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Welcome – Thanks for joining this ITRC Training Class

Permeable Reactive Barrier (PRB): Technology Update

ITRC Technical Regulatory Guidance Document:
Permeable Reactive Barrier:
Technology Update (PRB-5, 2011)

Sponsored by: Interstate Technology and Regulatory Council (www.itrcweb.org)
Hosted by: US EPA Clean Up Information Network (www.cluin.org)

A Permeable Reactive Barrier (PRB) is an in situ permeable treatment zone designed to intercept and remediate a contaminant plume to remediate groundwater. The treatment zone may be created directly using reactive materials such as iron, or indirectly using materials designed to stimulate secondary processes (e.g., adding carbon substrate and nutrients to enhance microbial activity). Since its first implementation in the early 1990s, over 200 PRB systems have been installed to treat groundwater contaminants and PRBs have become an important component among the various technologies available to remediate groundwater contamination.

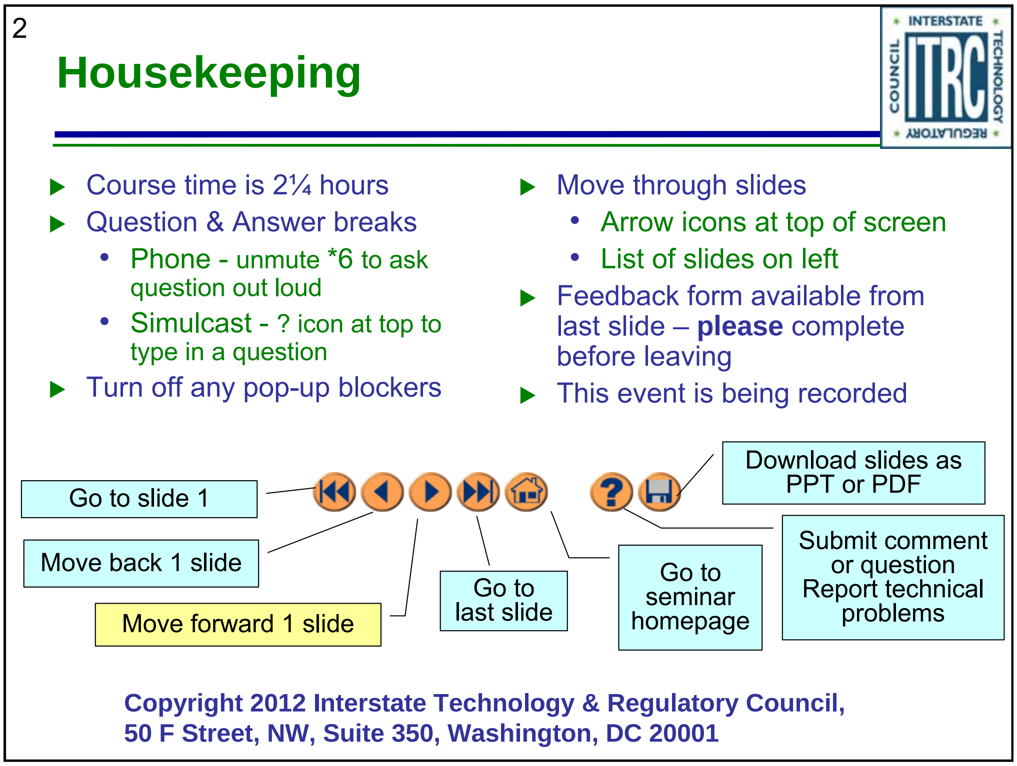
The ITRC Technical/Regulatory Guidance Permeable Reactive Barrier: Technology Update (PRB-5, 2011) and associated Internet-based training are intended to help guide state and federal regulators, consultants, project managers, and other stakeholders and technology implementers through the decision process when a PRB is being considered as a remedy, or part of a remedy, to address contaminated groundwater; and to provide updated information regarding several technical aspects of the PRB using information attained from the more than 15 years that the PRB has been a viable and accepted in situ remediation technology for contaminated groundwater. The guidance and training provides an update on PRBs to include discussions of additional types of reactive media and contaminants that can be treated, design considerations, construction/installation approaches and technologies, performance assessment, and longevity.

If you are unfamiliar with PRBs, we ask that you review background information on PRBs prior to attending the training class. Documents produced by the ITRC PRB team are available for review on the ITRC Permeable Reactive Barriers Guidance Documents page. You can access archives of previous ITRC trainings at http://www.clu-in.org/conf/itrc/advprb_032102/, http://www.clu-in.org/conf/itrc/prb_031902/, and http://www.clu-in.org/conf/itrc/prbll_061506/.

ITRC (Interstate Technology and Regulatory Council) www.itrcweb.org

Training Co-Sponsored by: US EPA Technology Innovation and Field Services Division (TIFSD) (www.clu-in.org)

ITRC Training Program: training@itrcweb.org; Phone: 402-201-2419



Although I'm sure that some of you are familiar with these rules from previous CLU-IN events, let's run through them quickly for our new participants.

We have started the seminar with all phone lines muted to prevent background noise. Please keep your phone lines muted during the seminar to minimize disruption and background noise. During the question and answer break, press *6 to unmute your lines to ask a question (note: *6 to mute again). Also, please do NOT put this call on hold as this may bring unwanted background music over the lines and interrupt the seminar.

You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments using the ? icon. To submit comments/questions and report technical problems, please use the ? icon at the top of your screen. You can move forward/backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our presentation overview, instructor bios, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation slides.

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ITRC (www.itrcweb.org) – Shaping the Future of Regulatory Acceptance

- Host organization (ECOS)
- Network
  - State regulators
    - All 50 states, PR, DC
  - Federal partners
    - DOE DOD EPA
  - ITRC Industry Affiliates Program (IAP)
  - Academia
  - Community stakeholders
- Wide variety of topics
  - Technologies
  - Approaches
  - Contaminants
  - Sites
- Products
  - Technical and regulatory guidance documents
  - Internet-based and classroom training

The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition of regulators, industry experts, citizen stakeholders, academia and federal partners that work to achieve regulatory acceptance of environmental technologies and innovative approaches. ITRC consists of all 50 states (and Puerto Rico and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and advance the regulatory acceptance of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision making while protecting human health and the environment. With our network of organizations and individuals throughout the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

For a state to be a member of ITRC their environmental agency must designate a State Point of Contact. To find out who your State POC is check out the "contacts" section at www.itrcweb.org. Also, click on "membership" to learn how you can become a member of an ITRC Technical Team.

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ITRC Course Topics Planned for 2012 – More information at www.itrcweb.org

Popular courses from 2011

- Bioavailability Considerations for Contaminated Sediment Sites
- Biofuels: Release Prevention, Environmental Behavior, and Remediation
- Decision Framework for Applying Attenuation Processes to Metals and Radionuclides
- Development of Performance Specifications for Solidification/Stabilization
- LNAPL 1: An Improved Understanding of LNAPL Behavior in the Subsurface
- LNAPL 2: LNAPL Characterization and Recoverability - Improved Analysis
- LNAPL 3: Evaluating LNAPL Remedial Technologies for Achieving Project Goals
- Mine Waste Treatment Technology Selection
- Phytotechnologies
- Permeable Reactive Barrier (PRB): Technology Update
- Project Risk Management for Site Remediation
- Use and Measurement of Mass Flux and Mass Discharge
- Use of Risk Assessment in Management of Contaminated Sites

New in 2012

- Green & Sustainable Remediation
- Incremental Sampling Methodology
- Integrated DNAPL Site Strategy

2-Day Classroom Training:

- **Light Nonaqueous-Phase Liquids (LNAPLs): Science, Management, and Technology**

October 16-17, 2012 in Novi, Michigan (Detroit Area)

More details and schedules are available from www.itrcweb.org.

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Meet the ITRC Instructors

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John Doyon has worked for the New Jersey Department of Environmental Protection's (NJDEP) Site Remediation Program since 1989 where his core responsibility is overseeing the remediation of contaminated sites. He has also been actively involved in the Development of Environmental Regulations for the State of New Jersey since 1993 and has been a member of the Interstate Technology Regulatory Council's Enhanced Attenuation of Chlorinated Organics Team since 2004. John earned a bachelor's degree in biology from Trenton State College in Ewing, New Jersey in 1986 and a master's degree in Environmental Policy from the New Jersey Institute of Technology in Newark, New Jersey in 2007.

Bruce Henry is a Project Manager and Principal Geologist. He has worked for Parsons since 1993 providing geological and engineering services for hazardous waste remediation. He is the primary author of the Tri-Services *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents* and the AFCEE *Technical Protocol for Enhanced Anaerobic Bioremediation Using Permeable Mulch Biowalls.* He is representing AFCEE as a member of the ITRC PRB team. He earned a bachelor's degree in geology from University of Colorado in Boulder, CO in 1981 and a master's degree in geology from Colorado State University in Fort Collins, CO in 1993. He is a professional geologist in Wyoming.

Cannon Silver is a Principal Environmental Engineer with CDM Smith, located in Columbus, Ohio. He has worked in the environmental field since 1994. Cannon designs, installs, and optimizes innovative remedial systems for industrial and federal clients, and specializes in technology transfer. He has authored or co-authored more than 15 technical presentations on innovative technologies. He has installed and evaluated the performance of multiple permeable reactive barriers (PRBs) at Air Force and Navy sites. In 2011, Cannon prepared a document for the Navy, comparing the cost, performance, and sustainability of various types of PRBs. He has served on ITRC's PRB Update Team since 2008. Cannon earned a bachelor's degree in Mechanical and Materials Engineering from Harvard University in Cambridge, MA in 1993, and a master's degree in Environmental Engineering from Stanford University in Palo Alto, CA in 1994, and is a registered professional engineer in California, Michigan, and Utah.

Scott Warner is a Principal Hydrogeologist and the Global Practice Area Leader in Environmental Engineering and Remediation with AMEC Environment and Infrastructure, located in Oakland, California. Scott has worked with the firm since 1991 specializing in groundwater remediation with specific expertise in enhanced bioremediation, permeable reactive barriers (PRB), and geochemical manipulation for treatment groundwater impacted by chlorinated and petroleum hydrocarbons, metals, and radionuclides. Scott has authored or co-authored more than 25 publications on the subjects of groundwater remediation, hydraulics, and geochemistry for both peer-reviewed journals and conference proceedings, and has given more than 50 presentations on these and related subjects. He is co-editor of an Oxford University Press book on dense non-aqueous-phase liquid (DNAPL) characterization and remediation and was the co-developer/co-instructor of national and international courses for the Remediation Technology Development Forum (RTDF), the U.S. Environmental Protection Agency (U.S. EPA), and the Interstate Technology Regulatory Council (ITRC) on the design and use of PRBs. Scott also is on the board of directors for the Bay Planning Coalition, a San Francisco Bay Area organization whose members represent industry, local governments and ports, recreational users, business and environmental organizations, landowners, and water-related companies that advocate balanced use and regulation of the San Francisco Bay and Delta resources. Scott has contributed to ITRC as a team member and instructor for ITRC's PRB teams since 1998. He earned a bachelor's degree in engineering geology from University of California, Los Angeles in 1983 and a master's in geology (hydrogeology specialization) in 1986 from Indiana University, Bloomington. Scott is a registered professional geologist in several states and is a certified/licensed hydrogeologist in California and Washington and a certified engineering geologist in California.

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PRB Update: Course Road Map

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- Introduction
- Regulatory Considerations
- Science of Permeable Reactive Barriers (PRBs)
- Reactive Materials
- Improved Construction Methods
- Performance Monitoring
- Longevity of PRBs
- Enhancing Effectiveness

No associated notes

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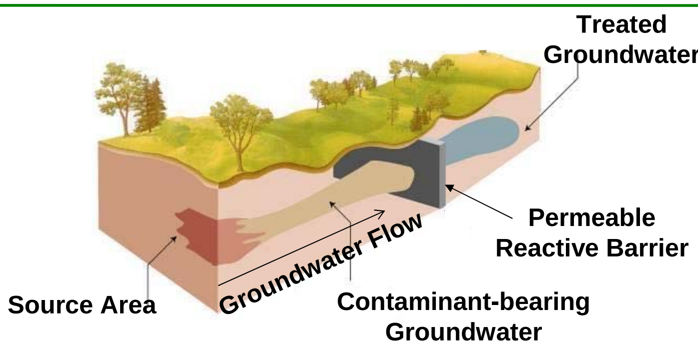
Permeable Reactive Barriers (PRBs)



- PRB is a continuous, in-situ permeable treatment zone designed to intercept and remediate a contaminant plume. Contaminants may be treated through physical, chemical, or biological processes
  - Uses a variety of materials and installation techniques
  - Treats an ever increasing list of contaminants
  - Part of an overall site close/exit strategy

In the broadest sense, a PRB is a continuous, *in situ* permeable treatment zone designed to intercept and remediate a contaminant plume. The treatment zone may be created directly, using reactive materials such as iron, or indirectly, using materials designed to stimulate secondary processes (e.g., adding carbon substrate and nutrients to enhance microbial activity). In this way, contaminant treatment may occur through physical, chemical, or biological processes. The term “barrier” is intended to convey the idea of a barrier to contaminant migration, but not to groundwater flow. The PRB is designed to be more permeable than the surrounding aquifer media so that groundwater readily flows through the barrier without significantly altering groundwater hydrology.

PRB – Example Installation

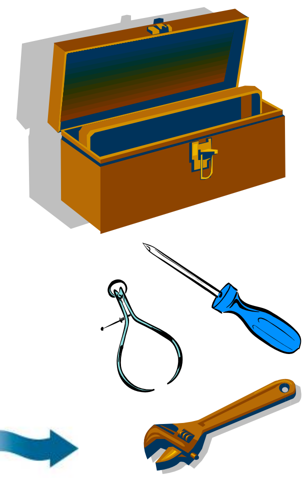
Installation of PRB at West Valley, New York

(photo courtesy of Dewind One-pass Trenching)

This photo illustrates the installation of a zeolite PRB to treat strontium 90 at the West Valley DOE site in New York. The PRB was installed to a maximum depth of 35 feet, but this trencher has the capability to install PRBs to as deep as 45 feet.

Tools for Your Remediation Tool Box

- Over 15 year of PRB lessons learned
- PRB advantages and limitations
- Application of new reactive materials
- Identify potential design and construction challenges
- Performance monitoring approaches
- Opportunities for enhancing PRB effectiveness



No associated notes

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ITRC Guidance/Training
Key to PRB Use/Acceptance

- 1999 - PBW- 1 Regulatory Guidance for Permeable Reactive Barriers Designed to Remediate **Chlorinated Solvents**
- 1999 - PRB- 3 Regulatory Guidance for Permeable Reactive Barriers Designed to Remediate **Inorganic and Radionuclide** Contamination
- 2000 - PBW- 2 **Design Guidance** for Application of Permeable Reactive Barriers for Groundwater Remediation
- 2005 - PRB- 4 Permeable Reactive Barriers: **Lessons Learned/New Directions**
- 2011 - PRB-5 Permeable Reactive Barriers: **Technology Update**

Over 15 Years of PRB Experience

Access documents at www.itrcweb.org under Guidance Documents then Permeable Reactive Barriers or directly at http://www.itrcweb.org/guidancedocument.asp?TID=5

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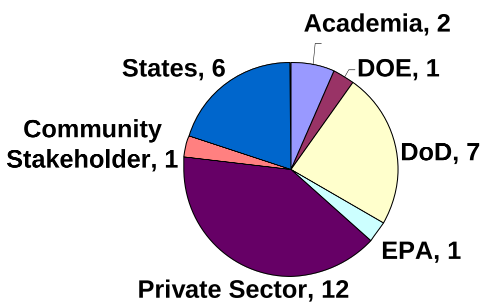
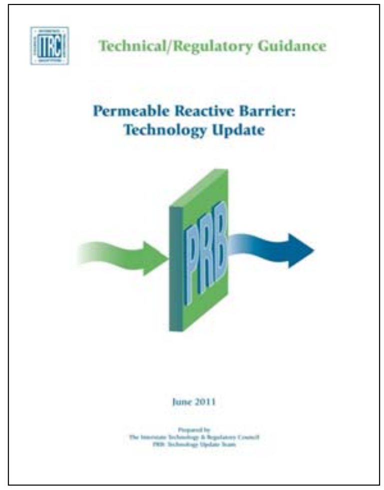
ITRC PRB Update Team and 2011 Guidance

Team Composition





ITRC Technical and Regulatory Guidance Permeable Reactive Barrier: Technology Update (PRB- 5, 2011)

Access PRB Team information and resources at http://www.itrcweb.org/prb/

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Key PRB Considerations

- Base technology is accepted as mainstream (almost)
- New media and new construction methods
- PRBs are addressing more contaminants and being installed deeper
- Combined with source area treatments (ITRC BIODNAPL guidance documents 2005 - 2008)
- Sequential aerobic/anaerobic treatment for multiple contaminants
- PRB as a green technology

No associated notes

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PRB Advantages and Limitations

Advantages

- Contains the plume while source is remediated
- Reduces mass discharge and accelerates monitored natural attenuation (MNA)
- Treats broad spectrum of contaminants
- Green and sustainable – low energy requirements
- Low operations and maintenance cost
- Long-term effectiveness
- System is unobtrusive once installed

Limitations

- Existing infrastructure
- Depth, hydraulic limits
- Performance may decrease over time

PRB-5: Figure 6-1. Horizontal PRB - treatment of septic system nitrate
(Courtesy of Septech, Inc., 2003)

PRBs are a proven technology and can be an integral part of an overall remedial strategy for groundwater restoration. They offer the following advantages:

- Contain the contaminant plume thus protecting groundwater receptors while source areas are being remediated

- Reduction in mass discharge to accelerate natural attenuation

- PRBs can be used for a broad spectrum of contaminants including all types of **organics** especially chlorinated solvents and fuel hydrocarbons, **inorganics** such as metals, radionuclides, and nitrate, and **energetics** such as perchlorate, RDX, TNT. PRBs can be used to treat a wide range of contaminants within single PRB.

Additionally, PRBs offer the following advantages:

- Green and Sustainable

- Long-lasting Performance

- Mass Flux Reduction

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Regulatory Considerations for PRBs

- In most cases, regulatory permits are not required for PRB operation, however:
  - Review of permitting issues should be conducted on a site-specific basis
- Permits may be necessary during construction, monitoring or closure of systems
  - Underground Injection Control (UIC) Permit – varies by state
  - Discharge Permits (NPDES) – may be required if excess fluid generated during construction

See PRB-5, Section 2 for Regulatory Considerations

See PRB-5, Section 2 for Regulatory Considerations

In most cases, regulatory permits are not required for the operation of a PRB. However, one or more permits may be necessary for the design, construction, monitoring, or closure of a PRB to the extent that the activity affects surface water, air, or groundwater quality or involves the management of hazardous waste. A thorough review of all permitting issues and state and local regulations should be conducted on a site-specific basis.

In addition to regulatory permits, PRB approval may occur through different regulatory mechanisms. The approval mechanism (e.g., approval letter or cleanup order) often depends on the regulatory program/process under which the site cleanup is managed (e.g., Resource Conservation and Recovery Act [RCRA], state Superfund, or voluntary cleanup programs). Various regulatory programs may require submittal of a work plan, corrective action plan, remedial action plan, feasibility study (FS), or similar regulatory planning document. Following are brief explanations of key potential regulatory permits that may be required for a PRB.

UIC permits are not typically required for PRBs; however, this requirement varies from state to state; therefore, a review of the pertinent regulations should be conducted during initial design stages of the project, especially if the reactive media is installed by a high-pressure jetting technique or by vertical hydraulic fracturing. If USEPA has not delegated the UIC program to the state, the regional USEPA office makes the determination.

National Pollution Discharge Elimination System (NPDES) permit authority resides within the federal Clean Water Act (CWA). The NPDES permit program controls water pollution by regulating point sources that discharge pollutants into waters of the United States. An NPDES permit may be required during construction if excess fluid (e.g., displaced groundwater or excess slurry) is generated. If it is necessary to dispose of the liquid or if there is potential that storm water generated during construction could carry pollutants or sediment into surface water bodies, then an NPDES permit from the state may be required. Additionally, many states now require storm-water pollution prevention plans, which require use of best management practices (BMPs) to manage storm-water discharges at construction sites 1 acre or larger.

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Regulatory Considerations for PRBs (continued)

- Downgradient groundwater quality issues (secondary water quality)
- Performance monitoring requirements
- Institutional controls
- Contingency planning
- Community considerations (public perception)

See PRB-5, Section 2 for Regulatory Considerations

PRB-5, 2011 Section 2: Regulatory Considerations

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Using PRBs: Your Remedial Strategy

- Selected as final remedy
  - Altus Air Force Base, Oklahoma
  - Seneca Army Depot, New York
- Selected part of overall remedial strategy
  - West Valley, New York
  - Offutt Air Force Base, Nebraska
- Remedy success example
  - Led to property transfer at large Naval facility in McGregor, Texas

Over 200 PRBs installed as of 2011

See PRB-5 Appendix A. Case Summaries

See more information in PRB-5 Appendix A. Case Summaries

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After this training class you should be able to……….

- Apply ITRC's PRB Guidance
- Understand basic PRB science and advantages/limitations
- Determine when PRBs should be considered
- Understand PRB use with other technologies
- Formulate questions to identify potential design and construction challenges
- Understand performance monitoring approaches and longevity considerations
- Access additional PRB resources

No associated notes

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PRB Update: Course Road Map

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- Introduction
- Regulatory Considerations
- Science of PRBs
- Reactive Materials
- Improved Construction Methods
- Performance Monitoring
- Longevity of PRBs
- Enhancing Effectiveness

This section is a review of the basic science of PRBs with a focus on the various PRB media currently being used and matching them to the appropriate contaminants. Design considerations and methods used for constructing for PRBs are also reviewed. These topics are covered in greater detail in Section 4 (Reactive Media and Treatment Processes), Section 5 (Design), and Section 6 (Construction and Cost Considerations) of the PRB Update document. Cost considerations are covered later in this training session. Access more ITRC PRB information at: http://www.itrcweb.org/prb/

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Science of PRBs
Key Concepts for Successful PRBs….

- Match the correct treatment media and degradation or removal process to the contaminant(s)
- Provide adequate contact/residence time to reduce the contaminants to target concentrations
- Intercept the plume without contaminant bypass
- Are effective long enough to achieve site-wide remedial objectives

The first step in designing a PRB system is to correctly match the reactive media to the contaminants to be treated, including any regulated degradation products, The design should allow for adequate residence time in the reaction zone to achieve target concentrations. This requires knowledge of peak concentrations, degradation or reaction rates for the media, and a good understanding of the site groundwater hydraulics. The design should ensure that contaminant bypass does not occur; for example, ensuring that the permeability of the PRB remains higher that the surrounding formation.

Beyond the design of a PRB, it is also necessary to integrate the PRB into a site-wide remedy, which often means that the PRB must be effective for long periods of time while other remedial strategies are being applied. Examples might include source reduction measures or natural attenuation of downgradient plume areas. ZVI PRBs have the longest record of operation, and the photo here shows installation of ZVI media in a supported trench.

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Matching the Media to the Contaminant

- How the material treats the contaminant
- The reaction kinetics (destructive) or treatment capacity (non-destructive)
- How site-specific geochemistry will affect the treatment process (e.g., potential for mineral passivation or biological sulfide toxicity)
- How to use new materials effectively– combined iron and carbon materials, zeolites, and organophilic clays

EHC® powder – combination plant fiber and zero-valent iron (ZVI)
(photo courtesy Adventus)

Matching the media to the contaminant or contaminant mixtures requires an understanding of how different media treat the contaminants, and the rates at which the contaminant is removed from groundwater. In some cases the material may have a limit to contaminant removal, for example materials like zeolite, apatite, or organophilic clays that remove contaminants by cation-exchange or sorption processes. Site-specific geochemistry should also be taken into account. For example the potential passivation of zero-valent iron by carbonates, or inhibition of biotic dechlorination due to high or low pH. New materials may require bench testing to thoroughly understand the removal pathways and reaction rates. Finally, many reactive media require special techniques to emplace the material in the subsurface.

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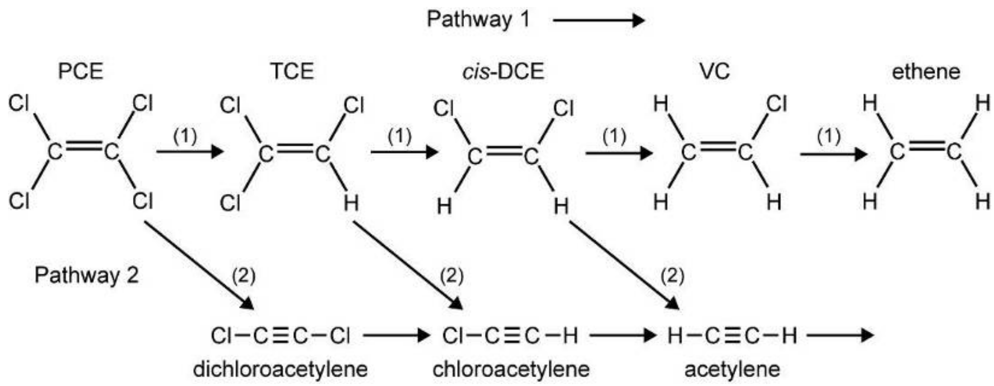
Destructive Processes to Treat the Contaminant

- Biotic degradation (e.g., dechlorination of solvents)
- Abiotic degradation to non-toxic end products (e.g., β-elimination of TCE by ZVI or iron sulfides)



PRBs treat contaminants by two general processes, either destructive processes where the contaminant is transformed into non-toxic end products, or non-destructive processes where the contaminant is removed by processes such as sorption or transformation to less mobile or less toxic forms.

Destructive processes may be abiotic (chemical or physical destruction) or biotic, or a combination of both. Pathway 1 shows the biotic sequential dechlorination of PCE and TCE to VC and ethene, while Pathway 2 shows an abiotic pathway where PCE and TCE are ultimately transformed to acetylene by reaction with reactive minerals or zero-valent iron. This is often referred to as the Beta-elimination pathway. In some cases the reactive mineral may be a reduced iron sulfide produced as a result of both biological and chemical processes, for example the biological reduction of sulfate to sulfide and the subsequent chemical reduction of ferric iron by sulfide to produce reactive iron mono-sulfides. This is a current area of research often referred to as “biogeochemical transformation.”

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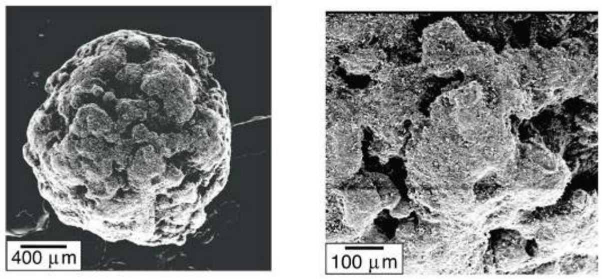
Non-Destructive Processes to Treat the Contaminant

- Sorption and surface complexation
- Cation exchange (e.g., Sr^{90} to zeolite or metals to apatite)
- Transformation to less toxic forms (e.g., reduction of Cr^{6+} to Cr^{3+} or NO_3^- to NO_2^-)



Electron micrograph illustrating morphology and micro porosity of apatite materials. Adapted from USEPA (2000).

Non-destructive processes may include sorption, cation exchange, surface complexation, and transformation to less mobile or less toxic forms. Radionuclides, in particular Uranium and Strontium-90, have been treated using zeolite. Uranium is removed from solution through precipitation or surface complexation.

Apatite materials (e.g., phosphate bone char) may have a high degree of micro-porosity and high surface area. These materials may be used to remove positively charged cations, for example removal of lead by precipitation as lead phosphate. The removal capacity of the material may be proportional to it's physical properties such as porosity and surface area

Reference:

USEPA. 2000. *Field Demonstration of Permeable Reactive Barriers to Remove Dissolved Uranium From Groundwater, Fry Canyon, Utah. Interim Report.* September 1997–September 1998. EPA 402-C-00-001. November 2000.

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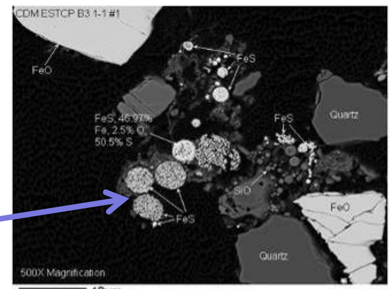
What Contaminants can be Treated?

- PRBs have commonly been applied to:
  - Organics (e.g., solvents/fuels/creosote)
  - Perchlorate and energetics such Royal Demolition Explosive (RDX) or Trinitrotoluene (TNT)
  - Inorganics (e.g., radionuclides, metals, anions)

  See Table 4.1 in the PRB document for an extensive list of media and contaminants
- Future PRBs to treat emerging contaminants
- Unique monitoring methods may be required to document the treatment process
  - Monitoring for toxic intermediates
  - Mineralogy and passivation



Reactive iron sulfides, for example framboidal pyrite (Lebron *et al*., 2010)

An expanding list of contaminants may be treated by PRBs, and it is anticipated that new materials will be developed to treat emerging or recalcitrant contaminants such as perfluorooctanoic acid/perfluorooctane sulfonic acid (PFOA/PFOS) and pharmaceuticals. This may also lead to more unconventional PRBs, for example to treat groundwater discharge or for surface water.

Table 4.1 in the PRB document has an extensive list of materials and the contaminants that they can treat.

Due to the difference in reactive material physical and chemical properties, unique monitoring methods and analyses may be required to evaluate PRB performance. For example, methods such as a scanning electron microprobe may be used to evaluate the presence of reactive iron sulfide minerals. The photomicrograph in this slide shows examples of framboidal pyrite.

Reference:

Lebrón, C., P. Evans, K. Whiting, J. Wilson, E. Becvar, and B. Henry. 2010. *In situ Biogeochemical Transformation of Chlorinated Ethenes Using Engineered Treatment Systems*. Prepared for NAVFAC ESC and ESTCP. February.

25

Treatment Materials and Mechanisms

(PRB-5: Section 4)

Media: Zero-Valent Iron (granular to nano-scale)

First used for: TCE (1997)

Contaminants Treated	Treatment Mechanisms
Chlorinated solvents	Abiotic reductive dechlorination
Energetics (TNT, RDX)	Reductive degradation
Redox-sensitive metals [Cr(VI)]	Reductive precipitation
Redox-sensitive oxyanions (U, Se)	Reduction, sorption, precipitation
Arsenic	Sorption and co-precipitation
Divalent metals (Cu, Zn)	Sorption, reduction, precipitation

Case Studies: Coast Guard Support Center, Elizabeth City, NC (TCE, CrVI)
Commercial Street Operable Unit, Sunnyvale, CA (TCE)
Cornhusker Army Ammunition Plant, NE (RDX, TNT)

Granular zero-valent iron (ZVI) is a common treatment media used to treat chlorinated solvents such trichloroethene (TCE) through an abiotic reductive dechlorination pathway. Recently ZVI has been demonstrated to be effective in reducing energetics such as TNT and RDX. The reducing properties of ZVI may also be used to treat redox-sensitive or divalent metals such hexavalent chromium, copper and zinc; arsenic and redox-sensitive oxyanions such as uranium and selenium may also be treated. Typically these elements are transformed to less mobile forms that are removed from groundwater by sorption or precipitations.

ZVI is also being applied in micro- and nano-scale forms that can e injected directly into the subsurface. Typically these forms of ZVI are used in a combined media such as the EHC® series of products or as emulsified zero-valent iron (EZVI).

For more information on treatment materials see Section 4 of Permeable Reactive Barriers Update (PRB-5). Several case studies of ZVI applications are included in an appendix in the PRB-5 document.

Example References:

Johnson, R. and P. Tratnyek. 2008. *Remediation of Explosives in Groundwater Using a Zero-Valent Iron Permeable Reactive Barrier*. Prepared for the ESTCP. Arlington, Virginia. ESTCP Project ER-0223, Final Report, May.

Wilkin, R.T., S.D. Acree, D.G. Beak, R.R. Ross, T.R. Lee, and C.J. Paul. 2008. *Field Application of a Permeable Reactive Barrier for Treatment of Arsenic in Ground Water*. EPA 600/R-08/093.

26

Treatment Materials and Mechanisms

(PRB-5: Section 4)

Media: Solid Organic Amendments (wood chips, leafy compost)

First used for: Nitrate (1995); Acid Mine Drainage (1997); TCE and perchlorate (1999)

Contaminants Treated	Treatment Mechanisms
Chlorinated solvents	Biological and abiotic dechlorination
Perchlorate	Microbial degradation
Energetics (TNT, RDX)	Reductive degradation
Nitrate	Denitrification (to nitrogen gas)
Sulfate	Reduction to sulfide

Case Studies: OU-1 Biowall at Altus AFB, Oklahoma (TCE and DCE)
Pueblo Depot Activity Biowall, Colorado (RDX)
Oklahoma Pork Facility, OK (nitrate)

Solid organic materials such as mulch and compost have been used to treat chlorinated solvents and perchlorate in biowall PRBs since 1999. Permeable mulch biowalls have also been demonstrated for RDX and TNT. Mulch has been used to reduce nitrate to nitrite since the mid-1990's, and may also be used to reduce sulfate and di-valent metals such as copper, and zinc.

Several case studies using solid organic substrates are included in the PRB-5 document, including treatment for chlorinated solvents, RDX, and nitrate.

Example References:

Robertson, W.D., J.L. Vogan, and P.S. Lombardo. 2008. "Nitrate Removal Rates in a 15-Year-Old Permeable Reactive Barrier Treating Septic System Nitrate," *Ground Water Monitoring and Remediation* **28**(3): 65–72.

AFCEE. 2008. *Technical Protocol for Enhanced Anaerobic Bioremediation Using Permeable Mulch Biowalls and Bioreactors*. Prepared by Parsons Infrastructure and Technology Group, Inc., Denver, Colorado. May.

GSI (Groundwater Services, Inc.). 2008. *Final Report - Treatment of RDX and/or HMX Using Mulch Biowalls.* Prepared for the Environmental Security Technology Certification Program, Arlington, Virginia. July.

27

Treatment Materials and Mechanisms
(PRB-5: Section 4)

Media: Phosphates (Apatite)
First used for: Uranium (1997)

Contaminants Treated	Treatment Mechanisms
Radionuclides (U, Sr)	Precipitation, surface complexation
Lead	Precipitation

Media: Zeolites
First used for: strontium-90 (1998)

Contaminants Treated	Treatment Mechanisms
Radionuclides (Sr)	Cation exchange
Ammonium and Perchlorate (lab only)	Cation exchange

Phosphates, in the form of natural or synthetic apatite, may be used to treat radionuclides such as uranium and strontium through precipitation or surface complexation processes. Heavy metals that may be treated with apatite include lead, zinc, and cadmium.

Zeolites are natural minerals that may similarly be used to treat radionuclides such as strontium by the process of cation exchange. Zeolites also have the potential to treat inorganic compounds such as ammonium and perchlorate, but to date this has only been demonstrated in the laboratory.

Example References:

Bowman, R.S., Z. Li, S.J. Roy, T. Burt, T.L. Johnson, and R.L. Johnson. 2001. "Pilot Test of a Surfactant-modified Zeolite Permeable Barrier for Groundwater Remediation," *Physical and Chemical Remediation of Contaminated Aquifers*. J.A. Smith and S. Burns (eds.). Kluwer Academic Publ./Plenum Press, New York: 161–85.

Conca, J.L. and J. Wright. 2006. "An Apatite II permeable reactive barrier to remediate groundwater containing Zn, Pb and Cd," *Applied Geochemistry* **21**(8): 1288–300.

Lee, D.R., D.J.A. Smyth, S.G. Shikaze, R.J. Jowett, D.S. Hartwig, and C. Milloy. 1998. "Wall-and-Curtain for Passive Collection/Treatment of Contaminant Plumes," Presented at the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, California. May 18–21.

Rabideau, A.J., J. Van Benschoten, A. Patel, and K. Bandilla. 2005. "Performance assessment of a zeolite treatment wall for removing Sr-90 from groundwater," *Journal of Contaminant Hydrology* **79**(1–2): 1–24

28

Treatment Materials and Mechanisms
(PRB-5: Section 4)

Media: Iron and Steel Furnace Slag
First used for: phosphate (1999)

Contaminants Treated	Treatment Mechanisms
Phosphate	Sorption; Precipitation of Hydroxyapatite
Arsenic	Sorption and precipitation
Divalent metals (lab only)	Sorption and precipitation
Chlorinated solvents (lab only)	Abiotic reductive dechlorination

Media: Organophilic Clays
First used for: creosote NAPL (2005)

Contaminants Treated	Treatment Mechanisms
Non-aqueous-phase liquids	Sorption
PAHs (lab only)	Sorption

Research has been conducted into the use of iron and steel furnace slag. Slag has been applied in a pilot-scale PRB applications for the treatment of arsenic (As) in groundwater and a full-scale slag PRB was installed in 2002 in East Chicago, Indiana, to treat As-impacted groundwater (Bain et al. 2006).

Organophilic clays have a high sorption capacity for oil and creosote, typically >50% by weight. Organophilic clay does not hydrate and swell with water, and has a hydraulic conductivity similar to sand. A field-scale PRB containing organophilic clay manufactured was installed at a former railroad tie treating facility in Escanaba, Michigan, in November 2005 (see Case Summary in Appendix A of PRB-5). The PRB was designed to control migration of a creosote DNAPL plume to surface water.

Example References:

Bain, J., D. Blowes, D. Smyth, C. Ptacek, J. Wilkens, and R. Ludwig. 2006. "Permeable Reactive Barriers for In-Situ Treatment of Arsenic-Contaminated Groundwater," *Remediation of Chlorinated and Recalcitrant Compounds—2006*. Proceedings of the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, California. May.

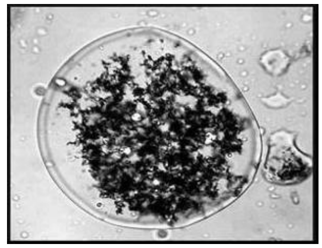
Benson, C.H., S. Lee, and A. Ören. 2008. "Evaluation of Three Organoclays for an Adsorptive Barrier to Manage DNAPL and Dissolved Phase Polycyclic Aromatic Hydrocarbons (PAHs) in Ground Water" Final Report (Redacted), University of Wisconsin, *Madison Geo Engineering Report* 8–24.

Metz, S. and C. Benson. 2007. "Iron Foundry Slags as Permeable Reactive Barrier Materials for Removing Arsenic from Groundwater," ASCE *Geotechnical Special Publication* **174:** 1–12.

29

New Reactive Materials

- Mixed iron and organic substrates
  - Use ZVI as reactive media and to lower redox state to enhance thermodynamics of degradation reactions
  - Examples – Duramend/EHC® products, ABC^{+} product
  - Emulsified Zero-Valent Iron (EZVI)
- Granular Activated Carbon impregnated with ZVI –
  - BOS 100® product - GAC has very high sorption capacity; may be difficult to evaluate sorption vs degradation



Micrograph of nanoscale iron within an emulsion droplet

Granular mixture of BOS 100®

Mixed iron and organic materials have been on the market for several years. In general these materials treat the same contaminants as ZVI or organic materials alone, primarily chlorinated solvents, perchlorate, and energetics compounds. In addition to being a reactive material, the presence of iron will drive the groundwater redox state lower than could be achieved by biological processes. This enhances the thermodynamics of the degradation processes, resulting in less formation of chlorinated intermediate products. This process is often referred to as in situ chemical reduction (ISCR). Other products combine micro-scale or nano-scale iron with emulsified vegetable oil (EZVI).

BOS 100® is another new product that is primarily granular activated carbon (GAC) impregnated with ZVI. Intended primarily for use with chlorinated solvents, the solvents are rapidly removed from groundwater by sorption, and then degraded by reaction with the iron.

The long-term performance of these products is still being evaluated, but should at least match that of emulsified vegetable oil products with which the iron products are often combined with. EHC products from Adventus, for example, have been shown to be effective for treating carbon tetrachloride for a period of over 5 years (Advents Technical Note, updated January 2011).

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PRB Design

- Importance of site characterization
  - adequate Conceptual Site Models
- Site-specific geotechnical and geochemical parameters
- Adequate residence time
- Use of treatability studies for design with new materials or emerging contaminants
- Considerations of current and future land issues
- Long-term operation
  - Can you build in flexibility or contingencies to sustain performance or to address hydraulic changes?
  - Designing for the future (e.g., >10-15 years)

Design considerations are covered in Section 5 of the PRB-5 document. When PRBs do not perform to expectations it is often a result of not adequately understanding site hydrogeological or chemical conditions. Therefore, developing a good conceptual site model continues to be emphasized for PRBs and other in situ remedial technologies.

For newer materials or for emerging contaminants, the use of bench-scale treatability studies or small scale pilot tests is advisable before proceeding to full-scale design.

Because PRBs may need to operate effectively for periods of 10 to 15 years or more, current and future land use must be considered as well as sustaining performance. Is there the potential for buildings or roadways to be built over the PRB? What load bearing properties may be required? How will settling and compaction be mitigated? Finally, can the ability to optimize, replenish, or other contingency to sustain performance be built into the design? The next section of this presentation covers some of these key topics.

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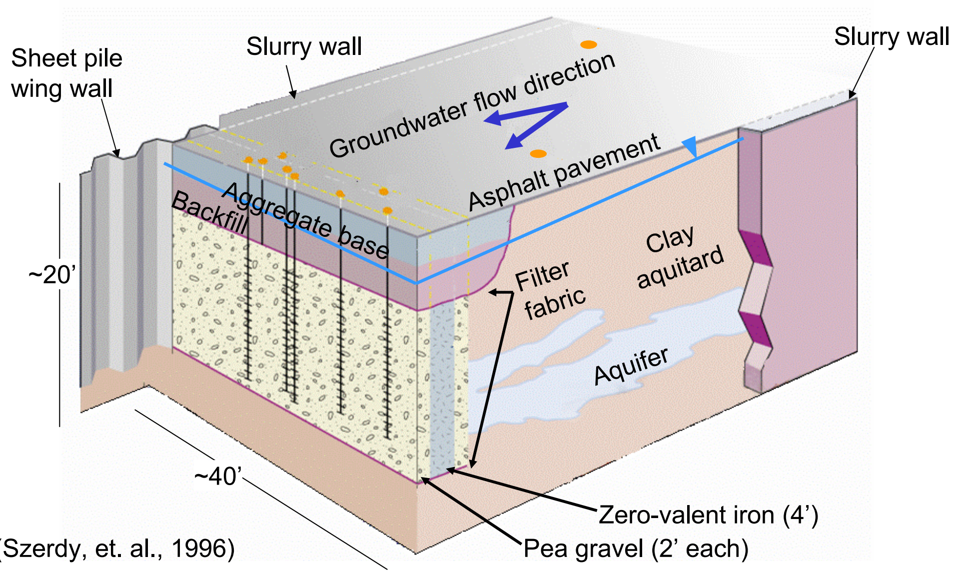
Layout of a Conventional PRB System



(Szerdy, et. al., 1996)

This figure is intended to illustrate many of the conventional components of a trench-and-fill PRB system. Each PRB is unique, so this diagram is not intended to represent all possible designs. Many PRBs use a slurry wall of sheet pile to channel flow through the reactive media. The thickness of the PRB treatment zone is proportional to the residence time in which contaminants are in contact with the reactive media, and this dimension is a critical design parameter.

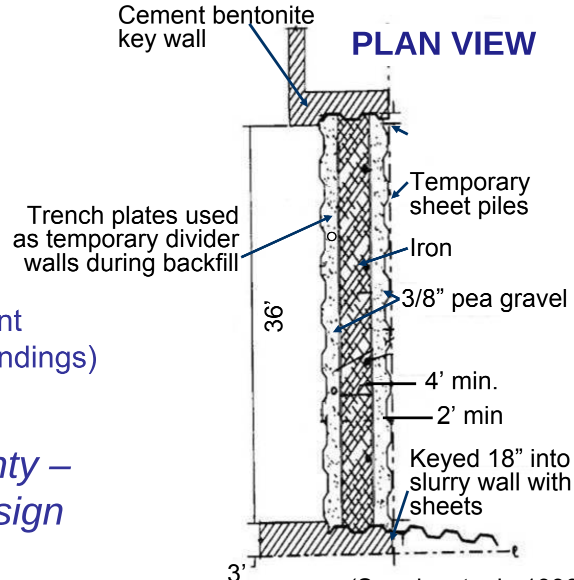
Reference: "In Situ Groundwater Treatment by Granular Zero Valent Iron: Design, Construction and Operation of an In Situ Treatment Wall." F. Szerdy, J.D. Gallinatti, S.D. Warner, C. Yamane, D.A. Hankins, and J.L. Vogan. Proceedings of the Non-Aqueous Phase Liquids (NAPLs) in Subsurface Environment: Assessment and Remediation, ASCE Specialty Conference, Washington, D.C. November 12-14, 1996.

32

Constructability –
Geotechnical and Structural Considerations

- Considerations
  - Sidewall integrity and smearing
  - Settlement and volume changes
  - Infrastructure and load bearing
- Geotechnical assessment (cone penetrometer soundings)

Reducing uncertainty – appropriate pre-design characterization



(Szerdy, et. al., 1996)

The ability to install a PRB (constructability) is dependent on the geotechnical properties of the subsurface soil or bedrock. The cohesive properties of the soil and integrity of the side walls may dictate what construction methods can be used, A supported excavation, for example with sheet pile, may be required. For interbedded sand and clays, smearing of clays across the sand horizons during excavation mat reduce the permeability of the clay, sometimes referred to as a “skin” effect.

Geotechnical surveys using direct-push methods, such as cone penetrometer soundings, may be used to reduce the uncertainty with subsurface conditions and provide greater confidence that the PRB can be installed as designed.

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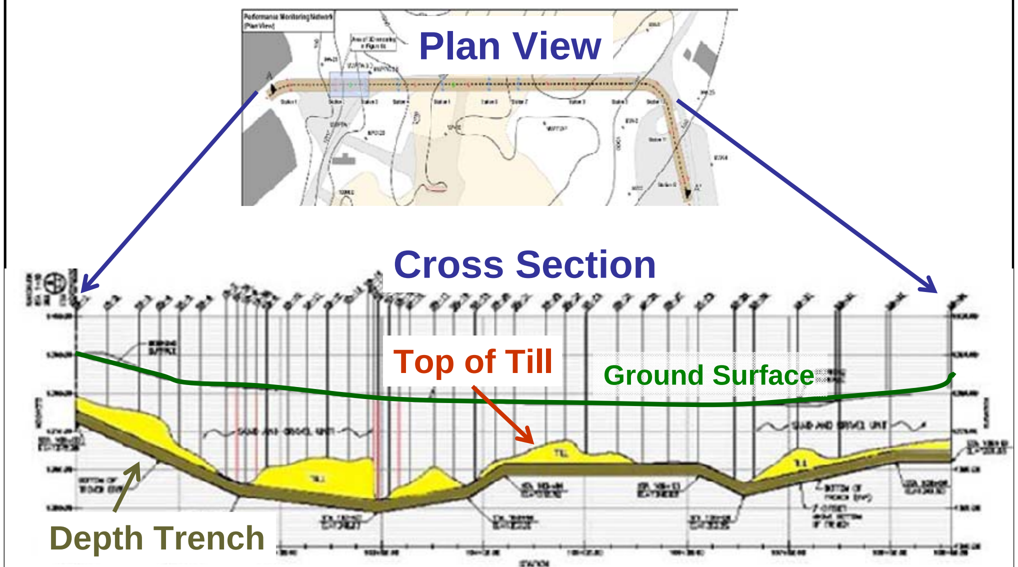
Geotechnical Design – Defining Lower Confining Unit with CPT Borings

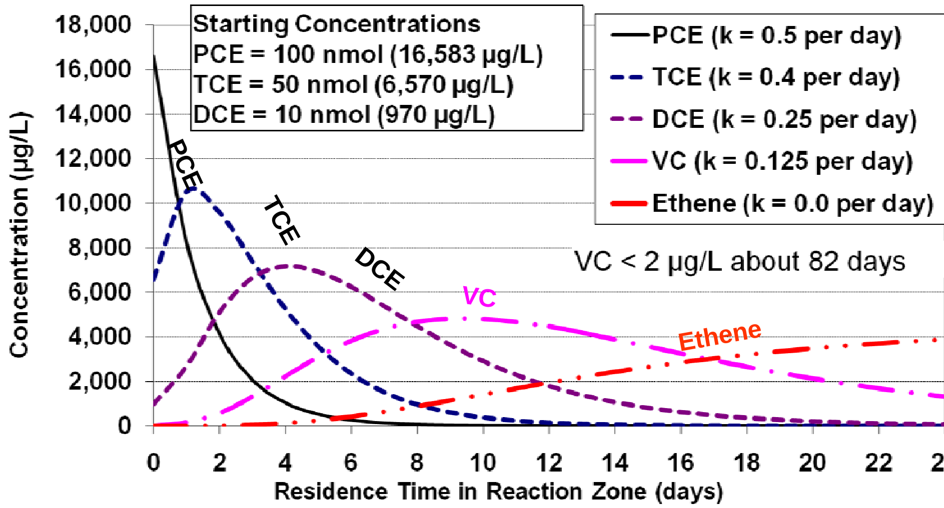


This cross section illustrates variations in the depth to a lower confining till (in yellow) at the West Valley Site in Western New York State based on a series of CPT borings. The depth of the trench (solid green line) was adjusted to ensure the PRB was installed to the lower confining unit along the entire length of the PRB. Without the borings it is likely that targeting a single depth would have left gaps in the PRB.

34

Residence Time – Impact of Sequential Reductive Dechlorination

Residence time may be estimated from reasonable first-order rate constants and maximum contaminant concentrations



The residence time necessary to reduce concentrations to a performance metric is typically calculated using a first-order decay rate. The solution to a first-order decay rate is:

$C_t = C_o e^{-(kt)}$ where

C_t is the concentration (mass per unit volume or µg/L) at time t (days)

C_o is the initial concentration (µg/L)

K is the first-order degradation coefficient (per day)

This equation can be rearranged to yield the time (t) to meet a target concentration as:

$t = -\ln (C_t/C_o) / k$

For example, to reduce the concentration of PCE from 10,000 µg/L (C_o) to 5 µg/L (C_t) at a first-order rate of 0.25/d (k) requires a residence time of approximately 30 days.

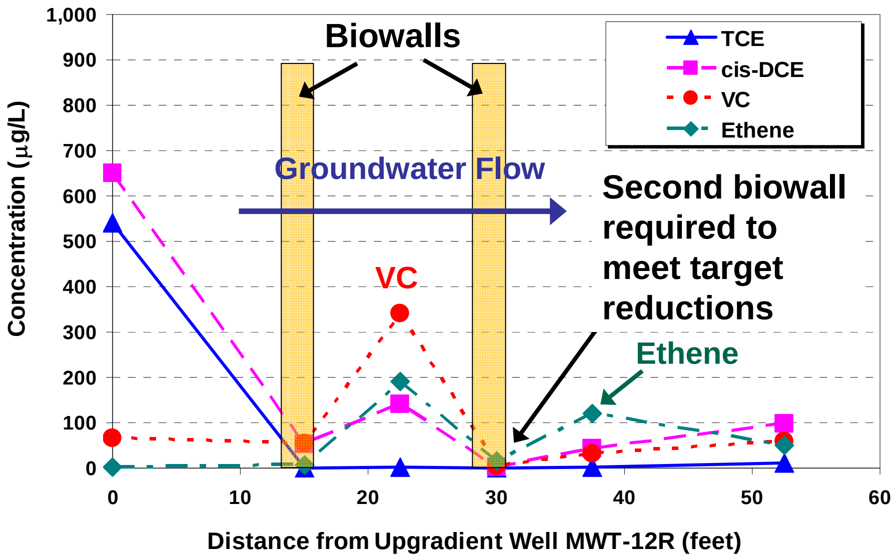
However, this plot shows the theoretical distribution of chloroethenes over time or distance when sequential reductive dechlorination occurs. Based on the initial concentrations of PCE, TCE, and DCE posted, and on typical degradation rates that may be achieved, the successive production and depletion of each intermediate dechlorination product is evident. Note that to completely degrade each dechlorination product to drinking water MCLs may take up to 82 days in this theoretical case. If the residence time in the reaction zone is not sustained long enough, DCE or VC may accumulate and persist in groundwater migrating downgradient of the reaction zone.

If there is a practical limit to the width of the PRB that can be excavated, then a second PRB may be installed to achieve a longer residence time. In addition, reaction rates between differing reactive media and different forms of a media may vary significantly.

Reference: AFCEE. 2008. *Technical Protocol for Enhanced Anaerobic Bioremediation Using Permeable Mulch Biowalls and Bioreactors*. Prepared for the Air Force Center for Engineering and the Environment by Parsons Infrastructure & Technology Group, Inc., Denver, Colorado. May.

35

Use of Multiple PRBs – Concentrations along Ash Landfill Biowall Transect



An example of concentrations across a dual biowall at the Seneca Army Depot Activity in New York are shown here for illustration. Concentrations of TCE and cis-DCE are reduced in the first biowall, but then VC is present as a dechlorination product after the first biowall. The concentration of VC is further reduced in the second biowall. Ethene is being produced, indicating a completed sequential degradation pathway from TCE to ethene.

It should be noted that if only a single biowall were installed, elevated concentrations of cis-DCE and VC would be present downgradient of the first biowall reaction zone. In this case, a second biowall is necessary to create sufficient residence time for TCE to be completely degraded to ethene.

36

Bench-Scale Studies to Estimate Reaction Rates and Media Requirements

Bench-scale test for perchlorate and TCE for Naval Weapons Industrial Reserve Plant (NWIRP) McGregor, TX (*Perlmutter et al., 2000*)

Mushroom Compost | Oil-coated Wood Shavings | Cotton Seed Meal | Granular Activated Carbon

Bench-scale studies may be used to estimate reaction rates and media requirements (or example the ratio of ZVI to sand) needed to met performance objectives. Bench-scale tests may be very useful for new PRB media or for unusual site conditions (for example sites with very low or high pH). When biowalls were first considered for treating perchlorate and TCE at NWIRP McGregor, Texas, a bench-scale test was conducted using site groundwater to evaluate different backfill mixtures. Other examples of bench-scale tests for mulch mixtures includes Shen and Wilson (2007) and Ahmad et al. (2007).

Bench-Scale References:

Ahmad, F., S.P. Schnitker, and C.J. Newell. 2007. Remediation of RDX- and HMX-Contaminated Groundwater Using Organic Mulch Biowalls. *Journal of Contaminant Hydrology*, Vol. 90(1-2):1-20.

Perlmutter, M.W., R. Britto, J.D. Cowan, M. Patel, and M. Craig. 2000. Innovative technology: In situ biotreatment of perchlorate-contaminated groundwater. In: *Air and Waste Management Association, 93rd Annual Conference and Exhibition*, Salt Lake City, Utah.

Shen, H., and J.T. Wilson. 2007. Trichloroethylene Removal from Ground Water in Flow-through Columns Simulating a Reactive Permeable Barrier Constructed with Mulch. *Environmental Science & Technology,* Vol. 41(11):4077-4083.

37

Construction Methods

- Conventional trenching methods
  - Conventional excavators to 25 to 30 feet
  - One-pass trenchers to 35 to 40 feet
  - Biopolymer slurry installation to >50 feet
- Injection methods
  - Pneumatic and hydraulic fracturing
  - New materials may require new injection methods
- Alternate methods
  - Deep soil mixing
- Other considerations
  - Permitting
  - Emplacement verification

Conventional trenching methods include backhoe excavators, one-pass trenchers, and use of biopolymer slurries with deep excavators to install PRBs deep below the water table. Alternative methods include direct injection, which may require pneumatic or hydraulic fracturing to emplace viscous or particulate media. Deep soil mixing is another alternative method to install reactive media to depth. The two photos in this slide show both unsupported excavation and excavation supported by trench boxes.

Bottom photo from Warner, et al., 1998, Journal of Environmental Engineering

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Continuous One-Pass Trenching

Conceptual One-Pass Installation

One-Pass Biowall Installation at Ellsworth AFB, South Dakota

Depths up to 45' deep
(Illustration courtesy Dewind One-pass Trenching)

Continuous one-pass trenchers have become a preferred method to install PRBs because they excavate and emplace reactive media in one continuous process without the need for a supported excavation. One-pass trenchers can reach depths of 45 feet, or even deeper if a bench can be excavated for the trencher. Trenching rates may be as high as 200 to 300 linear feet per day.

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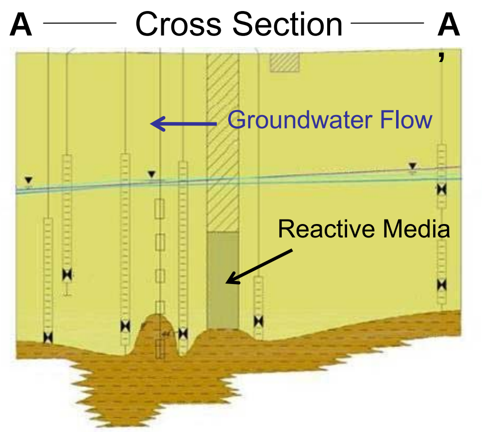
Deep Soil Mixing with BOS 100® at Site 15, Vandenberg AFB, California

Product mixed with soil at depths of 28 up to 70 feet



Where conventional trenching or injection techniques are not feasible, deep soil mixing is an alternative emplacement technique. BOS100® was selected at the reactive media for a pilot test at Site 15 at Vandenberg AFB, California. Heaving sands and depth to bedrock prevented the use of conventional trenching techniques at Site 15. Two phases of direct injection were attempted using traditional and high pressure injection techniques. Confirmation soil cores indicated that the granular product was not evenly distributed in the subsurface, likely due to the product being filtered out by the sandy sediments close to the point of injection. Deep soil mixing was selected at the best alternative to evenly distribute the product in the PRB treatment zone. Laboratory bench-scale column test and field test columns were conducted to determine optimal BOS100® loading parameters and number of auger strokes necessary for emplacement. Results determined a loading rate of 1.7 pounds BOS100® per gallon and 5 strokes would achieve homogeneous mixture of 6% by volume.

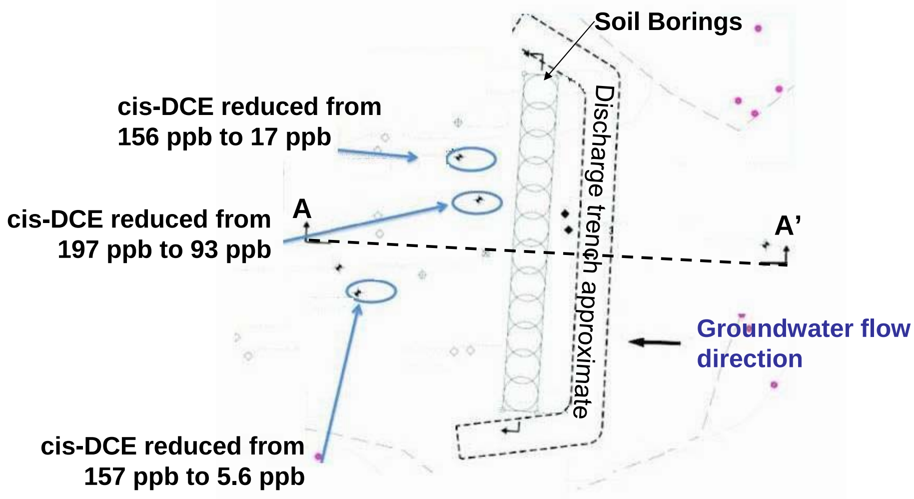
Reference:

Gerber, K., R. Mora, K. White, and S. Noland. Pilot-Scale Permeable Reactive Barrier Installation Using Deep Soil Mixing and BOS100®. Abstract and Presentation E-084, in K.A. Fields and G.B. Wickramanayake (Chairs), Remediation of Chlorinated and Recalcitrant Compounds—2010. *Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds* (Monterey, CA; May 2010). Battelle Memorial Institute, Columbus, OH.

40

Preliminary Results at Site 15

PRB 2 plan view with cis-DCE data (3-5 months)



BOS100® is a granular activated carbon impregnated with zero-valent iron. The carbon adsorbs contaminants such as chlorinated ethenes, which are subsequently abiotically dechlorinated by reaction with the zero valent iron. Dechlorination products such as vinyl chloride are typically not produced, which was confirmed with a bench test for groundwater from Site 15. Concentrations of chlorinated ethenes prior to PRB installation ranged up to 274 ppb of TCE, 381 ppb of cis-DCE, and 4 ppb of VC. The presence and slow degradation of guar used in construction temporarily delayed treatment for a minimum of 2 to 3 months.

Significant reductions have been observed at 5 months in approximately one-third of the downgradient wells, with no generation of cis-DCE or VC. Treatment in the deeper zone has yet to be observed. Sampling at 11 months shows similar results. Additional monitoring is being conducted to further evaluate treatment effectiveness and to determine whether the technology is suitable for full-scale application.

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Direct Injection

ZVI injection at Hunters Point Shipyard Parcel G, November 2008

Photos courtesy U.S. Navy

Direct injection may be used to inject viscous fluid media. The use of high pressure injection may be used to inject slurries such as micro- or nano-scale ZVI. The photos in this slide show an injection at the Hunters Point Shipyard, with a large mixing apparatus used to create a ZVI slurry which was then injected through direct-push borings installed with a Geoprobe rig.

42

Hydraulic Issues – Construction Related

- Aquifer sediments mixing with reactive media
- Reduced permeability zone at trench interface (smearing)
- Short-term effect on hydraulics
- Gaps in construction

Biopolymer slurry wall installation

Several hydraulic issues may arise due to the installation method used. Aquifer sediments may mix with the reactive media and reduce its effective permeability. Smearing may occur at the trench face. A filter cake may also form if make-up water migrates into the adjacent formation and leaves clay fines or particulate matter at the formation interface. The use of a biopolymer guar may result in a short-term reduction in permeability until it is broken down by injected enzymes. Gaps in construction may also occur, most often due to sloughing of the trench sidewalls. All this issues should be addressed during design and carefully monitored during construction. It is often difficult to evaluate hydraulic issues after construction.

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Construction Verification

- Distribution of media
- Hydraulics
  - Has installation disrupted groundwater flow?
  - Is water flowing through the PRB?
    - Changes in water levels and hydraulic gradient
    - Tracer testing (e.g. bromide, dyes)
- Geochemical parameters
  - pH
  - Redox (ORP)
  - Dissolved oxygen (DO)

Verifying that a PRB has been installed as designed can be a challenge. Uniform distribution of the reactive media is often the first concern due to the challenges of placing the media in the subsurface. Coring is one method to verify media distribution. The photo above shows the presence of emulsified zero-valent iron (EZVI) for cores from the Hunters Point Site. The product is preferentially distributed in coarser grained sands, but appears to be present along the entire length of the cores. For vertical trenches, coring can be performed with angled borings that cut through the trench.

Verifying that the hydraulic properties of the media mixture or PRB trench have not been compromised may be performed using tracer tests. But in most cases the changes in groundwater chemistry incurred by the reactive media provide a clear indication that groundwater is flowing through the trench.

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Example PRB System Costs
(from case studies in Appendix B of PRB-5)

SITE	MEDIA	METHOD	LENGTH (feet)	DEPTH (feet)	SYSTEM COST
Coast Guard Support Center, NC (1995)	ZVI	One Pass Trencher	150	24	$500K
Sunnyvale, CA (2003)	ZVI	Backhoe/ Sheet Pile	700	24 – 33	$2,100K
OU-1, Altus AFB , OK (2002)	Mulch	One Pass Trencher	455	24	$265K
Pueblo Chemical Depot, CO (2005)	Mulch	One Pass Trencher	105	14 – 24	$375K
Escanaba, MI (2005)	Organo-philic Clay	One Pass Trencher	270	11	$220K

Costs typically include design, monitoring system, and initial monitoring

Examples of PRB costs are included in PRB-5 in Section 6.4 and in the case studies in Appendix A. Several examples from the case studies are shown here. On a total system cost to linear foot basis, costs here range from $580 per foot for a biowall at Altus AFB, Oklahoma to $3,000 per foot for a ZVI PRB installed in Sunnyvale, California using a long-arm excavator with sheet piling. The reactive media and installation method are primary factors in the cost of constructing a PRB.

However, it is difficult to collect and compare PRB life-cycle costs due to 1) variability in the types and unit cost of media used and the quantity required for treating a given unit of contaminant mass, 2) different installation methods required depending on site-specific conditions, 3) operational requirements including monitoring and potential for replenishment or optimization, and 4) how cost data are reported.

Media costs cannot be compared directly on a per mass basis, as different mass of each specific reactive media may be required to treat a certain mass of contaminant (an “apples and oranges” comparison). Site-specific conditions will determine which installation methods can be used and what type of equipment is needed. Some PRBs such as ZVI walls may have higher up front material cost relative to a mulch PRB, but this may be offset by the need to replenish a mulch PRB. Finally, there is a relative lack of cost data in the literature and it is often not reported on a consistent basis. For example design, installation of monitoring wells, monitoring, and reporting costs are often not included.

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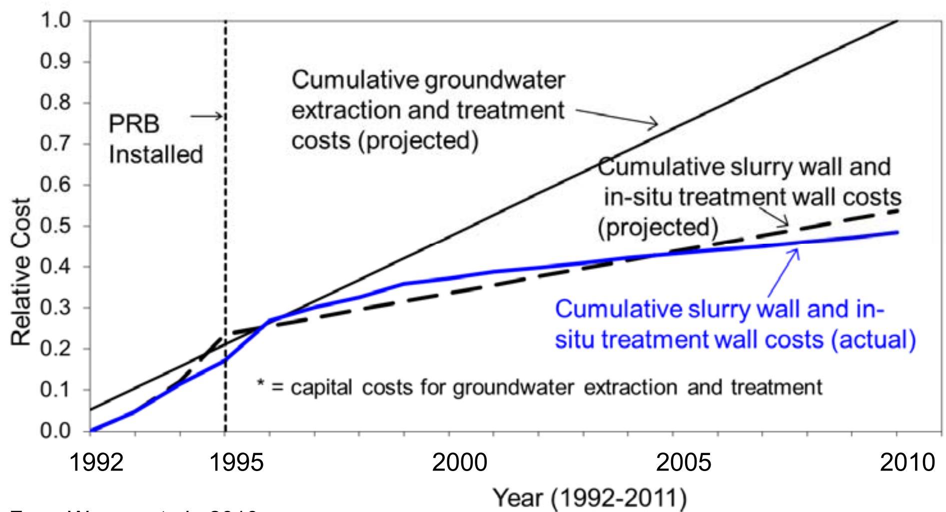
PRB Cost relative to Pump and Treat



From Warner et al., 2010

The relative cost of a PRB to other remediation alternatives provides a better comparison of PRB cost. A PRB was installed to replace a groundwater extraction and treatment system at a site in California in 1995. At that time a significant cost savings over time was anticipated due to the costs of operating the extraction and treatment system. The PRB remained effective for over 15 years and actual cost have tracked close to projected. Even though this PRB had a high capitol construction cost, the long-term cost over 15 years is approximately one-half of the pump and treat system.

Reference:

Warner, S.D., M. Zhang, J. Stimson, P. Bennett, and C. Mok. 2010. Practical Methods for Assessing PRB Performance and Longevity, presented at the *7th International Conference on Remediation of Chlorinated and Recalcitrant Compounds,* Monterey, California, May, 2010.

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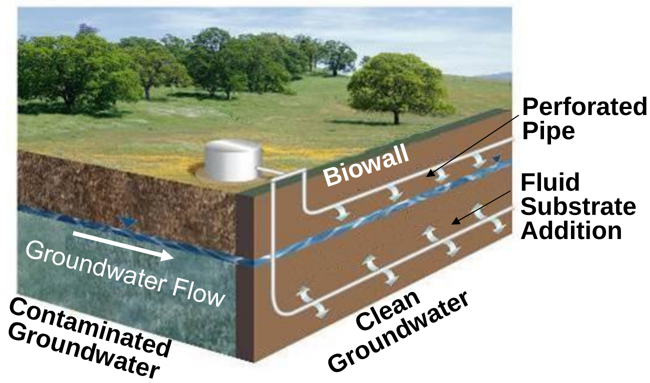
Permeable Mulch Biowalls

- Up to 8 years of monitoring indicates mulch will physically last at least 10 to 15 years, but may require replenishment every 4 to 6 years
- Can stimulate both biotic and abiotic degradation



Permeable mulch biowalls are a newer topic in the PRB-5 document. The next portion of this presentation focuses on a case study to illustrate aspects of operating biowall PRBs. One of the most significant differences between mulch and ZVI PRBs is the cost of the reactive media. Physically, the mulch should last 15 years or more (Robertson et al., 2008; Shen et al., 2010). However, monitoring of biowalls treating chlorinated solvents over the last 6 to 8 years indicates that for some sites the mulch may not be able to sustain the highly reducing conditions necessary for effective anaerobic degradation. Therefore, some mulch PRB systems may need to be replenished every 4 to 6 years.

References:

Robertson, W.D., J.L. Vogan, and P.S. Lombardo. 2008. Nitrate Removal Rates in a 15-Year-Old Permeable Reactive Barrier Treating Septic System Nitrate. *Ground Water Monitoring and Remediation,* Vol. 28(3):65–72.

Shen, H., C.J. Adair, and J.T. Wilson. 2010. Long-Term Capacity of Plant Mulch to Remediate Trichloroethene in Groundwater. *Journal of Environmental Engineering*, Vol. 136, No. 10, p. 1054-1062.

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Case Study – NWIRP McGregor, Texas

- Manufactured weapons and solid-fuel rocket motors from 1942 to 1992
- Ammonium perchlorate detected in groundwater
- Installed nearly 13,000 feet of biowalls along with 1,300 bioborings from 1999 to 2005
- Facility designated for closure and property transfer

High-Pressure Water Washout of Solid Propellant (photo courtesy US Navy)

Naval Weapons Industrial Reserve Plant (NWIRP) was operated for over 50 years as a manufacturing and decommissioning plant for solid-fuel rocket motors. Operations resulted in the release of perchlorate and chlorinated solvents (primarily TCE) to soil and groundwater. From 1999 to 2005, over 10,000 linear feet of biowall trenches and 1,000 bioborings were installed in rows that combined provide for over 3 miles of PRB treatment. Bioborings were installed in areas where trenching was not practical.

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Biowall Installation at NWIRP McGregor

Rock cutter for trenching in weathered limestone bedrock

Trench stays open for installation of perforated pipe and backfill material

Photos courtesy US Navy

A specialized, local rock cutting trencher was used at NWIRP McGregor to cut into soft, weathered limestone bedrock that was permeable to shallow groundwater flow. Even though the technology was relatively new at the time of installation, the biowalls were fitted with monitoring wells and piping for replenishing substrate over time. It was anticipated that the substrate would need to be periodically replenished to sustain performance until cleanup criteria were achieved.

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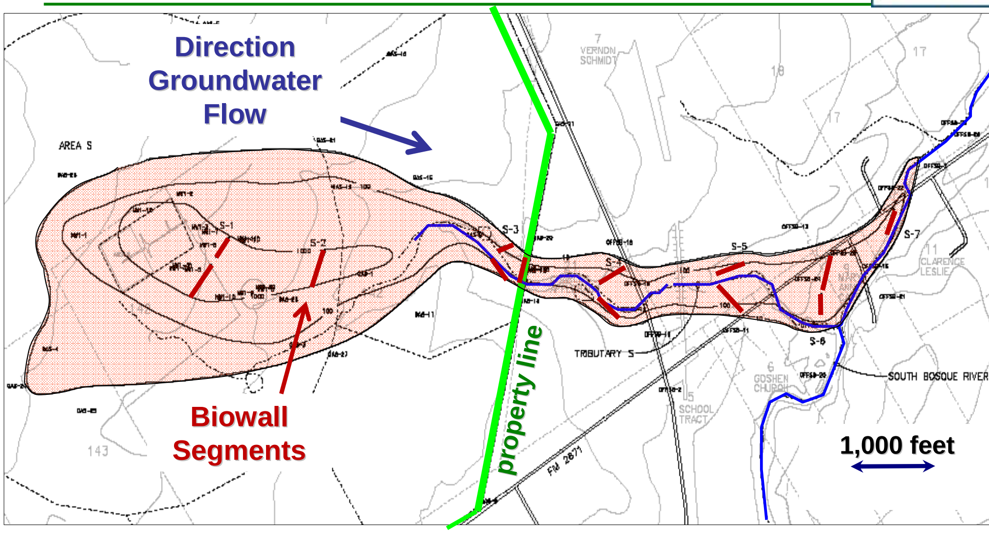
Area S Full-Scale Biowall Layout



Over 3,000 feet of trenches installed with subsurface piping system for substrate replenishment

There are three primary industrial areas at NWIRP McGregor where biowalls were installed. This slide illustrate the extent of the perchlorate plume at Area S. This plume is several thousands of feet long, and extends off site. The red lines are biowall segments, which were installed perpendicular to groundwater flow. For much of the downgradient portion of the plume, groundwater discharges to a local creek, The biowalls were installed along the length of the plume to cut it off and to achieve cleanup goals quicker.

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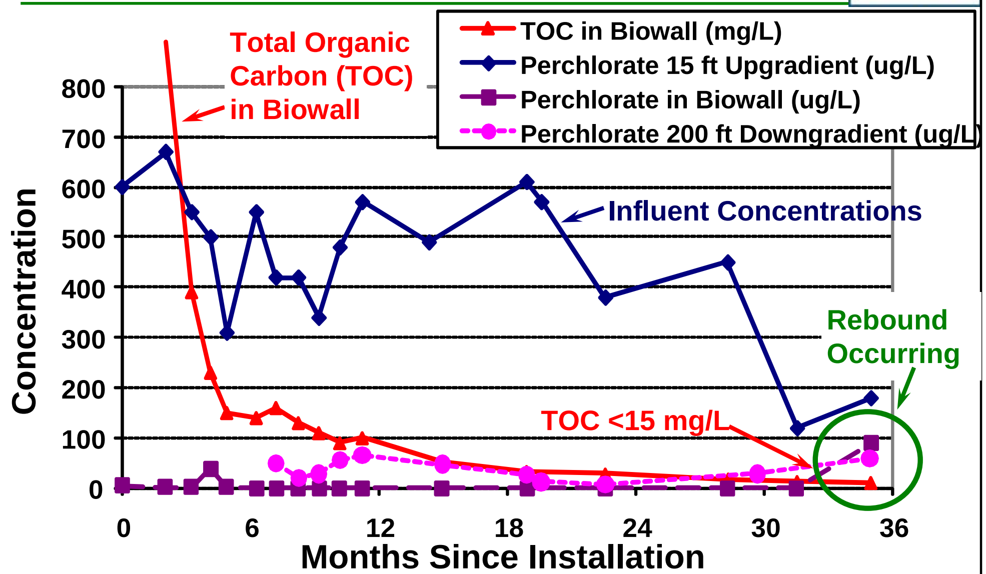
Trench 1 Perchlorate vs. Time

(Soybean Oil Saturated Wood Chips & Gravel)



(Modified from Naval Facilities Engineering Command, 2004)

This chart shows concentrations over time of perchlorate upgradient, within, and downgradient of one of the earliest biowall trenches. Total organic carbon (TOC) within the biowall trench is also plotted over time. Perchlorate within the trench was generally below detection, with the notable exception during the sampling event at approximately 3 years after installation. At that time the concentration of perchlorate began to rebound, corresponding to the concentration of TOC being depleted to less than 15 milligrams per liter (mg/L). This observation was later used to develop a scoring system to decide when to replenish substrate within the biowalls. The significant reduction in perchlorate relative to upgradient concentrations was a primary reason for expanding the NWIRP McGregor biowall system.

Reference: Modified from Naval Facilities Engineering Command. 2004. Passive In-situ Biotreatment of Perchlorate and Trichloroethene in Groundwater, Naval Weapons Industrial Reserve Plant (NWIRP), McGregor, Texas. Presentation at the 2004 Installation Restoration (IR) Conference. Port Hueneme, CA. February.

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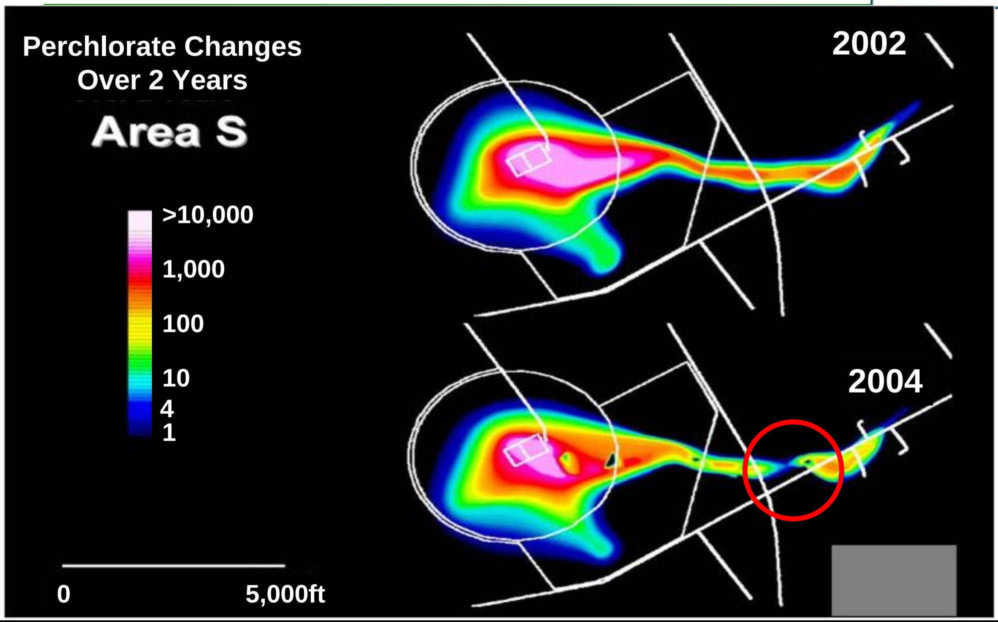
Plume Contraction at Area S

(Modified from Naval Facilities Engineering Command, 2004)



This graphic illustrates a contraction in the Area S perchlorate plume between 2002 and 2004. The plume has started to recede and appears at one place to be cut off. Concentrations in the source area (pink shaded area) are also contracting, and small “holes” in the plume are starting to appear immediately downgradient of a couple biowall trenches.

Reference: Modified from Naval Facilities Engineering Command. 2004. Passive In-situ Biotreatment of Perchlorate and Trichloroethene in Groundwater, Naval Weapons Industrial Reserve Plant (NWIRP), McGregor, Texas. Presentation at the 2004 Installation Restoration (IR) Conference. Port Hueneme, CA. February.

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OPS and Ready for Reuse

- Operating Properly and Successfully (OPS) granted by EPA because...
  - Three years of data showing biowall effectiveness
  - Natural attenuation (dilution) of perchlorate complementing engineered remediation
  - Facility shutdown and impacted soil removed
  - Human health and environment risks mitigated
  - Onsite plume management zones established
- Property transferred to City of McGregor for commercial development in October 2006
- Currently using an O&M plan to maintain long-term performance

A designation of operating properly and successfully (OPS) was granted by the USEPA in 2006 based on effectiveness of the remedy and development of a long-term operations and maintenance plan. The property is now being re-developed as a business park by the City of McGregor.

References:

EnSafe, Inc. 2005. *Operation and Maintenance Manual for Biowalls, NWIRP McGregor, McGregor, Texas.* Prepared for the Naval Facilities Engineering Command, North Charleston, South Carolina. December 19.

EnSafe, Inc. 2008. *Response Action Effectiveness Report*. Prepared for Naval Weapons Industrial Reserve Plant (NWIRP) McGregor, Texas and the Naval Facilities Engineering Command (NAVFAC), Jacksonville, Florida. July.

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Substrate Replenishment (2006)

- Area S – Oldest Biowalls
  - Test the method before O&M contractor took over
- Emulsified vegetable oil injection event conducted from August 14-18, 2006
  - 22,000 lbs (2,800 gallons) of undiluted EOS® 598 injected into 15 biowalls with 2,300 gallons chase water

Photo courtesy of CH2M Hill

Little need to rejuvenate; biowalls continue to effectively reduce perchlorate concentrations

While the biowalls did not necessarily need to be replenished at that time, the Navy wanted to test the injection system prior to a new contractor taking over long-term biowall maintenance.

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NWIRP McGregor Biowall Operations over Time

- Selected biowalls were replenished in Area M and Area S in 2008 and in 2009 (EnSafe and DSE 2010)
- Most recent Remediation Action Effectiveness Report (RAER) indicates that 11 biowall segments will need to be replenished in 2010
- Two biowall segments at Area A are ready to be decommissioned based on achieving groundwater standards for over 2 years

Several biowalls were replenished in 2008 and 2009 based on a scoring system developed in the O&M Plan that evaluates TOC and geochemical data in addition to concentrations of perchlorate. It now appears that biowall segments may need to be replenished on the order of every 3 to 4 years. At the same time, groundwater standards are beginning to be achieved at several areas, and some biowall segments are ready to be decommissioned based on 2 or more years of achieving groundwater targets.

Reference:

Ensafe Inc. and Dougherty Sprague Environmental, Inc. (Ensafe and DSE), 2010. *Response Action Effectiveness Report, NWIRP McGregor, McGregor, Texas.* July.

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Summary - What's New for Materials and Design

- ZVI treatment expanded to energetics (RDX, TNT), Cr(VI), and arsenic
- Increasing use of combined media, for example organic/iron combinations such as EHC® and EZVI
- Improved understanding of treatment mechanisms, for example abiotic reactions with reduced iron-sulfide minerals
- Mulch biowalls and future designs using iron and sulfate amendments
- Deeper trenching equipment, improved hydraulic and pneumatic injection techniques, use of deep soil mixing

To summarize, there is an ever increasing variety and differing forms of media being used to construct PRBs, and an expanding list of contaminants that can be treated.

Improvements in the treatment mechanisms and how the media sustains degradation or removal over time are being used to optimize PRB systems, for example the injection of emulsified vegetable oil into mulch biowalls to sustain or improve performance.

As longer-term monitoring data are made available, future designs are anticipated to be more robust with greater confidence in how they will perform.

Finally, improvements in media and installation methods will increase the number of sites where PRBs may be applied.

Questions & Answers

- Introduction
- Regulatory Considerations
- Science of PRBs
- New Reactive Materials
- Improved Construction Methods
- Performance Monitoring
- Longevity of PRBs
- Enhancing Effectiveness

Question & Answer Break

No associated notes.

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PRB Update: Course Road Map

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- Introduction
- Regulatory Considerations
- Science of PRBs
- Reactive Materials
- Improved Construction Methods
- Performance Monitoring
- Longevity of PRBs
- Enhancing Effectiveness

This section examines two key questions after PRB installation:

1)What to monitor to assess whether the PRB is performing as designed?

2)How long will the PRB last?

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Performance and Longevity: Intro

- Performance Monitoring (PRB-5, Section 7)
  - Overview of objectives, network design, parameters, downgradient water quality
  - What's new?
- Longevity (PRB-5, Section 8)
  - Theoretical
  - Observed
  - Factors impacting longevity
- Sustainability (PRB-5, Section 9)

Each of these topics is covered in more depth in ITRC PRB-5: Sections 7, 8, and 9.

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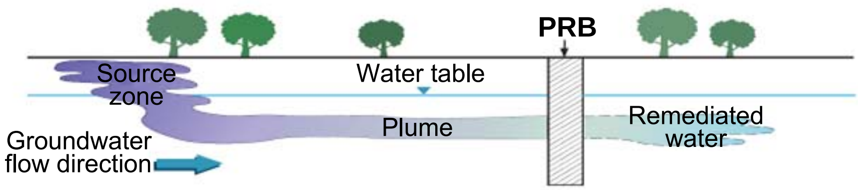
Defining Performance and Longevity



- Performance
  - How the system meets design intent or functional requirements
    - Attainment of water quality objectives
    - Hydraulic system performance
    - Financial goal attainment
    - Sustainability goal attainment
- Longevity
  - Duration and durability of the treatment
    - Treatment media life span
    - Rejuvenation options, cost and effectiveness
    - Geotechnical sustainability / durability
    - Sustainability goal attainment

Performance and longevity are not necessarily the same thing, but they do go hand-in-hand. Performance evaluation is the comparison of our expectations to actual performance. Longevity is the duration or time over which the PRB reactive media will perform as expected.

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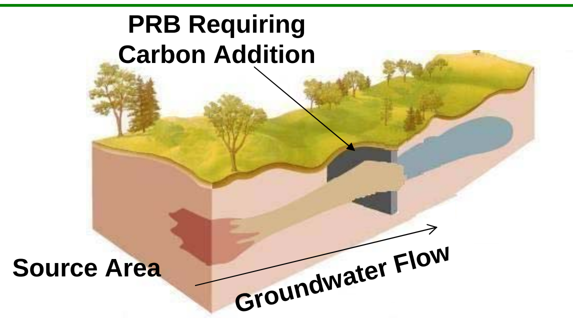
Examples of Perceived Failures



- Performance
  - Flow around the PRB due to insufficient site characterization or changing flow directions
- Longevity
  - Rejuvenation required prior to anticipated life time

If expectations are not set properly, there may be a "perceived" failure with regards to either performance or longevity, which may not be the fault of the PRB itself. Examples of each include:

1)A perceived failure with respect to performance: poor site characterization or changing conditions may lead to a PRB design that does not intercept the entire plume; this may lead to the perception the wall is not functioning as designed. In reality, the PRB is working quite well in those portions of the aquifer where it was installed.

2)A perceived failure with respect to longevity: there may be a "perceived" failure that the wall does not last as long as expected, when in reality the biodegradable portions of the PRB can be replenished and maintain performance throughout an extended time period.

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Performance Monitoring

PRBs need to be monitored because hydrology and geochemistry can change

- Proven methods
  - Baseline characterization (Section 7.1)
  - Monitoring network design—locations, frequency, and duration (Section 7.2)
  - Hydraulic performance (Section 7.3)
  - Concentration-based (Section 7.4)
    - Primary contaminants
    - Geochemical (Table 7-1)

See PRB-5, Section 7 Performance Monitoring Design and Assessment

Goal during monitoring is building multiple lines of evidence to demonstrate to stakeholders that the PRB system is meeting design and compliance objectives, or, if not, to be able to answer why not. Section 7 discusses the range of monitoring metrics, and which may be needed for each type of PRB, including:

•Baseline characterization (Section 7.1) includes groundwater contours, contaminant concentrations, and geochemical conditions. Can include evaluation of soil mineralization or innovative geophysics.

•Monitoring network design (Section 7.2):

- •Upstream & downstream monitoring through conventional monitoring wells
- •Piezometers or direct push sampling within the barrier
- •Multiple vertical intervals

•Hydraulic performance (Section 7.3) includes:

- • Seeing potentiometric lines showing flow through, not around, the PRB
- • Vertical hydraulic gradient showing flow through, not under, the PRB
- • Advanced tools, including tracer tests

•Concentration –based monitoring (Section 7.4)

- •Changes in concentration vs. time or distance
- •Changes in total molar concentration and molar fractions

•Choice of geochemical parameters (Section 7.4) will depend on the COCs and reactive media used at the site.

See ITRC PRB-5: Table 7-1

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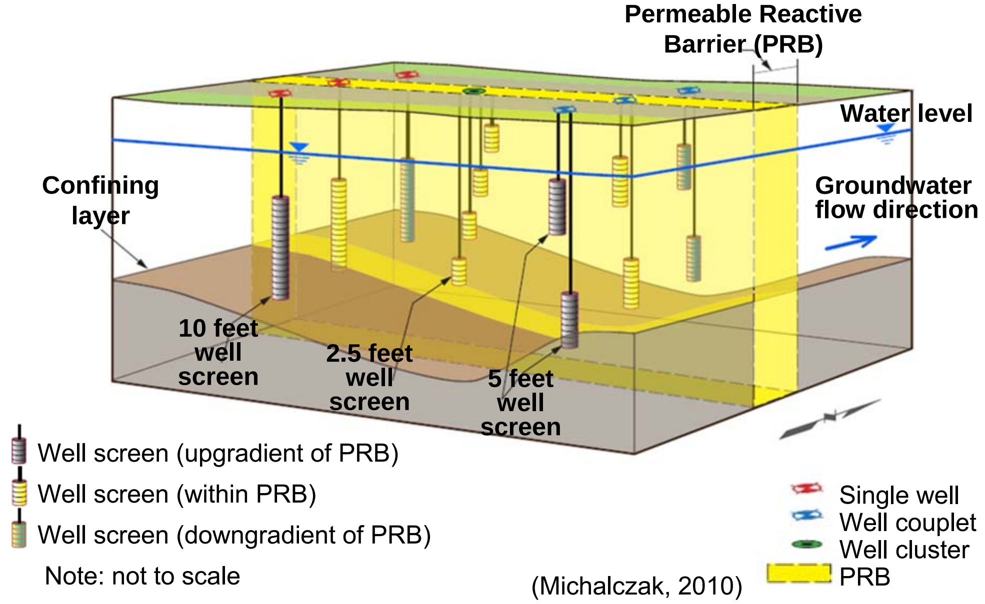
Monitoring Well Configurations

Conceptual 3D Rendering Performance Monitoring Well Network



(Michalczak, 2010)

This figures illustrates some of the possible monitoring well configurations available for a site.

•On the left shows single MWs upgradient, within, and downgradient of the PRB

•In the middle, well clusters with shorter well screens placed at multiple vertical depths → key when site may exhibit high degree of heterogeneity

•On the right, shows well couplet formation

•Not shown: cross-gradient wells or wells screened under the PRB to monitor potential bypass around or under the PRB; downgradient wells

Reference: L.M. Michalczak, “North Plateau Permeable Treatment Wall Performance Monitoring Plan,” WVDP-512, West Valley Demonstration Project (2010)

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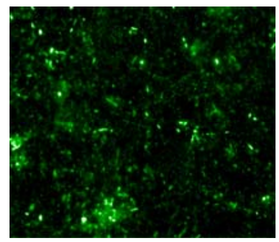
Performance Monitoring (continued)

- New approaches
  - Alternative compliance monitoring metrics (Section 7.5)
  - Geochemistry and microbiology (Section 7.6; Table 7-2)
    - Biogeochemical transformations
  - Improved analytical monitoring tools (Section 7.7)
    - Molecular biological tools (MBTs)
    - Compound-specific isotope analysis (CSIA)
  - Secondary water quality (Section 7.8)
    - Regulated parameters (Table 7-3)
  - O&M plans with monitoring protocols to evaluate when a PRB should be optimized

MBT showing presence of *Dehalococcoides*



(Photo courtesy Idaho National Laboratory)

New topics in the ITRC PRB-5 include:

•Using Mass flux/mass discharge and toxicity reduction as alternative compliance monitoring metrics (Section 7.5)

•See also *ITRC Use and Measurement of Mass Flux and Mass Discharge* MASSFLUX-1, August 2010) and free internet based training available at www.itrcweb.org

•Broader monitoring of geochemistry to evaluate the contributions of various biogeochemical transformations (Section 7.6); for example:

•Analysis of iron and sulfide mineralogy to evaluate biogeochemical transformation processes.

•Use of scanning electron microprobes (SEM) or other advanced analytical methods to evaluate formation of precipitates.

•Advanced analytical monitoring tools (Section 7.7)

•MBTs are generally used to evaluate whether the desired microorganisms that facilitate contaminant degradation are present and active.

•Bio-molecular techniques and tools will be discussed more in an upcoming ITRC document on MBTs.

•CSIA may help determine whether a compound has undergone a chemical or biological transformation rather than a nondestructive physical process such as dilution or sorption.

•Increased understanding of secondary water quality implications

•Downgradient concentrations may remain elevated for some time due to portion of the plume that already passed the PRB, with contributions from back diffusion

These additional tools are particularly useful when performance is not what is expected, and additional lines of evidence are helpful to decipher what is indeed going on. More detail is available within the ITRC PRB-5 throughout Section 7.

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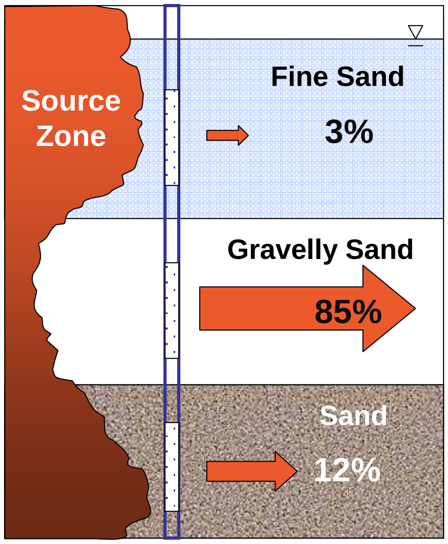
Mass Flux and Concentration



Concentration (C) = 10,000 μg/L
Hydraulic gradient (i) = 0.003 m/m
Mass Flux = KiC

Hydraulic conductivity (K) = 1.0 m/day
Mass Flux = 0.03 g/day/m^2

K = 33.3 m/day
Mass Flux = 1 g/day/m^2

K = 5.0 m/day
Mass Flux = 0.15 g/day/m^2

Figure ES-2 from ITRC *Use and Measurement of Mass Flux and Mass Discharge* (MASSFLUX-1, August 2010)

One of the new approaches to monitoring is using alternative compliance monitoring metrics, such as mass flux. Illustrative example of an aquifer with identical concentrations and hydraulic gradients in three sandy layers. However, mass flux varies a factor of 30 between layers, because the hydraulic conductivity varies by several orders of magnitude. Therefore, 85% of the flux is through only one layer. Even in unconsolidated aquifers, 80-90% of the mass flux may be through only 10-20% of the total plume volume.

ITRC, 2010. Use and Measurement of Mass Flux and Mass Discharge

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What is PRB Longevity?

- Definition of PRB longevity
  - How long a PRB will perform as designed or expected in terms of hydraulic capture, residence time, and reactivity without requiring major maintenance or replacement of the reactive media
- Calculated longevity*
  - For ZVI, theoretical lifetime is 80-400 years
  - For biowall, theoretical lifetime 29 years

(* Reardon, E.J., 2005 and 1995; Shen et al, 2010)

See PRB-5, Section 8 Longevity

Longevity calculations are based on ideal situations. In actuality, PRBs age and performance decreases over time based on media usage and passivation.

Sources for longevity calculations:

•Reardon, E.J., 2005, Zero Valent Irons: Style of Corrosion and Inorganic Control on Hydrogen Pressure Buildup, *EST*, 39: 7311-7317

•Reardon, E.J., 1995, Anaerobic Corrosion of Granular Iron: Measurement and Interpretation of Hydrogen Evolution Rates, *EST*, 29: 2936-2945

•Biowall: Shen, H., C.J. Adair, and J.T. Wilson. 2010. Long-Term Capacity of Plant Mulch to Remediate Trichloroethene in Groundwater. *Journal of Environmental Engineering*, Vol. 136, No. 10, p. 1054-1062.

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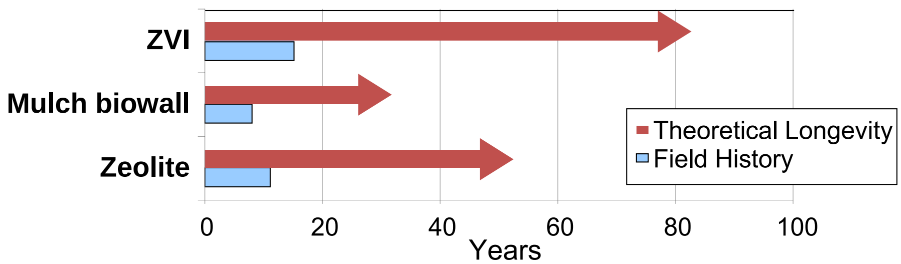
Observed Longevity

- ZVI PRBs
  - Majority of PRBs still going strong after 15 years of field experience
- Mulch biowall
  - 8+ years of monitoring indicates mulch will last at least 10 to 15 years, but some require replenishment after 4 to 6 years
- Other emerging reactive media
  - Zeolite—11+ years
  - Apatite—varies
  - Slag—5+ years



Comparison of actual longevity observed in the field for three different types of PRBs. The “blue bar” represents number of years of field experience with each technology compared to the projected theoretical longevity (the red bar).

Field experience basis:

ZVI PRBs: full-scale since 1995 (15+ years)

Mulch biowalls: full-scale since 2002 (8+ years)

Other Emerging Reactive Media: varies (longer-term field data generally unavailable; 11+ years for zeolite materials)

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Factors Influencing PRB Longevity

PRB Type	Factors Impacting Reactive Media Longevity
ZVI	Precipitation; passivation
ZVI (Injected)	Mass and uniformity
Mulch Biowalls	Carbon substrate bioavailability
Mineral Media	Contaminant loading; precipitation

This table summarizes for each main PRB category the key factors that have been observed to influence reactive media longevity.

The following slides focus on these factors reducing the longevity of the reactive media, along with some examples of each.

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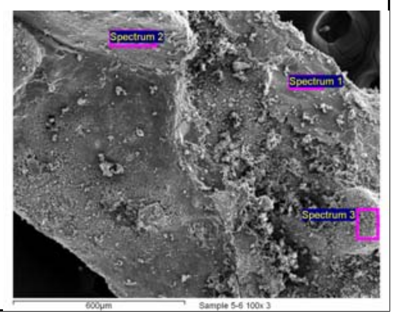
Factor: Precipitation and Passivation of ZVI

- Normally, ZVI corrodes, forming divalent iron species and reducing groundwater conditions
  - Conducts electrons
- Flux of native inorganic species may:
  - Precipitate, occupy pore space, and block flow
  - Insulate the ZVI ("passivation")

SEM image of hydrated iron, Hill AFB



See PRB-5, Sections 5.2 and 8.2

The changes in dissolved groundwater species upon contact with ZVI are described in detail in ITRC PRB-5: Section 5.2.

As the iron corrodes, divalent iron oxides/hydroxides form which are conductive and allow electron transfer between the ZVI and contaminants. These conductive precipitates may include iron sulfides and green rusts. The figure illustrates a scanning electron microscope (SEM Spectrum 3) detection for iron mono-sulfide, which is formed when sulfate precipitation occurs and is highly reactive with many contaminants.

Precipitates such as calcium carbonates can potentially form in great enough quantity to cause permeability losses and preferential flow pathways. Field observations and modeling have shown that in many cases this loss of porosity and permeability will occur at relatively low rates.

Also, some precipitates are more insulating and cause passivation or loss of reactivity of ZVI surfaces. These include trivalent iron oxides/hydroxides.

In general, ZVI PRBs have proven to be a relatively robust technology and have functioned for years in a variety of geochemical environments.

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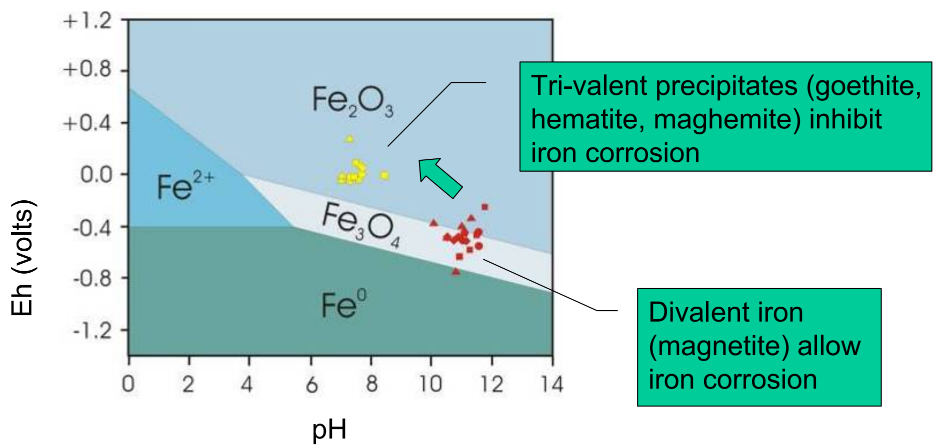
Factor: Passivation of ZVI Surfaces

- Nitrate, silica, and phosphate increase the groundwater reduction potential E_h (ORP), allowing trivalent iron oxide films to inhibit iron corrosion and electron transfer



In the context of corrosion, passivation is the spontaneous formation of a hard non-reactive surface film that inhibits further corrosion. This layer is usually an oxide or nitride that is a few nanometers thick.

“Reduction potential," is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. “Reduction potential" is also known as “redox potential,” “oxidation/reduction potential (ORP), or E_h, and is measured as either volts or millivolts (mV).

> To convert from ORP measured in the field, using a reference solution of 4 M concentration of potassium chloride (KCl) Ag/AgCl, to the standard reduction potential (E_0) measured using a standard hydrogen electrode (SHE) reference, add 200 mV to the field output.

The presence of nitrate or other oxidizing inorganics can shift reduction potential higher and prevent auto-reduction of trivalent iron oxide films present on most manufactured ZVI. This passivating layer therefore remains on the iron surfaces, preventing electron transfer and contaminant reduction.

For more information, see ITRC PRB-5: Section 5.2.

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Example of ZVI PRB Longevity

Elizabeth City Coast Guard Station, North Carolina

- ZVI PRB installed in 1996 to treat TCE, Cr(VI)
  - 140-ft long, 2-ft thick, and 22-ft deep
- Some precipitates on ZVI surface
- No evidence of decline in PRB performance in 13 years groundwater sampling
- Only known PRB where monitoring discontinued after meeting remedial objectives

See PRB-5 Appendix A. Case Summaries

One of the first iron PRBs ever installed, but only one of several case studies highlighted in ITRC PRB-5: Section 8. PRB cores analyzed using microscopy detected a range of precipitates, including calcium carbonates, iron hydroxyl-carbonate, carbonate green rust, hydrous ferric hydroxide, ferric oxyhydroxide, and iron monosulfides.

Chromium in less-soluble trivalent oxidation state

Detected mostly at upgradient aquifer-ZVI interface.

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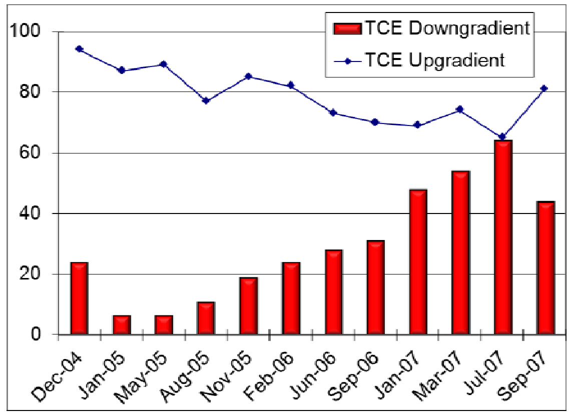
Example of ZVI PRB Reduced Longevity

Hill AFB OU-12, Utah

- 0.5 m (1.5 ft) thick ZVI PRB installed November 2004 to treat TCE
  - Iron 37%; equivalent iron thickness 17 cm (0.55 feet)
- Nitrate 2 to 13 mg/L
- Decreasing performance noted in 2005
- Passivation rate 3.8 cm/yr (1.5 inches/yr)

TCE Concentrations (µg/L) Over Time



See PRB-5, Section 8.2.2 Field Experience

pH neutral; sulfate content moderate at 70 mg/L, nitrate low between 2 and 13 mg/L.

Over this time, influent TCE concentrations held steady around 80 µg/L

Downgradient TCE concentrations increased beginning in 2005.

No safety factor; potential passivation of 3.8 cm/year (1.5 inches) calculated using reference: EnviroMetal Technologies Inc. (ETI). 2007. Technical Note 2.08. *Nitrate Reduction on Granular Iron and the Effects on Chlorinated Volatile Organic Compound Degradation*.

Recommendations: if nitrate present, include safety factor with 2-3 times additional iron, remove the nitrate upgradient, or flush with nitrate-free water (see PRB Sections 5.1.5 "Safety Factors" and 5.2 under "Nitrate").

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Factor: ZVI Mass and Distribution within Injected PRBs

- Over 100 sites with micron- or nano-scale ZVI injected since 2002
  - Most sites targeted 0.4 to 0.8% ZVI by soil mass
    - TCE, chloroform concentrations reduced
    - ORP reduced to less than -200 mV
    - Heterogeneous ZVI distribution
- Recommend targeting >1% ZVI to achieve true 0.4% iron distribution and beta-elimination pathway

(Photo courtesy US Navy)

Greater reducing conditions (lower ORP) will maximize beta-elimination pathway and minimize formation of daughter products (cDCE, VC). At Hunters Point Naval Shipyard site, even when ORP reached -400 mV, suggesting beta-elimination pathway, within weeks or months ORP returned to -200 mV, suggesting hydrolysis reactions and formation of lower-chlorinated compounds. However, TCE removal has been sustained through 2010, suggesting longevity of injected iron.

New injection methods being developed (e.g., hybrid fracturing) will allow injection of greater quantities of reactive media.

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Factors Influencing Longevity of Mulch Biowalls

- Initial quantity and bioavailability of organic substrate
- Rate of groundwater flow
- Electron acceptor demand
- Availability and utilization of iron and sulfate

Example of Biowall PRB Materials

Two factors most impact the longevity of mulch biowalls: (1) bioavailability of the carbon source and (2) carbon demand based on groundwater flow rate and electron acceptor demand.

Bioavailability depends on relative quantities of cellulose and lignin, with cellulose being more biodegradable and lignin providing longer term structure. Compost has more cellulose and less lignin. This photo gives an example of biowall materials locally available, including compost.

Iron and sulfate may increase longevity by further stimulating abiotic reactions. Sand may contain iron.

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Examples of Mulch Biowall Carbon Substrate Bioavailability

- Altus AFB OU-1, Oklahoma
  - TCE removal for 7 years without rejuvenation
- Offutt AFB B301, Nebraska
  - Continued TCE removal after 5+ years monitoring without rejuvenation
- NWIRP McGregor, Texas
  - No rejuvenation required during first 4 years
  - Since then, 13 of 34 biowalls rejuvenated with vegetable oil at frequency of 1-3 years
  - Some biowalls met remedial goals without rejuvenation; monitoring discontinued

Rejuvenation more likely needed in areas of the wall or at sites with higher groundwater flow and higher carbon consumption rates.

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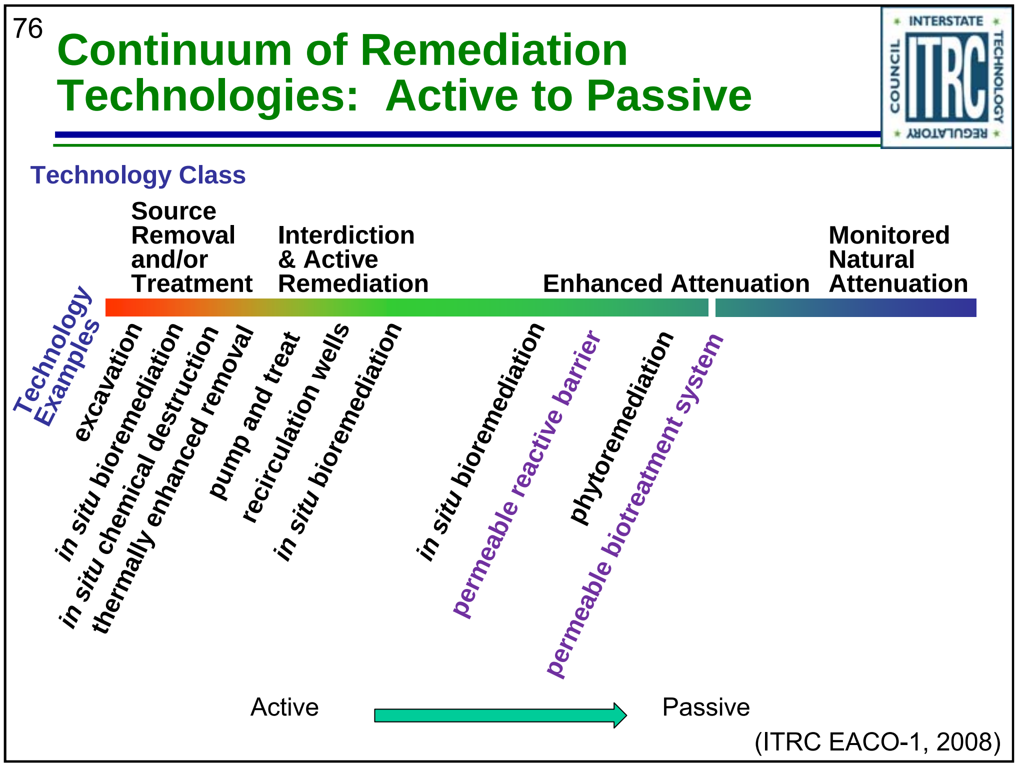
Examples of Observed Longevity for Mineral Media PRBs

- Apatite PRB
  - Mixed performance
    - Success Mine PRB: no reduction in treatment efficiency for pH and metals from 2001 to 2004
    - Other apatite PRBs less successful
- Zeolite PRB
  - Chalk River PRB effectively removed Sr-90 from groundwater for 11+ years with no reduction in efficiency
- Slag PRB
  - East Chicago PRB was effectively removing Arsenic (As) 5 years after installation (2002-2007)

Performance of apatite depends on the pH, mineral solubility, specific surface area, and competing cations. See PRB-5: Section 8.5 for more discussion of factors influencing performance of mineral media PRBs.



The continuum of Remediation Technologies on this graphic ranges from “active” to “passive” technologies (left to right). Two types of PRBs (shown in purple) are included under “Enhanced Attenuation” Technologies, among the more passive remedial technologies. Passive technologies generally have a smaller environmental footprint (e.g., use less energy) than more active remedies. However, other site-specific considerations (e.g., community benefits of unrestricted site closure) may make a more active remedy more sustainable for that site.

Figure source: ITRC IBT training, Technical & Regulatory Guidance for Enhanced Attenuation: Chlorinated Organics (EACO-1, 2008)

A Site Management Tool, www.cluin.org

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Sustainability of PRBs

- Generally passive treatment systems with little or no operation or maintenance (O&M) costs
- Tools available to evaluate site-specific sustainability
  - See ITRC *Green and Sustainable Remediation: State of the Science and Practice* (GSR-1, May 2011) and ITRC *Green & Sustainable Remediation: A Practical Framework* (GSR-2, November 2011)
  - PRBs generally more sustainable than other groundwater plume containment options (e.g., pump and treat)
  - Production and transportation of reactive media primary contributor to "footprint"

See PRB-5, Section 9 PRB as Green and Sustainable Technology

Sustainability evaluated in terms of environmental footprint, energy usage, air emissions, water resource impacts, impacts to land and ecosystems, material consumption and waste generation, and impacts on long-term stewardship. See ITRC PRB-5: Section 9 for more details.

Comparison using SiteWise™ performed by Battelle (Navy document to be released by 2012) between different types of PRBs and pump and treat systems noted:

1) Material production and transportation the greatest contributor to the environmental footprint; and

2) Among these PRBs, biowalls were comparably the most sustainable remedial groundwater containment option, even when considering periodic rejuvenation with vegetable oil.

However, the most sustainable technology will depend on the site. Therefore, performing site-specific assessments are recommended; tools exist to perform these assessments, see ITRC Technical and Regulatory Guidance for Green and Sustainable Remediation *(GSR)* document: ITRC Green and Sustainable Remediation: A Practical Framework (GSR-2, 2011) and ITRC Green and Sustainable Remediation: State of the Science and Practice (GSR-1, 2011).

For more information see: http://www.itrcweb.org/teampublic_GSR.asp.

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PRBs Ability to Use Recycled Media

- Reactive media may consist of recycled "waste" material

Recycling Storm Waste for a Biowall at Altus AFB, Oklahoma

(Photo courtesy US Air Force)

Therefore, attention should be paid to determine the optimum type and quantity of media. The PRB may be more sustainable if material is generated on site or is local to site.

This photo gives an example of biowall materials gathered locally after a storm event.

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Longevity Advantages of PRBs

- Initial capital cost and footprint of PRBs is offset by the long passive operating life
  - Very low O&M labor and material costs
  - Life spans reaching decades
  - Technologies to rejuvenate PRBs expanding

Site-specific sustainability evaluations should be performed using tools outlined in the ITRC Technical and Regulatory Guidance for Green and Sustainable Remediation *(GSR)* document: ITRC Green and Sustainable Remediation: A Practical Framework (GSR-2, 2011) and ITRC Green and Sustainable Remediation: State of the Science and Practice (GSR-1, 2011).

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Summary of "What's New" for PRB Performance and Longevity

- More available monitoring tools and protocols
- Growing confidence in the reliability of PRBs
  - ZVI—now 200+ applications during 15+ years
  - Mulch biowalls—now 8+ years monitoring

…how to optimize

- Best management practices during construction
- For biowalls, consider availability of sulfate and iron, and carbon replenishment (e.g., every 3 to 6 years)

…and how to make even more sustainable

- Use of recycled or locally-available material

See PRB-5: Section 8.2, Boxes A and B

See PRB-5, Section 7 and Section 8.2 Box A "Key Findings on the Longevity of ZVI PRBs" and Box B "Key Findings on the Longevity of Mulch Biowalls."

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PRB Update: Course Road Map

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- Introduction
- Regulatory Considerations
- Science of PRBs
- Reactive Materials
- Improved Construction Methods
- Performance Monitoring
- Longevity of PRBs
- Enhancing Effectiveness

This section is focused on lessons learned and considerations for assuring that the performance intent of the PRB system is achieved. “Enhancement” refers to assuring a positive outcome of the construction and does not refer to maintenance activities. This discussion will, however, introduce various long-term technical needs to enhance reactions and performance.

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Enhancing Long-Term Performance and Cost Effectiveness

Focus areas

- Designing for site objectives
  - Short-term goals vs. long-term goals
- Designing for site conditions
  - Site characterization for design purposes
- Considering "secondary" site issues
  - Stormwater management
  - Long-term site use
  - Constructability

For considering enhancements to performance, the design should focus on the key areas that lead to a successful system: Objectives, Site conditions, secondary issues. For each area, identifying both the long and short term issues are important so as to focus on areas where efficiency, cost effectiveness, technical flexibility, and other areas can be used to identify performance enhancements. ITRC PRB-5: Section 8, for example, does provide areas where technical longevity "tricks" can be considered based on past performance and current and anticipated research.

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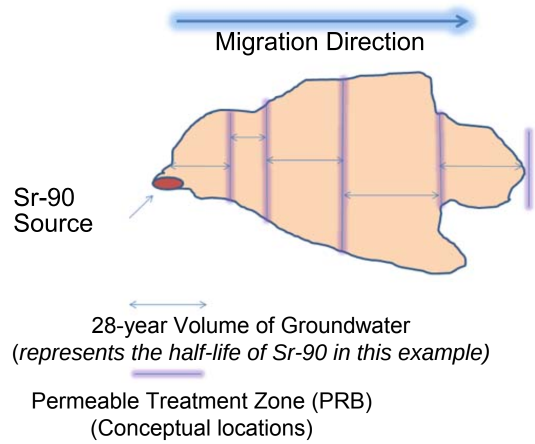
Designing for Site Objectives

- Define short-term goals vs. long-term goals
- Determine goals based on the needs to promote (for example)
  - Source control
  - Receptor protection
  - Longevity
  - Imminent protection
  - “Buying time”



Perhaps the most important initial consideration is to design the PRB specific to the Site Objectives. Under this consideration, both short-term and long-term goals must be identified. Even if goals change, there should be a starting point for working up the design; if there is uncertainty in long-range goals, for example, a consideration should be given to allowing for contingencies to be built into the design, or in the site management approach. Key considerations for helping with identifying both short term and long term goals is to determine if the PRB is intended to: for example, provide source control (and for how long), provide receptor protection (and for how long), provide imminent protection (and for how long), “buy time” (that is, mitigate contaminant migration for a long-enough period to allow a longer-range remedial approach to be implemented). For the example above of a radioactive strontium-90 plume, both short-term and long-term goals are important – there is a need to stop the distal end migration from impacting a down-gradient receptor, and there is acknowledgement that Sr-90 decays with a 28 year half life. Thus the longer term objective may be to systematically establish treatment cells within the plume to shorten the overall remediation time). Failure to explicitly consider short and long term goals in the design will lead to unintended performance – good evaluation of these issues in the design is likely to increase system effectiveness and lengthen the duration of satisfactory performance.

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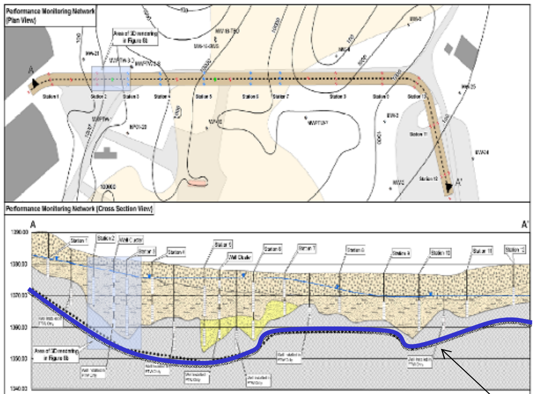
Designing for Site Conditions

- Site characterization for design purposes
  - Good characterization leads to sustainable design



Example: note non-uniform plume distribution and variable at-depth low-permeability boundary

PRB design depth

Key Parameters:

Geology
- Stratigraphy
- Grain size/pore space
- Boundaries

Hydrology
- Hydraulics (Gradient/K)
- Flux
- Seasonal Variability

Chemistry
- Chemical Distribution & Occurrence
- Chemical Fate

Unintended performance of a PRB system can almost always lead back to inadequate site characterization activities. The corollary to this is thus that highly accurate and effective site characterization will likely lead to a highly effective and sustainable PRB system. Each PRB is unique, and must be designed for specific short and long term objectives consistent with the site conditions for which a PRB is intended. These conditions include effective site hydrogeological evaluations – including physical characteristics of the stratigraphy AND groundwater hydraulic information (including rate of chemical migration and aquifer hydraulics). Early breakthrough or inadequate hydraulic capture will be caused in many cases by inadequate site characterization – designing for long-term variable hydraulic conditions can be an effective investment in allowing a PRB to be effective for decades.

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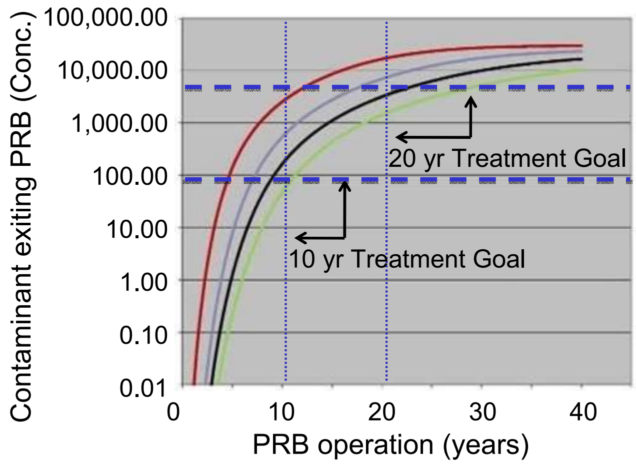
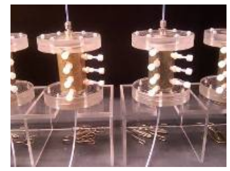
Designing for Site Conditions (continued)

- Laboratory-based longevity studies





Results of column testing to assess treatment under different scenarios.

NOTE: Curve colors represent different scenarios, i.e.,
a.High/low flow rates
b.High/low cation-exchange capacity

Laboratory studies – primarily column tests to assess effectiveness over time, including the rate of mineralization, rate of destruction, and rate of ion exchange, for example, can provide indications as to how a PRB performance could be enhanced using difference in treatment media type or amounts (as an example). Effective laboratory tests are an investment to assure a successful implementation, however, the test must be designed correctly (including being designed for short term and long term requirements).

For the example shown, each color curve represents the treatment effectiveness over time under different scenarios – that is, different combinations of flow rate through a column with different treatment materials, where each material has a different cation exchange capacity. Review of these curves then tell us for how long each material should be effective (i.e., treating to the water quality goal – in this case 8,000 (units) at 20 years and 100 (units) at 10 years) under different conditions. Concentration units can be any denomination – PPM, PPB, PCi/L, etc.

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Longevity Predictions
Fe-based PRB – Corrosion (example)

Chemical Reactions – Secondary conditions to evaluate

$$Fe_{(s)} + 2H_2O_{(l)} \longleftrightarrow Fe^{2+} + 2OH^{-} + H_{2(g)}$$

- Dissolved hydrogen in pore water
  - 800, 000 nM (approximate solubility)
    - Effect on permeability
    - Stimulation of biological processes
- Corrosion rate
  - Theoretical lifetime of iron = 80 – 400 years *
    - Specific surface area of iron granule
    - Changes in redox (Eh/Ph) conditions
    - Mineralization rate (e.g., as affected by pH)

(* Reardon, E.J., 2005 and 1995)

Reardon, E.J., 2005, Zerovalent Irons: Style of Corrosion and Inorganic Control on Hydrogen Pressure Buildup, EST, 39: 7311-7317

Reardon, E.J., 1995, Anaerobic Corrosion of Granular Iron: Measurement and Interpretation of Hydrogen Evolution Rates, EST, 29: 2936-2945

This discussion is based in part on information in 4.2.2 of the ITRC document. Theoretical calculations indicate that granular iron, as one PRB media example, can be effective for many decades. This is an important consideration in enhancing effectiveness, but not the only one. Different media age differently; and other chemical considerations, such as mineralization, blinding, porosity loss, can lead to reduced duration of effectiveness. Secondary chemical processes, such as gas production, pH shifts, etc. also are important considerations. By knowing these likely conditions during the design phase of a project, certain design schemes could be developed to limit negative effects or reduce their potential shortening of treatment efficacy. Examples include moderating pH shifts using less wt/vol of a reactive media (i.e., Fe), creating transition zones between the aquifer and core of the PRB, using treatment material that by their nature have less severe secondary geochemical impact. The reader is referred to the Reardon document and additional references on secondary processes associated with the iron-water reaction as provided in Section 12 of the Guidance document.

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Considering "Secondary" Site Issues

- Stormwater management
- Long-term site use
- Constructability

Example
Project Site

Wetland area – transportation corridor – commercial sector – residential sector

Secondary issues, including land use, storm water management, constructability, can impact the PRB design, as well as bias (positive or negative) short and long term objectives. These issues can change over time as well. A key design consideration is to build in contingencies that would provide value if land issues change. Also, unintended performance can occur if a PRB system design is compromised (ex: shorter or smaller treatment zone) due to land use issues.

Constructability

- Lower impact and “surgical” construction
- Sustainable (i.e., durable) materials

PRB Trench Within Building

Granular Iron

Sand

Durability of treatment materials is an important, but perhaps not highly considered parameter for PRB use. Fining of treatment materials intended to maintain a certain effective porosity my reduce the hydraulic performance and reduce the longevity of the PRB system.

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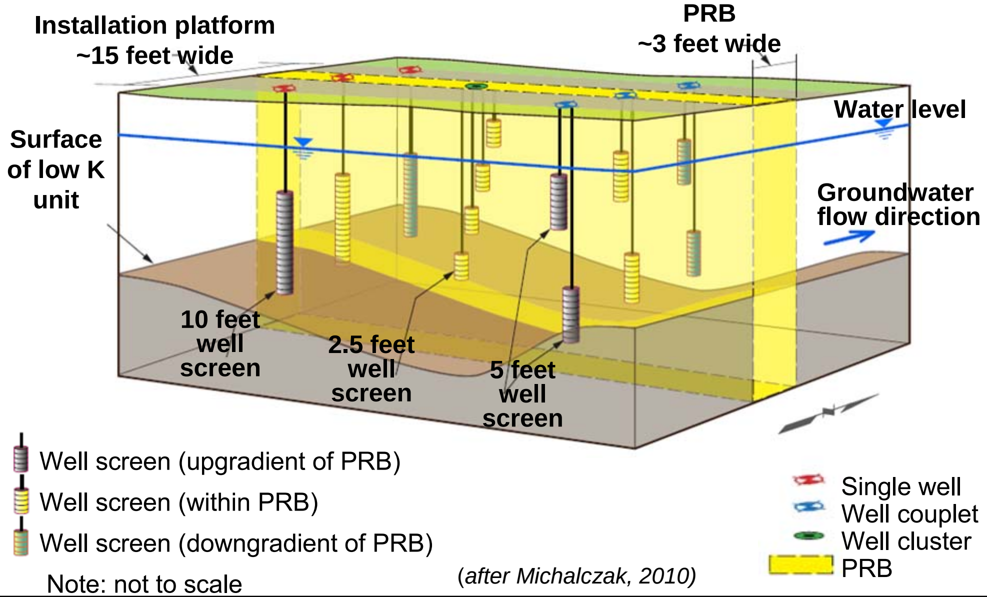
Focused and Design Specific Monitoring Program



(*after Michalczak, 2010*)

Refer back to monitoring section – key and focused monitoring will allow an effective evaluation of the system to made regularly. The ability to "surgically" repair portions of the PRB without the need to replace an entire system, or large section of a system should provide cost value and long-term effectiveness. Monitoring also should be designed to assess variability in both hydraulic and chemical conditions. The monitoring program should remain dynamic over time; as the PRB system ages, the monitoring plan will likely require adjustments as well.

Reference: Reference: L.M. Michalczak, "North Plateau Permeable Treatment Wall Performance Monitoring Plan," WVDP-512, West Valley Demonstration Project (2010)

What is on the Horizon for PRBs?

- Treatment of multiple/emerging contaminants
- Identification of additional treatment materials
- Faster reaction rates without loss of efficiency
- Innovative emplacement (e.g., deeper, targeted)

See PRB-5, Section 11 Conclusions (What's Next?)

See PRB-5: Section 11 Conclusions (What's Next?) for details and discussion of these topics.

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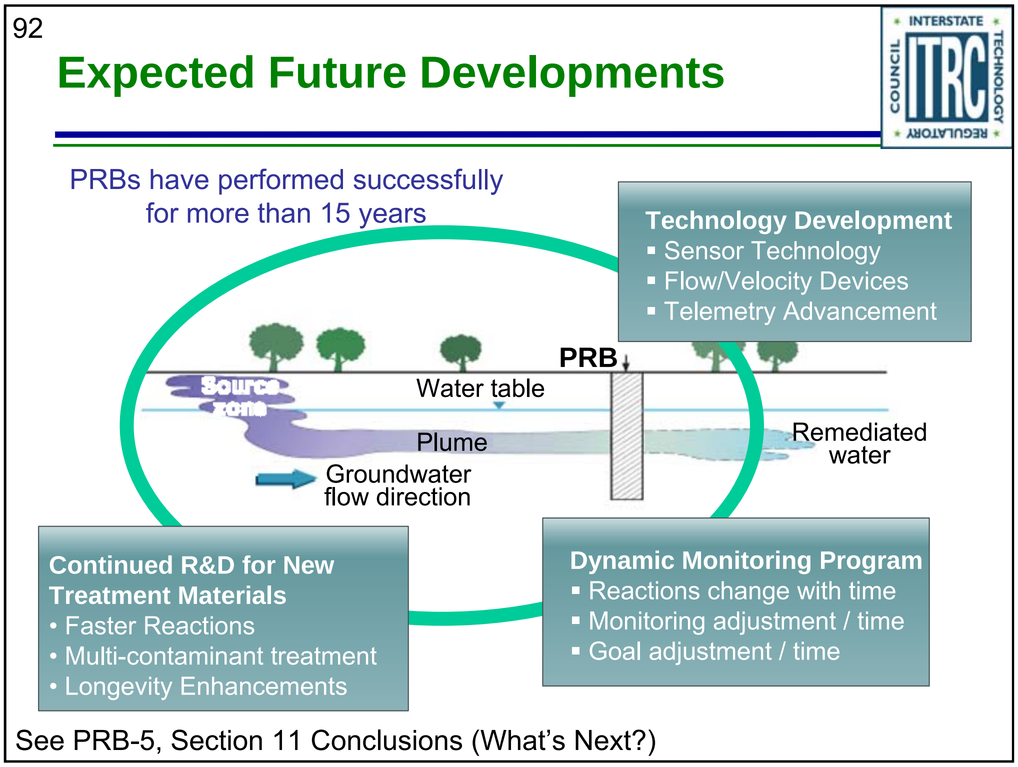
What is on the Horizon for PRBs? (continued)

- Hydraulic design
- Monitoring
- Closure and decommissioning

See PRB-5, Section 11 Conclusions (What's Next?)

See PRB-5: Section 11 Conclusions (What's Next?) for details and discussion of these topics.



See PRB-5: Section 11 Conclusions (What's Next?) for details and discussion of these topics. This figure is not provided in the Guidance document but is a compilation of topics provided throughout the document as well as the specific topics in Section 11.

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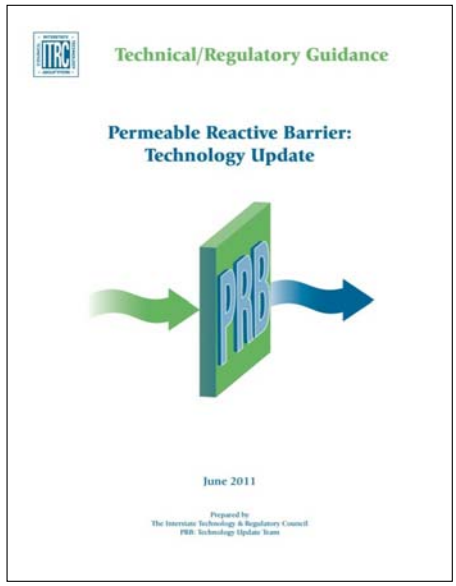
Improve Site Decision-Making: Use ITRC's PRB Guidance

ITRC Technical and Regulatory Guidance Permeable Reactive Barrier: Technology Update (PRB- 5, 2011)



See more ITRC PRB Information at:
http://www.itrcweb.org/prb

See more ITRC PRB Information at: http://www.itrcweb.org/prb

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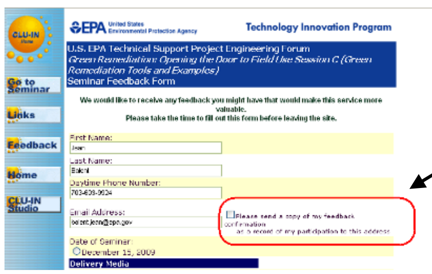
Thank You for Participating

- **2nd question and answer break**
- **Links to additional resources**
  - http://www.cluin.org/conf/itrc/prbtu/resource.cfm
- **Feedback form – *please* complete**
  - http://www.cluin.org/conf/itrc/prbtu/feedback.cfm



Need confirmation of your participation today?

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Links to additional resources:
http://www.cluin.org/conf/itrc/prbtu/resource.cfm

Your feedback is important – please fill out the form at:
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The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

✓Helping regulators build their knowledge base and raise their confidence about new environmental technologies

✓Helping regulators save time and money when evaluating environmental technologies

✓Guiding technology developers in the collection of performance data to satisfy the requirements of multiple states

✓Helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations

✓Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

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✓Use ITRC products and attend training courses

✓Submit proposals for new technical teams and projects