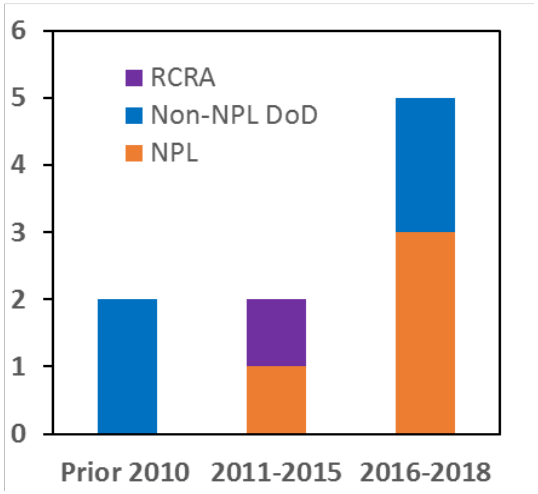


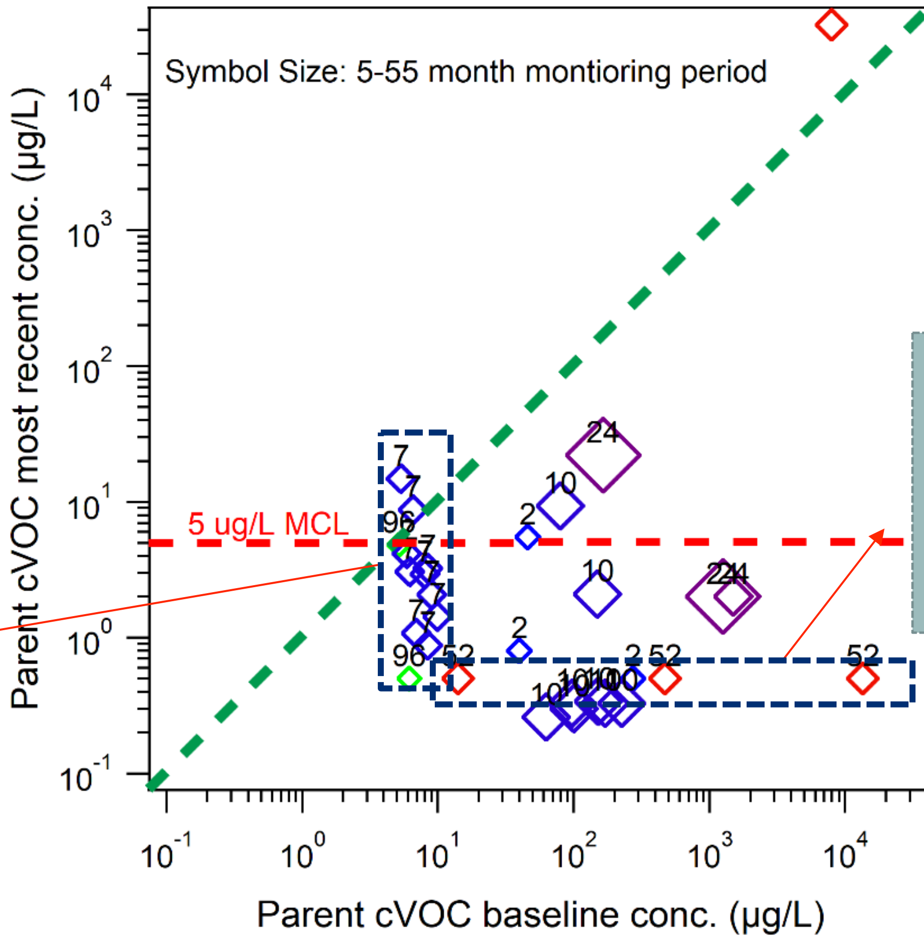
Two sites applied AC w/o reactive amendments to prevent (1) VC production and (2) remobilization of Mn and As

Rationale for Selecting AC-based Technology

- Technologies could not achieve remediation goal or determined to be not suitable:
  - At the former Lowry AFB, addition of alkaline-activated persulfate resulted 70% CT concentration reduction in bedrock aquifer after injection but showed rebound after 6 month.
  - At the former Intel SC3 facility NPL in R9, multiple attempts have been tried to reduce TCE concentrations below MCL in all monitoring wells in the tailing part of the plume, including ISCO, MNA and P&T. One well is resistant to all treatments.
  - At the East 67th Street NPL in R6, injection of EVO for bio impacts water quality and requires ongoing maintenance due to biofouling of injection wells. P&T limited by property access.
  - At Vandenburg AFB and FCX NPL site, production of VC and high groundwater velocity adjacent to surface water are concerns that prevent selection of bio or ISCO.

Overview of Treatment Performance





Two sites that applied AC only without adding reactive amendments

A site AC-based amendments applied at multiple areas

Benefits to Superfund

- Reduce risks of plume offsite migration
  - Rapid adsorption of contaminants

- Reduce long term mass flux from SZ
  - Coupled with other aggressive source treatment technology

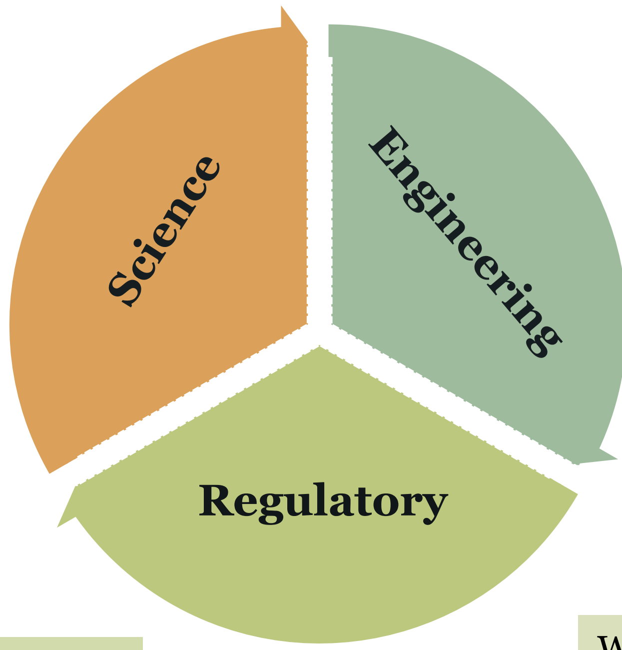
- Address difficult/returning sites more effectively
  - Possible longevity advantage for combating back diffusion
  - In situ bioreactor to enhance biodegradation (biofilm)

- Accelerate cleanup and save long-term cost

Concluding Remarks

Biogeochemical processes involving AC:

- ❖ Electric properties of carbonaceous material for contaminant degradation
- ❖ Interactions between AC and microorganisms and the resulting effects on contaminant degradation.
- ❖ Desorption kinetics/risks



Evaluation and optimization of long-term performance

- ❖ How to differentiate contributions between adsorption and degradation?
- ❖ How to optimize the persistence of degradation in long term?
- ❖ How to couple with other technologies?

Categorization of the technology

What monitoring frequency or parameters we need to require?