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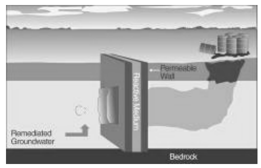
Permeable Reactive Barriers: Lessons Learned & New Directions



ITRC Technical and Regulatory Guidance on
Permeable Reactive Barriers:
Lessons Learned / New Directions

This training is co-sponsored by the EPA Office of Superfund Remediation and Technology Innovation

Presentation Overview:

A permeable reactive barrier (PRB) is a continuous, in situ permeable treatment zone designed to intercept and remediate a contaminant plume. PRBs are often intended as a source-term management remedy or as an on-site containment remedy. Over the past 10 years, the use of iron-based PRBs has evolved from innovative to accepted standard practice for the containment and treatment of a variety of groundwater contaminants. Reactive media such as carbon sources (compost), limestone, granular activated carbon, zeolites, and others had also been deployed in recent years to treat metals and some organic compounds. Research and deployment of bio-barrier systems is also growing in recent years, particularly for treatment of chlorinated solvents and petroleum hydrocarbon constituents.

This training presents updated information regarding new developments, innovative approaches, and lessons learned in the application of PRBs to treat a variety of groundwater contaminants. The information will be presented by reviewing the approaches and results at several sites where PRBs have been deployed. The training is based on the ITRC guidance document titled Permeable Reactive Barriers: Lessons Learned/New Directions (PRB-4, 2005). Case studies from around the country are included in the training to show various designs, contaminants, reactive media, and cost data for PRB systems. The training provides new information on iron-based PRB systems while providing a solid introduction to the non-iron PRBs. As a prerequisite to this course, we ask that you review background information on PRBs as presented in the material from earlier ITRC PRB training courses. You can access archives of these trainings at http://www.clu-in.org/conf/itrc/advprb_032102/ and http://www.clu-in.org/conf/itrc/prb_031902/. Three other documents produced by the ITRC PRB team are also available for review. They can be downloaded from www.itrcweb.org under 'Guidance Documents.'

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

Training Co-Sponsored by: EPA Office of Superfund Remediation and Technology Innovation (www.clu-in.org)

ITRC Course Moderator: Mary Yelken (myelken@earthlink.net)

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

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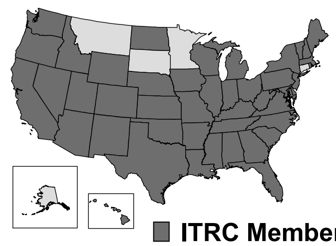

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The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition of regulators, industry experts, citizen stakeholders, academia and federal partners that work to achieve regulatory acceptance of environmental technologies and innovative approaches. ITRC consists of 45 states (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 approaching 7,500 people from all aspects of 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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•We recommend you check with the local and state laws and experts.

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ITRC Course Topics Planned for 2006

Popular courses from 2005

- Alternative Landfill Covers
- Constructed Treatment Wetlands
- Environmental Management at Operational Outdoor Small Arms Ranges
- DNAPL Performance Assessment
- Mitigation Wetlands
- Perchlorate Overview
- Permeable Reactive Barriers: Lessons Learn and New Direction
- Radiation Risk Assessment
- Radiation Site Cleanup
- Remediation Process Optimization
- Site Investigation and Remediation for Munitions Response Projects
- Triad Approach
- What's New With In Situ Chemical Oxidation

New in 2006

- Characterization, Design, Construction and Monitoring of Bioreactor Landfills
- Direct-Push Wells for Long-term Monitoring
- Ending Post Closure Care at Landfills
- Planning and Promoting of Ecological Re-use of Remediated Sites
- Rads Real-time Data Collection
- Remediation Process Optimization Advanced Training
- More in development…….

Training dates/details at www.itrcweb.org

Training archives at http://cluin.org/live/archive.cfm

More details and schedules are available from www.itrcweb.org under "Internet-based Training."

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Permeable Reactive Barriers: Lessons Learned & New Directions

Logistical Reminders

- Phone line audience
  - ✓ Keep phone on mute
  - ✓ *6 to mute, *7 to un-mute to ask question during designated periods
  - ✓ Do NOT put call on hold
- Simulcast audience
  - ✓ Use ? at the top of each slide to submit questions
- Course time = 2¼ hours

Presentation Overview

- Hydraulic issues
- Performance issues
- Iron and zeolite case studies
- Questions and answers
- Bio-barrier case study
- Compost wall case study
- Links to additional resources
- Your feedback
- Questions and answers

No associated notes.

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Meet the ITRC Instructors

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Scott Warner
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Mike Duchene is a senior engineer at EnviroMetal Technologies Inc. (ETI) with more than 10 years consulting engineering experience in the environmental field. He received both his Bachelors of Applied Science and Masters of Applied Science in Civil Engineering from the University of Waterloo. He joined ETI in October 1999. Prior to joining ETI, Mike worked primarily as a design engineer and designed and operated several groundwater remediation systems. At ETI, his responsibilities include managing various engineering aspects of the design and installation of PRBs. Mike is primarily involved in assisting clients in the detailed design of PRBs including detailed assessments of groundwater hydraulics, assessment and specification of potential construction techniques, and construction QA/QC protocols. He is also involved in the development and evaluation of innovative construction methods and the interpretation of chemical and hydrogeological performance data for completed PRBs.

Scott Warner (Vice President and Principal Hydrogeologist) joined Geomatrix in August 1991 and is the managing principal for the firm's largest office in Oakland, California. Mr. Warner has been practicing as a professional hydrogeologist and environmental consultant since January 1987. Mr. Warner is an experienced hydrogeologist and environmental consultant whose practice has evolved from designing and performing highly quantitative hydrogeological characterization and analysis work for several radioactive waste repository assessment programs (including those in the United States, Great Britain, Canada, and Sweden), to designing, implementing, and consulting on innovative in situ groundwater remediation technologies. Mr. Warner also has provided expert witness and litigation support services to the legal community and has been qualified in court as an expert in hydrogeology and groundwater remediation. Mr. Warner has developed a wide range of experience in assessing the fate and transport of key environmental contaminants including methyl tertiary butyl ether (MTBE), perchlorate, arsenic and other metals, industrial solvents (including trichloroethylene and vinyl chloride) and a variety of xenobiotic compounds. Mr. Warner has published widely and has presented to professional, academic, government, and international audiences on innovative groundwater remediation methods. He served on both the Remediation Technologies Development Forum and Interstate Technology Regulatory Council (Permeable Reactive Barrier [PRB] subcommittees) and was a co-developer and instructor for EPA-supported national short courses on PRB technology.

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Meet the ITRC Instructors

Alec Naugle
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Alec Naugle is an Engineering Geologist in the Groundwater Protection Division at the California Regional Water Quality Control Board, San Francisco Bay Region. Mr. Naugle oversees solvent and petroleum hydrocarbon cleanups and waste disposal activities at industrial facilities and landfills. He is also co-chair of the Region's groundwater committee, which was formed to support the Board's Basin Planning process with respect to groundwater quality issues and beneficial use region-wide. Mr. Naugle has an MS in Groundwater Hydrology from the University of California at Davis, and a BS in Chemistry and Geology from Marietta College in Ohio. Prior to joining the Board in 1999, Mr. Naugle worked both as a consultant on various military and private sites in California and the Northeast, and as a regulator in the UST program.

David Smyth received his B.Sc. (Earth Sciences, 1979) and M.Sc (Hydrogeology, 1981) from the University of Waterloo. Between 1981 and 1987, he worked as a hydrogeologist in the Toronto area for an international geotechnical and environmental consulting firm. Since 1988, he has worked at the University of Waterloo, first as Manager of Waterloo Centre for Groundwater Research, then as Manager of the University Consortium Solvents-in-Groundwater Research Program until 1998 and recently as a Research Hydrogeologist. He currently works under the direction of Dr. David Blowes on a wide range of projects related to the in situ remediation of metals and inorganic contaminants in groundwater using permeable reactive barriers. He has participated in activities of the RTDF and ITRC permeable reactive barrier teams since the mid-1990s.

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What You Will Learn…

- Update on the general performance of PRBs from over the last 10 years
- Specific details on the design, operation, monitoring, and assessments of PRBs presented as four case studies
    - Iron PRB for treatment of VOCs
    - Sorption barrier for treatment of radionuclides
    - Bio barrier for treatment of VOCs
    - Solid organic carbon barrier for treatment of acid mine drainage

Presentation Format:

Mike Duchene - Performance assessment of PRBs

Scott Warner - Long-term performance of the first iron PRB for treatment of VOCs at Sunnyvale, CA and lessons learned from the design and operation of a pilot-scale PRB using clinoptilolite to treat Sr-90

Alec Naugle - Case study of a bio-barrier to treat VOCs

David Smyth - Case study of a compost based PRB for treatment of acid mine drainage

The primary document sections within Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) that are discussed in this training course include:

1.2: PRB Definition and Application

2.2: Treatment Materials

2.5.3: Oxygen for Fuel Sites

2.5.7: Organic Carbon Media for Denitrification, Sulfate Reduction, and Perchlorate Destruction

2.6 Deployment Tables

3.2: Hydrogeologic Data

4.2: PRB Construction

4.3 Lessons Learned from PRB Design and Construction

5: Performance Assessment

6.2 Monitoring

6.2.5: Sampling Frequency

10: Cost

11: Conclusions and Recommendations

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History of PRBs and the ITRC PRB Team

- PRB technology (iron-based)
  - 10 years of data
  - Has evolved from innovative to accepted standard practice
- ITRC PRB Team
  - Created in 1996
  - Produced 4 ITRC guidance documents
  - Collaborated on 2 additional guidance documents with DoD, DOE, and EPA
  - Delivered 14 classroom training sessions
  - Created 3 Internet-based training courses delivering more than 20 classes

Guidance Documents (available at www.itrcweb.org):

PRW-1 - Regulatory Guidance for Permeable Barrier Walls Designed to Remediate Chlorinated Solvents (2nd Edition), December 1999

PRB-2 - Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation, March 2000. With the Air Force Research Laboratory.

PRB-3 - Regulatory Guidance for Permeable Barrier Barriers Designed to Remediate Inorganic and Radionuclide Contamination, September 1999

PRB – 4 - Permeable Reactive Barriers: Lessons Learned/New Directions, 2005

EPA/600/R-03/045, August 2003, Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Ground-Water Remediation available at http://www.epa.gov/ada/pubs/reports.html

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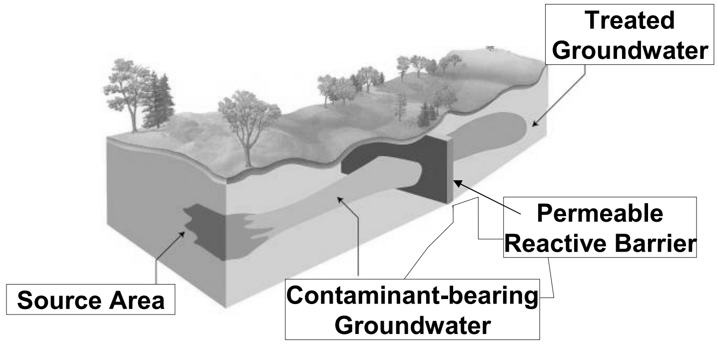
Definition of a PRB



- A continuous, in-situ permeable treatment zone designed to intercept and remediate a contaminant plume
  - … may be created directly using reactive materials, or indirectly using materials designed to stimulate secondary processes

Refer to PRB definition in Section 1.2 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

PRBs are intended to reduce contaminant mass flux.

The primary document sections within Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) that are discussed within this portion of the training course include:

1.2: PRB Definition and Application

2.2: Treatment Materials

2.6 Deployment Tables

4.3: Lessons Learned from PRB Design and Construction

5: Performance Assessment

6.2: Monitoring

10: Cost

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Treatment Materials

Treatment Material	Contaminants Treated
Zero-valent iron (granular iron)	▶Chlorinated solvents ▶Reducible metals (Cr(VI), As)
Basic oxygen furnace slag	▶Arsenic ▶Phosphorous
Solid organic amendments (wood chips, leaf compost)	▶Acid mine drainage (Fe, Zn, etc.) ▶Nitrate ▶Biologically degradable compounds
Liquid organic amendments (lactate, molasses, propylene glycol)	▶Biologically degradable compounds
Gas amendments (oxygen, hydrogen)	▶Biologically degradable compounds
Zeolites	▶Sr, Pb, Al, Ba, Cd, Mn, Ni, Hg
Phosphates	▶Mo, U, Tc, Pb, Cd, Zn, Sr

For more information on treatment materials see Section 2.2 of of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

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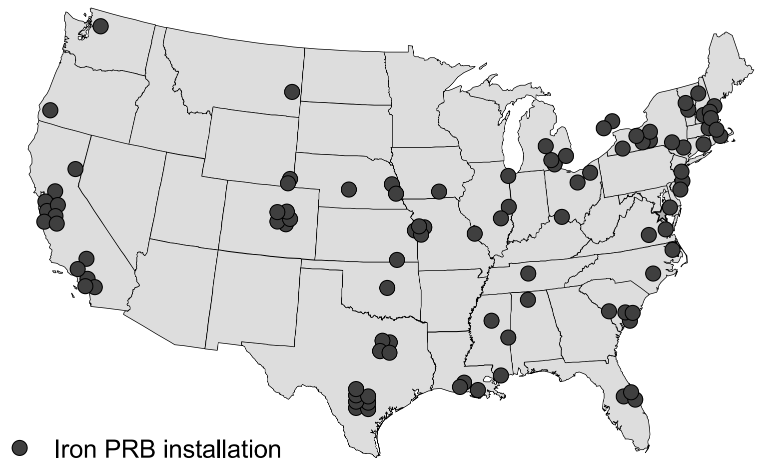
Iron PRBs for VOC Treatment



Total 98 full and pilot scale PRBs
(as of December 2005)

Information in presentation slide updated with data as of December 2005.

See Table 2.3 in Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) for a complete list of installations (as of December 2004). As of December 2004, there were 91 full-scale PRBs installed world wide (using granular iron for treatment of VOCs). Of these, 55 have been installed long enough to have meaningful data available.

PRB assumed to be in compliance if:

- Current information shows compliance
- Initial data showed compliance, no new data available
- No data received

Subjective analysis to an extent - No phone call, assumed site meeting objectives

Results show 48 of the 55 PRBs are meeting the site objectives. Most common issue is hydraulics.

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Performance Assessment

- Four types of assessment
  - Chemical (contaminants of concern)
  - Hydraulic
  - Geochemical
  - Microbial
- Assessments are interdependent
- Section focuses on granular iron PRBs for VOC treatment

Performance assessment is addressed in Section 5 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

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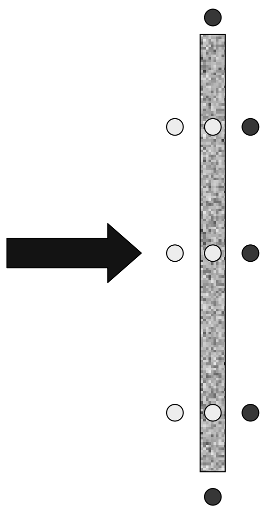
Monitoring Programs



- Compliance monitoring (● wells)
  - Driven by regulatory requirements
  - Typically only contaminants are regulated
- Performance monitoring (○ wells)
  - Identify any changes in system that may affect treatment effectiveness and longevity

Monitoring is addressed in Section 6.2 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

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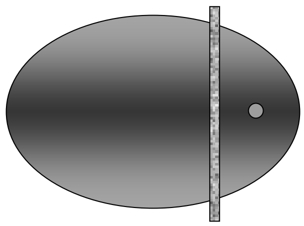
Downgradient Concentrations



- Compliance wells installed in contaminated aquifer downgradient of PRB
- Time required for ‘flushing’ of contaminants in downgradient aquifer
- Varies at each site
- Challenge for assessment

Effect of aquifer contamination in the downgradient aquifer addressed in Section 6.2.1.1 Compliance Monitoring of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4)

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Hydraulic Performance

- Deviation from hydraulic design performance caused by one or more of the following
  - Sewer lines influencing flow
  - Construction artifacts altering flow
- Result can be
  - Reduced residence time leading to insufficient treatment
  - Plume bypass

Hydraulic performance is addressed in Section 5.1 Hydraulic Assessment of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4)

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Hydraulic Issues - Characterization

- Thorough site characterization required as PRBs are not easily modified
- Past characterization issues include
  - Incomplete plume capture in 3 dimensions
  - Variation in seasonal flow direction
  - Variation in hydraulic gradient and permeability
  - Incorrect groundwater flow velocity / variation along PRB alignment
  - Influence of sewer lines

See Section 4.3 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) for lessons learned related to PRB design and construction.

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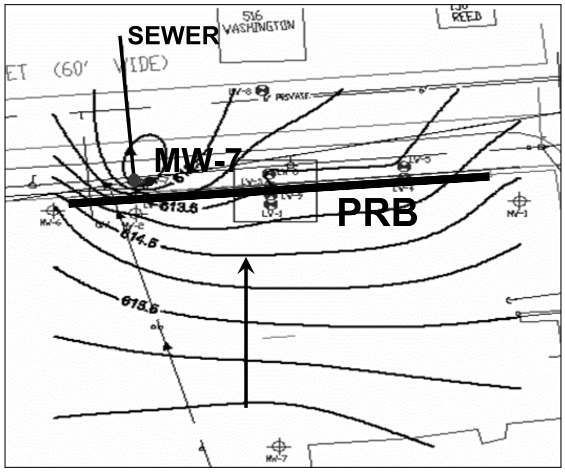
Hydraulic Issues – Sewer Line



Source: Stantec, 2003

PRB installed at a former dry cleaner site. Sewer (identified in red) does not intersect PRB but is close enough to influence flow in the vicinity of the PRB.

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Hydraulic Issues – Construction Related

- Aquifer sediments mixing with reactive media
- Reduced permeability zone at interface
- Short-term effect on hydraulics

See Section 4.3 Lessons Learned (Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4)) from PRB Design and Construction for more information.

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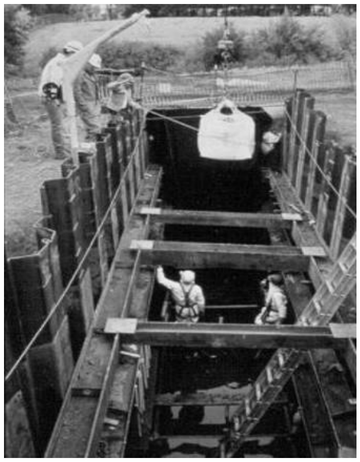
Hydraulic Issues – Funnel and Gate PRBs



- Inadequate funnel length
- Flow over reactive material in gate
- Reduced hydraulic conductivity zone at gate entrance
- Flow beneath funnel sections

See Section 4.3 Lessons Learned (Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4)) from PRB Design and Construction for more information.

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Geochemical Performance

- Reactions within PRB result in change in geochemistry
  - Provides evidence treatment process is working
    - Increase in pH, decrease in redox potential (Eh)
    - Reduction in carbonate concentration
- Provides data to assess longevity of PRBs

See Section 5.2 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) for more information on geotechnical assessment.

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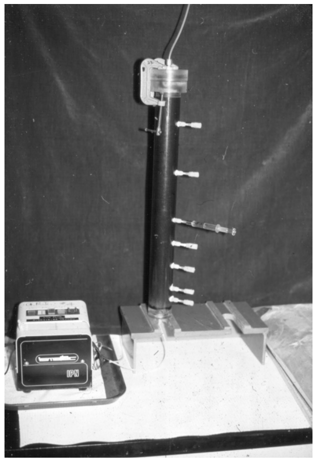
Geochemical Performance



- Carbonate precipitates may drive long-term performance (sulphides in some cases)
- Precipitate build-up begins at upgradient interface
- Long-term lab simulations show some permeability loss and significant reactivity loss in precipitate zones

See Section 5.2.4 (Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4)) for more information on the assessment of longevity.

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Geochemical Performance

- No indication to date that precipitates causing sufficient loss of reactivity requiring rejuvenation and/or iron replacement
- Flow through PRBs at field sites to date much less than simulated flow through laboratory columns
- Estimate of >10-15 years before refurbishing at most sites appears reasonable
  - Dependent on mass flux of carbonate

See Section 5.2.4 (Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4)) for more information on the assessment of longevity.

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Microbial Assessment

- Microbial activity does occur in iron PRBs
- No indication of significant biomass buildup
  - Exception is Denver Federal Center – attributed to low-flow conditions and high sulfate
- Shift in populations to sulphate reducers and anaerobic metal reducers
- Potential beneficial effects

See Section 5.3 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) for additional discussion of Microbial Assessment

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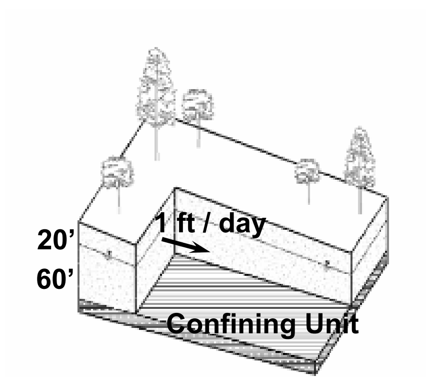
PRB Cost Comparison



- Economic analysis by DuPont for EPA/RTDF training
- Evaluated
  - PRB
  - PRB with natural attenuation
  - Pump and treat
  - Monitored natural attenuation

Economic comparison prepared by Rich Landis, DuPont for the US EPA PRB Short Course, 2000, EPA542/B-00/001

Additional information on the cost of PRBs can be found in Section 10 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

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Cost Comparison Details

- Plume
  - TCE=10,000 ppb, cDCE=1,000 ppb, VC=100 ppb
- Treatment to federal MCLs
- Capital costs
  - Design and construction of PRB or pump and treat system
  - Monitoring wells
- Operating costs
  - Sampling and analysis
  - Operations for pump and treat system

Economic comparison prepared by Rich Landis, DuPont for the US EPA PRB Short Course, 2000

PRB cost components

PRB emplacement

Granular iron

Licensing fee

Up front engineering

Monitoring wells

Pump and treat cost components

Capital investment per installed gpm

Operating costs

Annual monitoring cost per well ($2500)

Pump and treat - $20 per 1000 gallons treated

Additional information on the cost of PRBs can be found in Section 10 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

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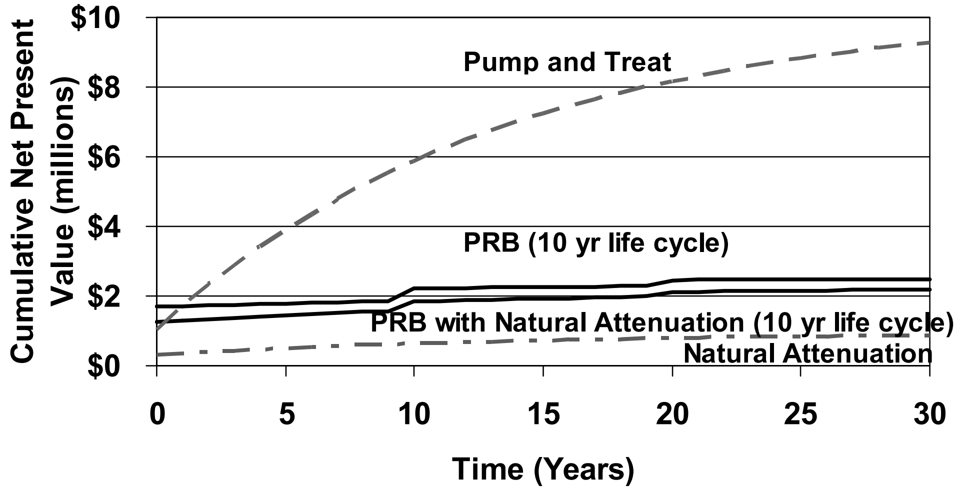
PRB Cost Comparison



Source: EPA 542/B-00/001

Analysis completed on a net present value approach where annual costs are discounted to present value at a rate of 12% and adjusted for inflation at an assumed rate of 4%.

Additional information on the cost of PRBs can be found in Section 10 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

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Summary

- Of the few systems with inadequate performance, system hydraulics are the main cause
- Ongoing refinement/improvement of construction methods is minimizing adverse impacts due to construction
- Estimate of >10-15 years before refurbishing at most sites appears reasonable

No associated notes

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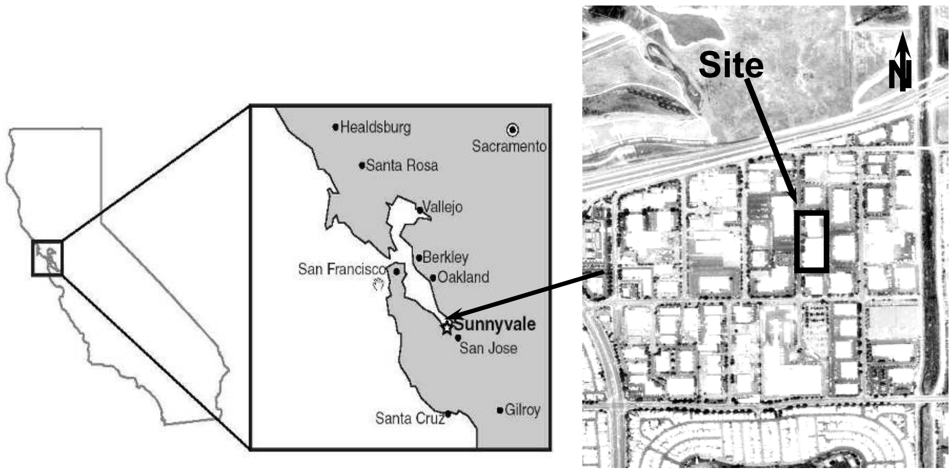
First Commercial Granular-Iron PRB 10 Year Update



Santa Clara County, California

This section of the presentation provides a summary of the first commercial granular-iron PRB to be designed and installed in the United States. The installation occurred in November 1994; the site remains the longest active and successful PRB system of its kind in North America. The PRB system was designed to treat groundwater affected by chlorinated ethenes (e.g., TCE, DCE, and vinyl chloride) as well as freons. The site has achieved regulatory success since being installed more than 10 years ago.

The primary document sections within Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) that are discussed within this portion of the training course include:

3.2: Hydrogeologic Data

4.2: PRB Construction

4.3 Lessons Learned from PRB Design and Construction

5.1: Hydraulic Assessment

6.2 Monitoring

6.2.5: Sampling Frequency

10: Cost

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Site History

1983-1987	Site characterization, source remediation, pump and treat implementation
1991-1993	PRB concept, design work, regulatory process
Nov 1994 - Feb 1995	PRB construction
1999	Five-year effectiveness evaluation
2004	Ten-year effectiveness evaluation
Historical notables	• Hydrogen gas monitoring, passive diffusion bag sampling • Slurry wall breach and repair, system alarm installation

Basic Site History. A recent summary of performance was presented at the First International Symposium on PRBs held in March 2004 in Belfast, Northern Ireland. The title for the paper is "Warner, S.D, Longino, B.L., Zhang, M., Bennett, P., Szerdy, F., and L. Hamilton. The First Commercial Permeable Reactive Barrier Composed of Zero-Valent Iron: Hydraulic and Chemical Performance at 10 Years of Operation."

Focus of Case Study Presentation

- Layout
- Hydraulics
- Geochemical conditions
  - pH
  - Redox
  - Inorganic character
- Dissolved gas measurements
- Economic performance

No associated notes.

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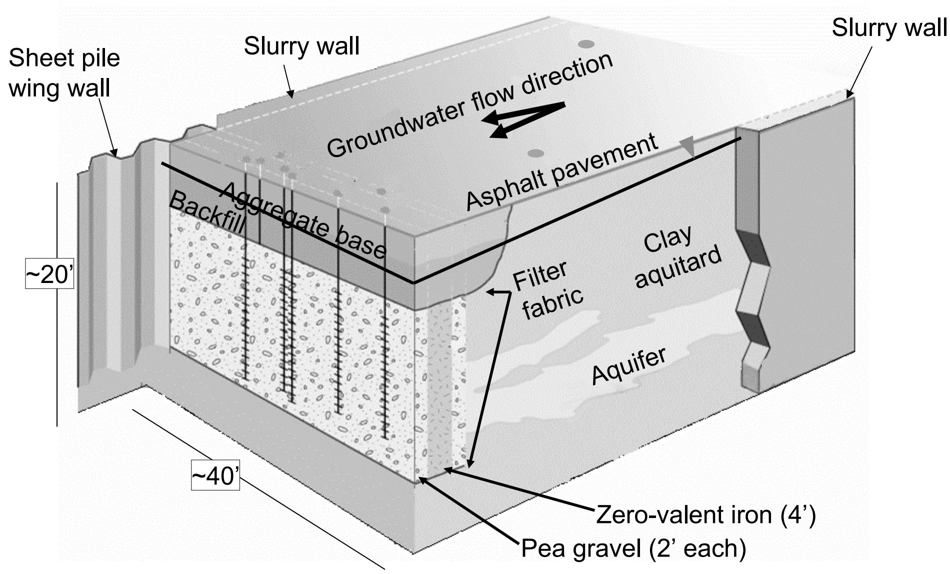
PRB Layout



No associated notes.

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PRB Emplacement - Treatment Section

2 feet | 4 feet | 2 feet

Photo from Warner, et al., Jour. Envir. Engineering, 1998

This photograph is of the PRB as it was being installed in November 1994. The PRB zone includes two -2 foot thick pea gravel zones sandwiching the 4-foot thick 100% zero-valent iron zone. The system extends from a depth of approximately 5 feet bgs to 22 feet bgs and is approximately 40 feet long. The PVC monitoring wells (in white) were emplaced during construction. The materials were placed in 1 foot lifts and tamped during construction. The reference is for the paper

"Considerations for Monitoring Permeable Ground-Water Treatment Walls," S.D. Warner, C.L. Yamane, J.D. Gallinatti, and D.A. Hankins, 1998, Journal of Environmental Engineering (ASCE), Vol. 124, No. 6, pp 524-529.

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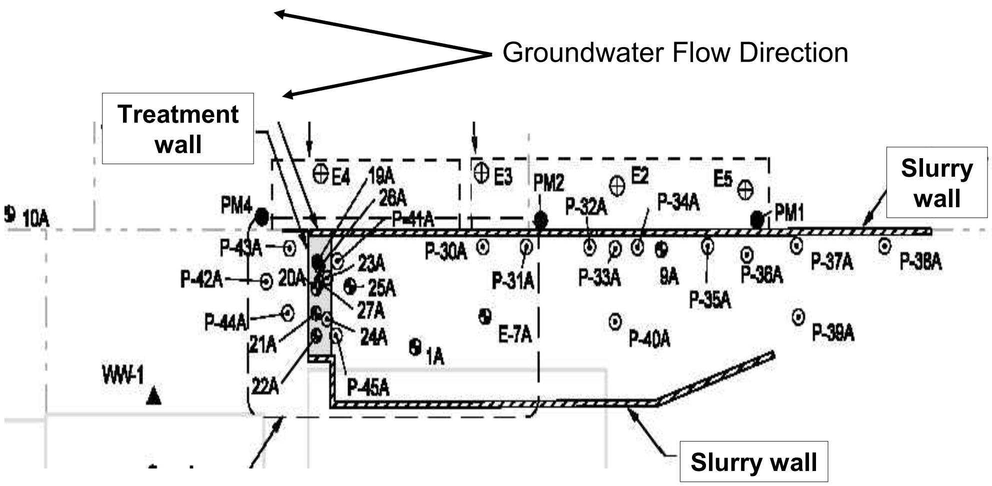
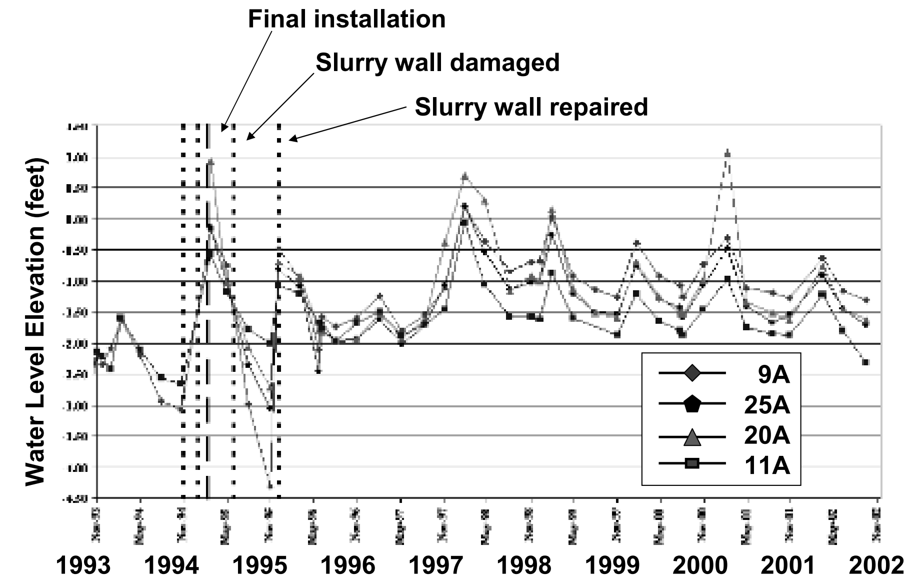
PRB Layout - Plan View



Layout includes lateral soil-cement-barriers walls to route flow through the PRB. Monitoring well and piezometers are shown at the site. Lateral piezometers intended to assess hydraulic conditions along the upper SCB low K wall. For more detailed information on monitoring see Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) section 6.2 (Monitoring).

34

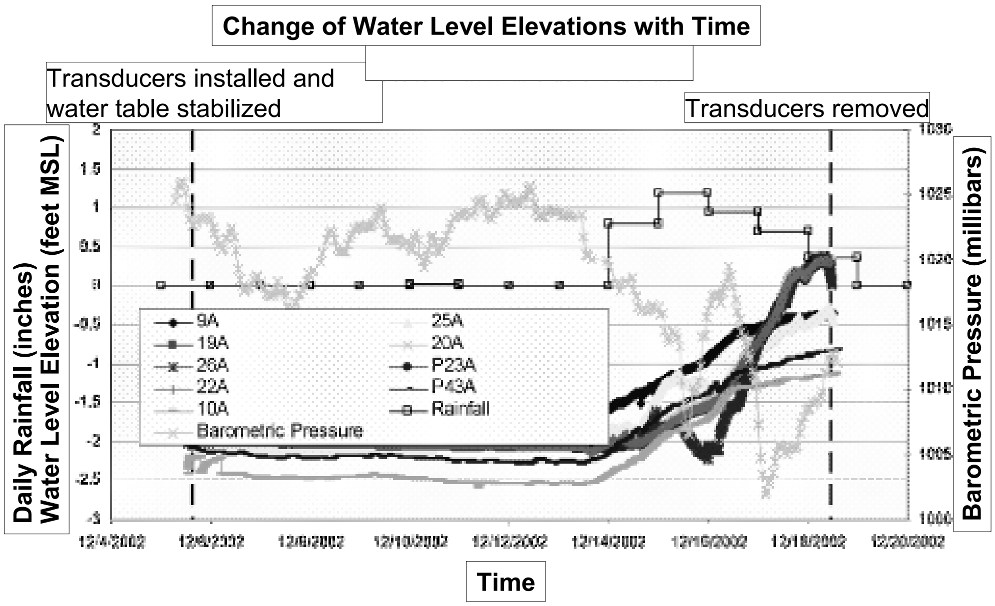
Monitoring Water Levels



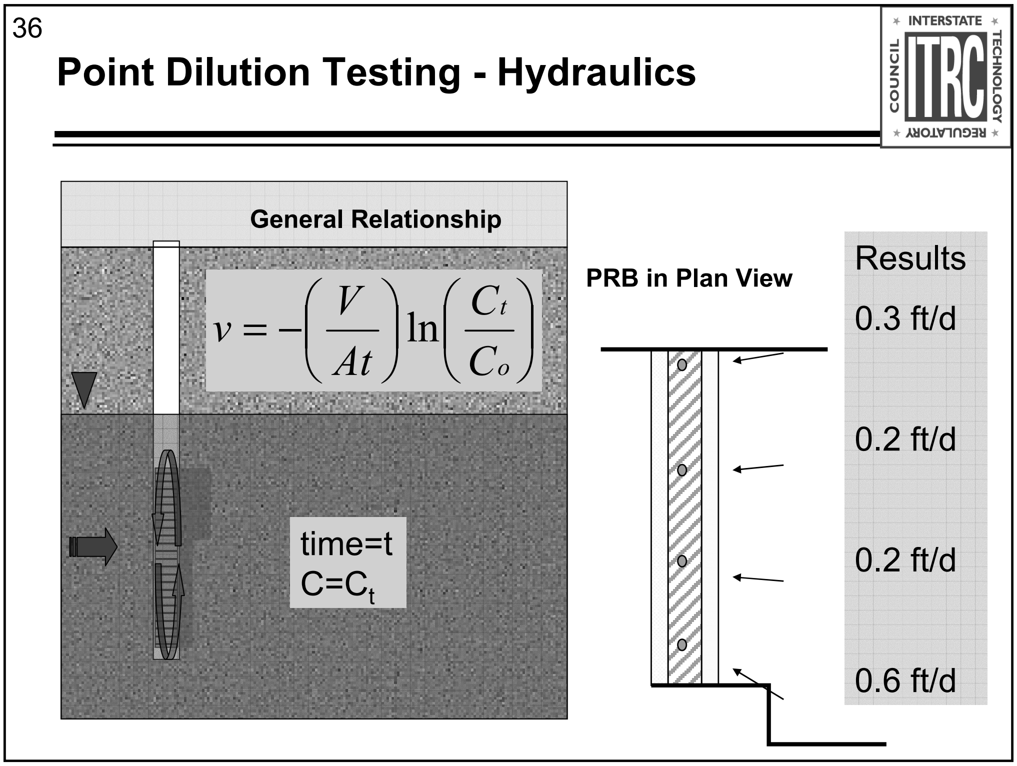
Historical water levels indicating seasonal conditions. Early depression caused by unintended breach of lateral slurry wall by neighboring construction. Repair of the slurry wall occurred successfully through grout injection. For more detailed information on water level monitoring see Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) section 6.2.5 (Sampling Frequency).

35

Monitoring Transient Hydraulics



No associated notes.



The borehole dilution test involves the introduction of a pre-determined mass of inorganic salt [sodium bromide (NaBr)] into a known volume of groundwater. The sodium bromide tracer is introduced and mixed into the well with minimal disturbance to hydraulic head. Dilution of the bromide tracer occurs as groundwater moves through the well screen. The decrease in bromide concentration over time is measured with a bromide-specific electrode. The measured decrease in bromide concentration over time is directly related to the horizontal groundwater velocity by the equations on the slide

where

Vb=borehole velocity (linear velocity of groundwater at the center of the test interval)

V=measuring volume of test interval

A=cross-sectional area of the test interval perpendicular to the groundwater flow direction

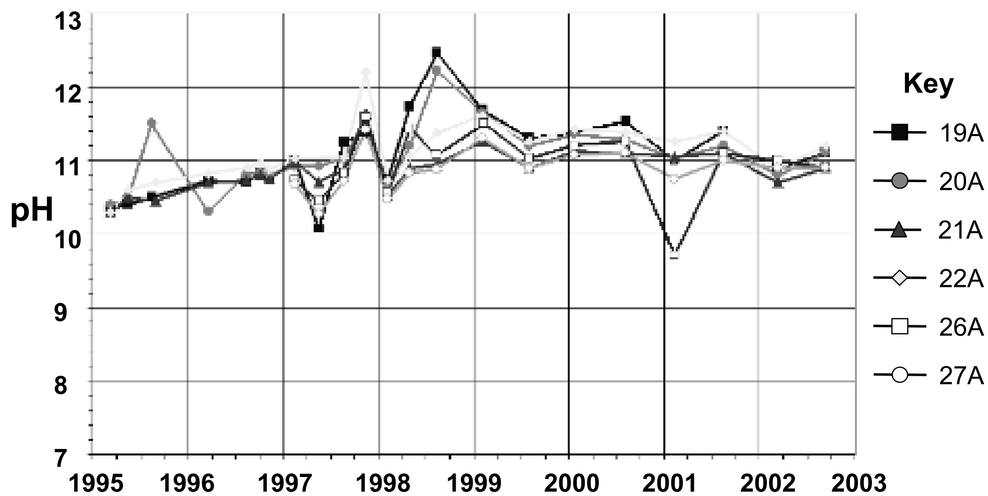
t=time since introduction of NaBr

C=concentration of sodium bromide at time “t”

Co=concentration of sodium bromide at time zero, or start of test (Co>C except at t=0, where Co=C)

37

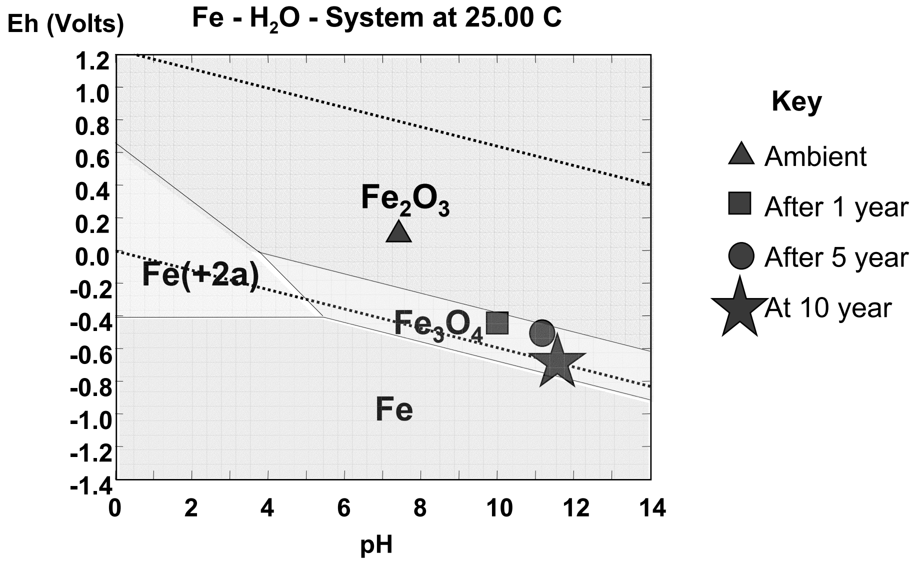
Trend in pH Conditions



pH data remains in the 10 to 11 range within the PRB; these are typical and expected conditions.

38

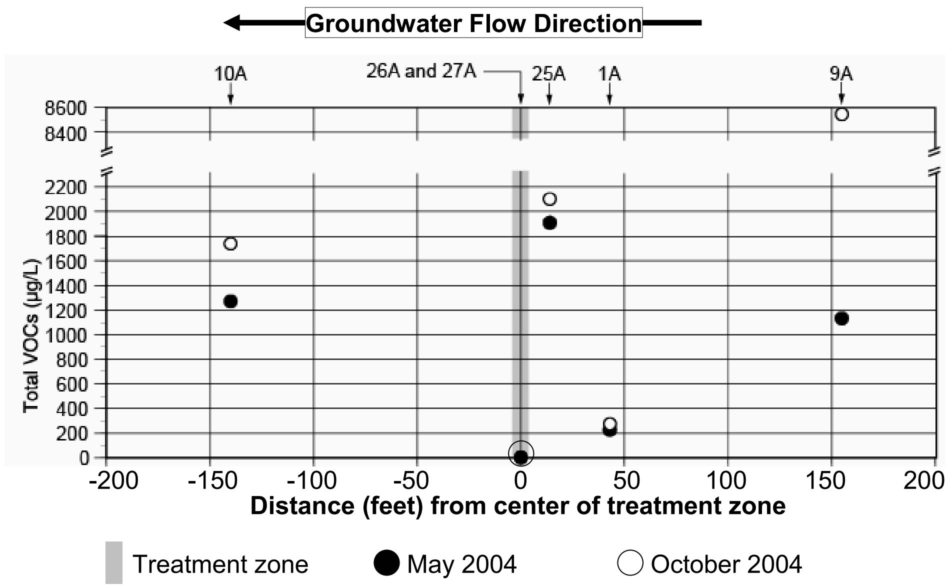
Eh- pH Relationship



Historical Eh-pH relationships. Apparent drift toward more reducing and higher pH conditions are being evaluated.

39

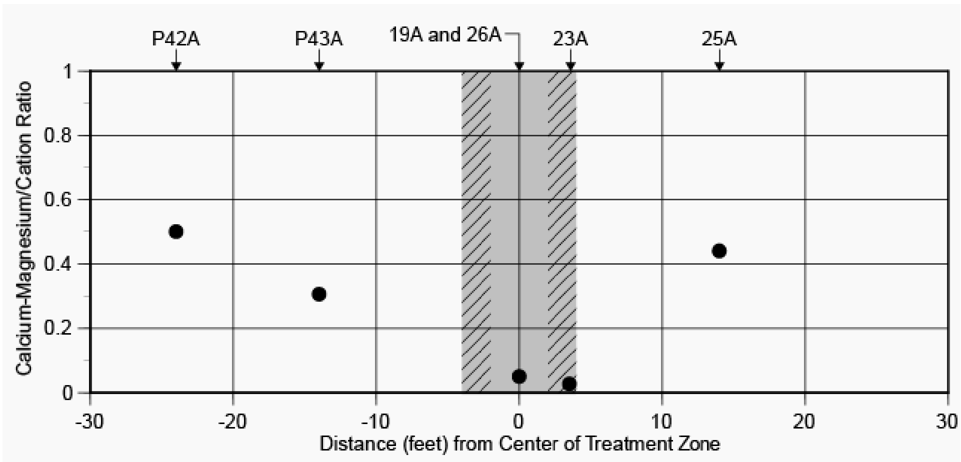
Monitoring Total VOC Concentration



No associated notes.

40

Monitoring Inorganic Chemistry



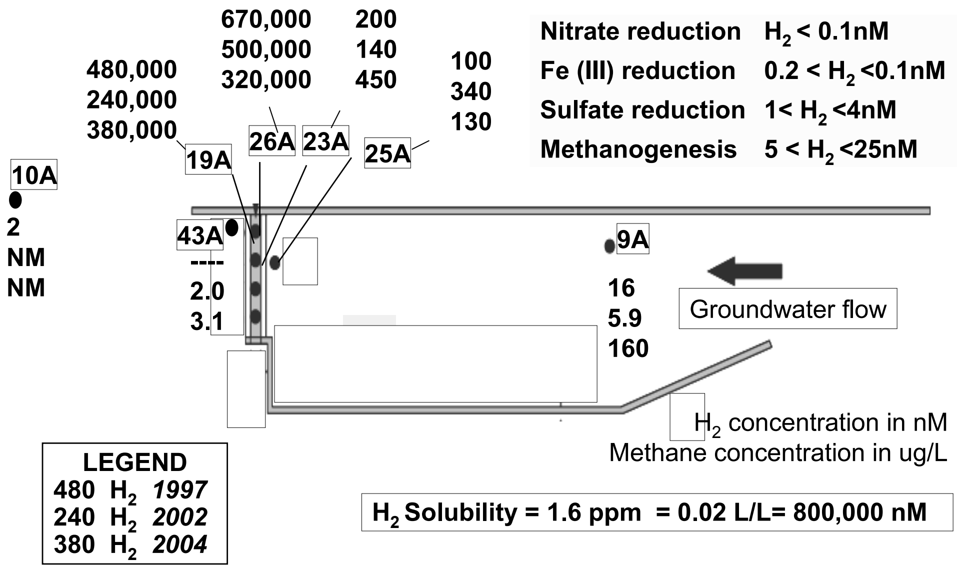
Ca + Mg / Total Cations (meq/L)

Treatment zone   Transition zone   October 2004

No associated notes.

41

Dissolved Hydrogen Gas Monitoring



No associated notes.

Economic Assessment

Historical cost assessment for the PRB remedy 1992-2004

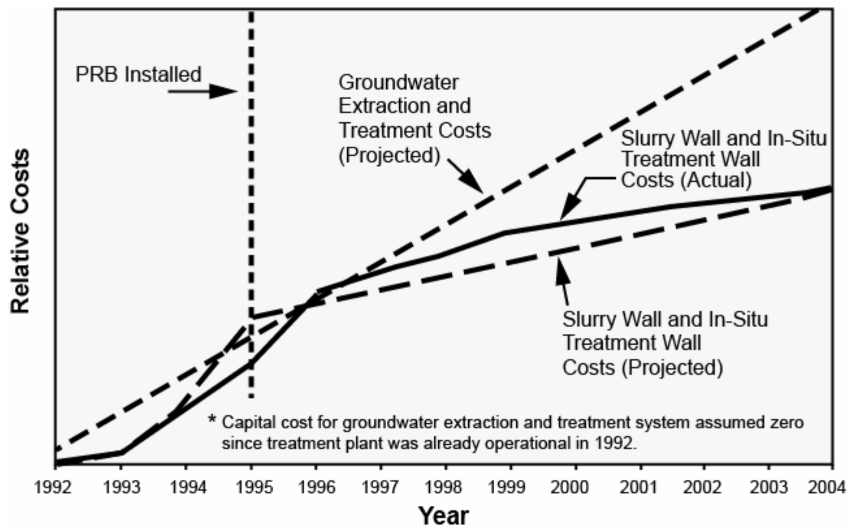


Figure indicates that the actual PRB costs approximate the predicted costs and are well below the anticipated future costs that would have been associated with continuation of the pump and treat system. For more detailed information on cost see Section 10 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

43

The First Zero-valent Iron PRB at 10 Years

- Remedial intent is being achieved
- Economic property use has been restored
- Geochemical conditions confirm remedial process
- Mineralization likely; no significant affect - yet
- Hydrogen shows effect beyond PRB boundary
- Hydraulic conditions are transient
    - Flow conditions appear to be maintained

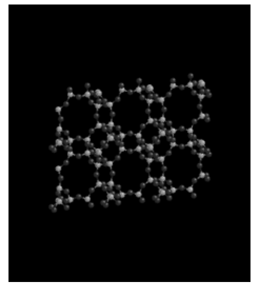
No associated notes.

44

Performance of a Zeolitic PRB
West Valley, New York

Zeolite (clinoptilolite)

$(Na, K, Ca)_2\text{-}3Al_3(Al, Si)_2Si_{13}O_{36}\text{-}12H_2O$

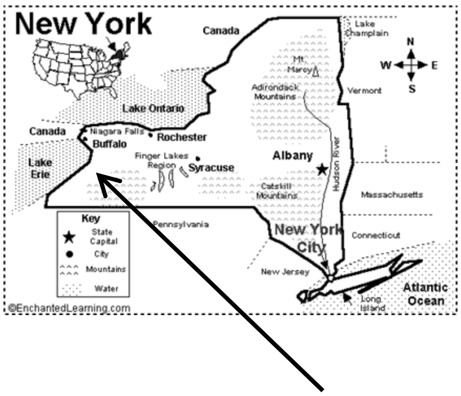


Specific Gravity = 2 to 2.5
Cation Exchange Capacity = 1.7 meq/g
Sorption capacity 2350 mL/g
Bulk Density 0.8 g/mL
material testing by University at Buffalo

The project involved assessing the performance of a reactive barrier composed of the zeolite clinoptilolite for removing Sr-90 from groundwater.

45

Site Background



Site Location

- West Valley Demonstration Project
- 30 miles south of Buffalo, NY
- Department of Energy Vitrification Pilot Plant
- Sr-90 in groundwater from 1960s process water line break
- PRB pilot test using a zeolitic material (approximately 85% clinoptilolite) to promote removal of Sr-90 through ion exchange
- Sr-90 decay rate 6.59 x 10^{-5} per day

Site is located in western New York State south of Buffalo. This was the first pilot test in the U.S. of a reactive barrier using the zeolite material to promote ion exchange of Sr-90.

46

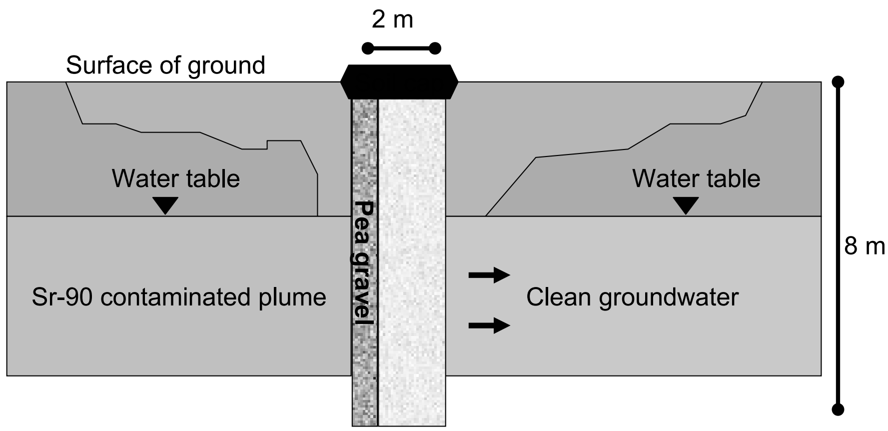
Case Study Focus Areas

- Hydraulic performance anomalies
- Post construction evaluation
- Monitoring of inorganic performance parameters
- Consideration of hydraulic improvements – if needed
- Reassessment of performance – long-term
- Evaluating success of the pilot program with respect to developing a potential full-scale design

This study began after the pilot test began. Hydraulic performance anomalies were apparent, and questions arose as to how well the treatment process was working to remove Sr-90 from the groundwater. The study also was tasked with identifying those elements important for designing a full-scale system, if appropriate.

47

PRB Concept



Idealized layout of the pilot system. The system had a cross-flow length of approximately 10 meters, and a flow through thickness of approximately 2 m; an upgradient pea gravel section (approximately 0.3 m) was installed and completed with a horizontal dewatering pipe for use in developing the PRB system after construction.

48

Construction

Construction pictures. Note the sheet pile system used to form the outline of the PRB prior to excavation.

49

Construction

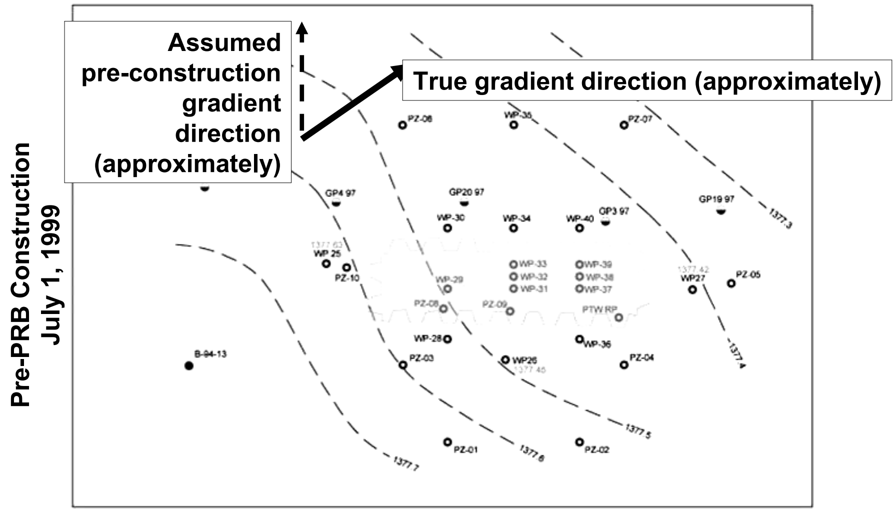
Excavation

Gravel and Zeolite Placement

For additional information on PRB construction see Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) section 4.2. For PRB design and construction lessons learned see section 4.3. Photographs show excavation of material within sheet-piled section (on left). Photograph on right is of the upgradient section showing pea gravel and zeolitic material (white).

50

Pre-construction Gradient Direction; Gradient Direction Based on Fewer Number of Wells



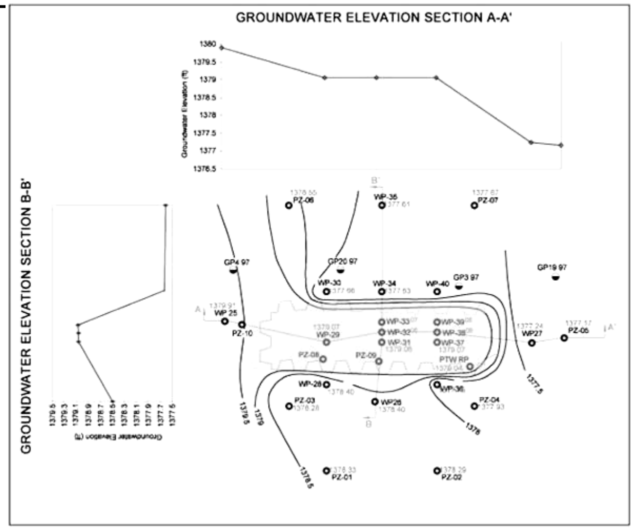
Source: Topographic Survey for the North Plateau Barrier Wall, Nussbaumer & Clarke, Inc, October 31, 1994. Horizontal datum New York State Plane Coordinate System, NAD West Zone

The original interpretation of the pre-construction gradient indicated a more northerly direction (noted by dashed arrow); however, the true gradient direction appears to have been more toward the northeast and at an angle to the orientation of the length of the PRB system.

51

Post-construction Gradient Direction

Post-PRB Construction, Pre-development
May 30, 2000



Source: Topographic Survey for the North Plateau Barrier Wall, Nussbaumer & Clarke, Inc, October 31, 1994. Horizontal datum New York State Plane Coordinate System, NAD West Zone

Measurements of groundwater elevations beginning soon after construction indicated the presence of an apparent hydraulic mound; the study was aimed at identifying the cause of this unanticipated condition. Potential causes of the mound included: surface drainage; skin effects from construction; hydrogeologic conditions.

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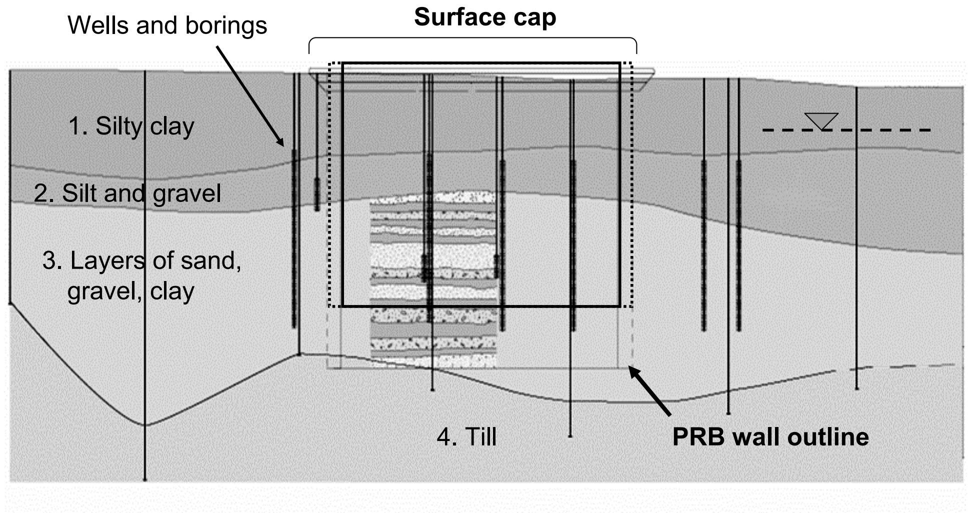
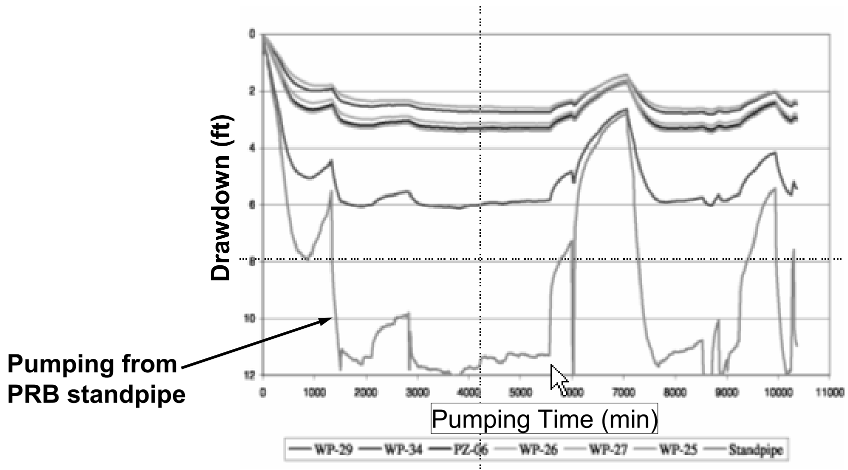
Hydrostratigraphic Cross-section



Review of the boring logs and logs from cone penetrometer test holes showed that primary flow system was composed of a highly heterogeneous layer cake of fine and course sediments. The potential of skin effects from construction may have caused diversion of flow and contaminant migration pathways.

53

Hydraulic Communication

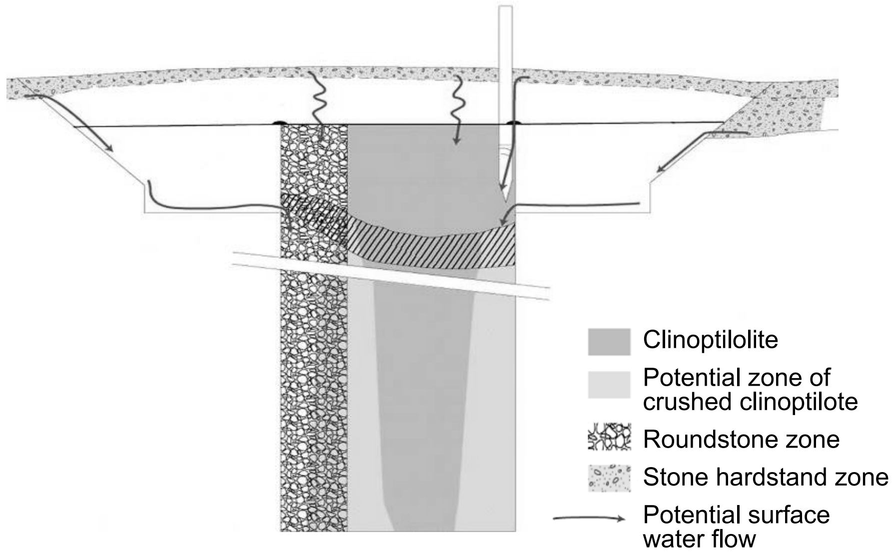


Note: Data from the January 2001 PRB river pipe pumping test
Source: Data provided by West Valley Nuclear Service

Assessment of whether the PRB was in hydraulic communication with the aquifer system was performed by pumping within the pea gravel standpipe and monitoring the water level in neighboring wells. The monitoring data does show that hydraulic effects were observed well outside the limits of the PRB.

54

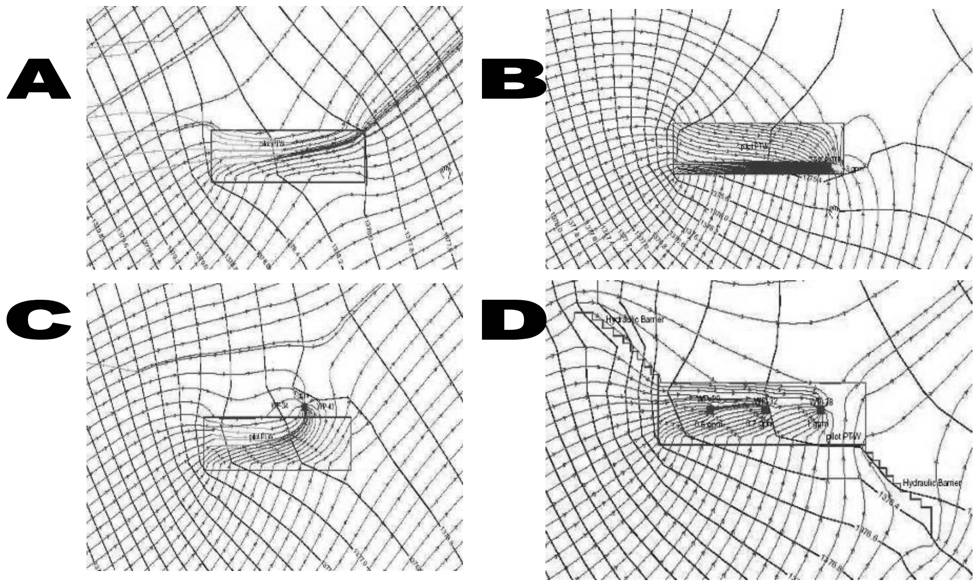
Factors Affecting PRB Performance - Material Conditions and Construction



During construction, several factors can lead to unanticipated conditions. These potential effects include: 1. crushing of the treatment material leading to a finer than designed media; 2. surface drainage into the PRB can cause transient (or sustained) hydraulic mounding; 3. smearing of permeable flow zones with fine materials during emplacement and extraction of sheet piles; potential hanging of PRB above a portion of the underlying lower conductivity aquitard zone.

55

Assessing Potential Hydraulic Enhancements using Analytical Modeling



This figure represents potential modifications to enhance the hydraulic performance of the PRB, if needed. This was created as an analytical element model in 2 dimensions, but the flow from two zones is represented by the different colors of the pathlines due to vertical movement of particles.

The ambient system is indicated in this figure. Equipotentials are at 90 degrees to flow lines. Each tick represents a time of 1 day.

Enhancing flow using by pumping the drain system installed in the upgradient pea gravel.

Enhancing flow from a pumping well installed just downgradient of the PRB

Enhancing flow from pumping at 3 interior wells within the PRB. Also, not the addition of low K wing walls at the corners of the PRB.

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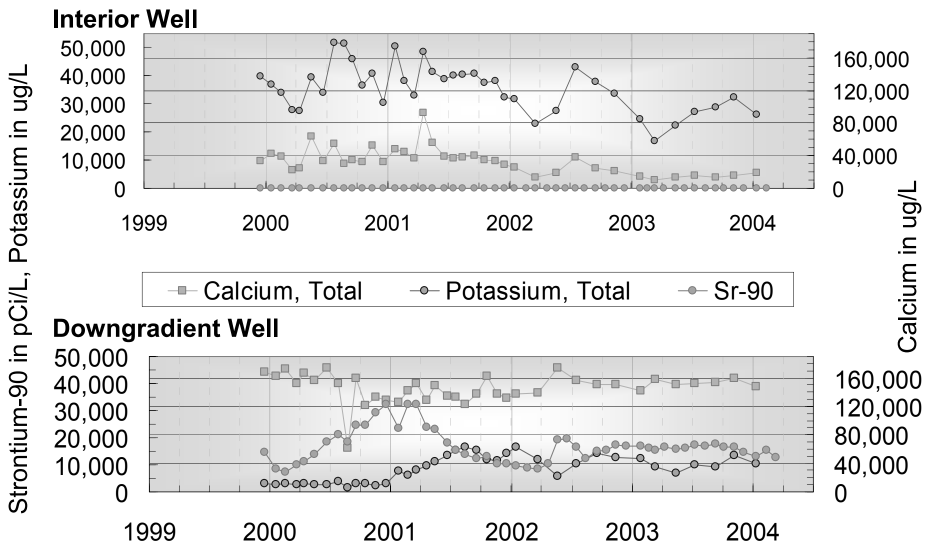
Monitoring Results



Additional information about monitoring can be found in section 6.2 of Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4).

Analytical results.

Blue = potassium (mg/L)

Green = calcium

Orange/Red = Strontium 90

Graph on the top is an interior well

Graph on the bottom is a downgradient well

Note the nondetection of SR in the interior well (expected if ion exchange is occurring)

Note the eventual decrease in SR and increase in potassium in the downgradient well. This is expected from the exchange of Sr for K in the zeolite. Important to note that this PRB was located within a pre-existing plume; thus the chemical signature of groundwater is consistent with the plume characteristics before initiative of the PRB pilot test.

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Lessons Learned

- Site characterization
  - Hydraulic conditions
  - Vertical and lateral heterogeneity
- Pilot testing objectives
- Construction methods
- Details for potential full-scale installation

Key lessons learned fall in the areas of:

Site characterization – completeness for the intended remedial objectives

Define pilot testing objectives for the purpose of obtaining data for a final design; the pilot needs not to work perfectly to meet these objectives

Understand the potential affects of construction on the flow system and contaminant migration pathways

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Questions and Answers

No associated notes.

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Bio-Barriers: In-Situ Bioremediation Using a Permeable Reactive Barrier Design

Presentation Overview:

- **What is a bio-barrier?**
- **Typical "amendments" for in-situ bioremediation**
- **Case example**

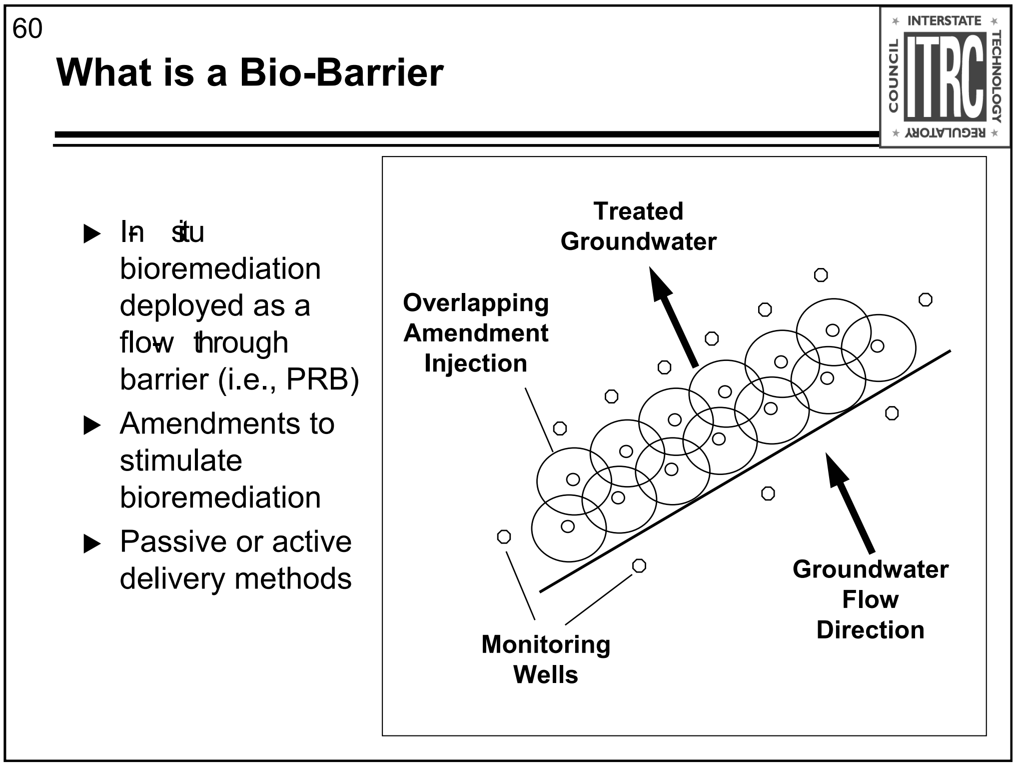
This presentation will discuss the following topics:

What is a bio-barrier?

Typical "amendments" used in bio-barriers

A case example of a large bio-barrier installation to treat chlorinated solvents at an industrial facility in California. Highlights include:

- Permitting
- Monitoring
- Performance evaluation
- Operation and maintenance



An introduction to bio-barriers is presented in **Sections 1.2 and 2.5** of the guidance document.

- "Bio-barrier" refers to a contiguous, linear zone where microbiological activity is enhanced to treat various pollutants.
- Bio-barriers are finding increased use for the treatment of degradable pollutants such as chlorinated solvents, MTBE, BTEX, and also for metals precipitation via pH/redox adjustment.
- Bio-barriers are unique types of PRBs (**see PRB definition, Section 1.2**):
    1. PRB design (i.e., flow-through barrier) applied to in-situ bioremediation remedy
    2. Relies on amendments to stimulate secondary processes (i.e., microbial degradation) rather than materials like iron that have a direct effect on contaminants.
    3. May rely on "passive" delivery systems such as slow continuous release of gases or liquids, or "active" delivery systems such as injection and circulation of amendments

Many different bio-barrier designs:

1. Overlapping amendment injection points:
    - Goal is to achieve the proper spacing to create continuous zone of biological activity
    - Aligned perpendicular to groundwater flow to create flow-through treatment barrier
    - Passive or active injection of amendments
    - Could use sheet piles to "funnel" groundwater through barrier
2. Subsurface circulation system:
    - Goal is to circulate amendments laterally and vertically in the subsurface via opposing injection and extraction
    - Hydraulic capture functions like funnel and gate PRB design
    - Good for treatment in multiple aquifers/depth zones
3. Trench and fill design
    - Amendments added directly into trench
    - Aligned perpendicular to groundwater flow
    - Good for relatively shallow groundwater treatment

Examples of Sites with Bio-barriers (see Table 2-4 and Appendix D for more information):

1. Nickel Rim Mine Site, Sudbury, Ontario. Organic carbon to threat nickel, iron & sulfate. Full Scale since 1995. Ref: http://www.rtdf.org/public/permbarr/prbsumms/default.cfm
2. Zeneca / Campus Bay, Richmond, California. Leaf compost with soil/sand mix and sulfate-reducing bacteria to treat acid mine drainage (low pH, iron, mercury, copper, arsenic, zinc). Full scale since Oct 2002 – contact Peter Zawislanski, LFR, peter.zawislanski@lfr.com, 510.596.9685.
3. Naval Base Ventura County Port Hueneme Naval Base, Ventura County California. Microbes and oxygen to treat MTBE & BTEX. Full Scale since 2000 – contact: Karen Miller, U.S. Department of the Navy, Naval Facilities Engineering Service Center, karen.miller@navy.mil, (805) 982-1010. Ref: Naval Facilities Engineering Service Center; Johnson, P.C., Bruce, C.L, Miller, K.D., June 2003, ESTCP Cost and Summary Report, In-Situ Bioremediation of MTBE in Groundwater, (ESTCP Project No. CU-0013), Technical Report TR-2216-ENV, pgs. 1-118.
4. Vandenberg Air Force Base, Lompoc, California. Dissolved oxygen to treat MtBE via a polyethylene tubing flow-through barrier. Contact: Beatrice Kephart, 805-605-7924. Ref: Wilson, R. D., D. M. Mackay, and K. M. Scow. In Situ MTBE Degradation Supported By Diffusive Oxygen Release. Environmental Science and Technology, 36(2): 190-199, 2002.
5. The Dow Chemical Company, Pittsburg, California. Propylene Glycol, Sodium Lactate, and Nutrients to treat chlorinated volatile organic compounds (PCE, TCE, DCE, Ctet, Chloroform) via a subsurface circulation system (39 circulation wells screened over two zones: 40-80 ft and 110-130 ft.). Full Scale since 2002. Contact: Alec Naugle, S.F. Bay Water Board, anaugle@waterboards.ca.gov, 510.622.2510. http://www.bcilabs.com/monterey2.html, http://www.bcilabs.com/monterey1.html
6. Altus Air Force Base, Oklahoma. Cotton Gin Compost, Sand, and Shredded Bark Mulch used to treat Chlorinated VOCs. Full Scale since 2002. http://www.afcee.brooks.af.mil/products/techtrans/bioremediation/downloads/AltusBiowallPaper-163PEHa.pdf
7. McGregor Naval Weapons Plant, Texas. Solid Carbon Substrate to treat Perchlorate. Full Scale Field Demonstration since 2002. http://www.afcee.brooks.af.mil/products/techtrans/perchloratetreatment/permeablereactivebarriers.pdf
8. Moss-American, Milwaukee, Wisconsin. Air and Nutrients to treat Polycyclic Aromatic Hydrocarbons (PAHs), BTEX. Full Scale since 2000. Ref: Federal Remediation Technologies Roundtable (2004)
9. Dover Air Force Base, Delaware. Soybean Oil to treat Chlorinated VOCs. Pilot Scale in 2000. http://www.afcee.brooks.af.mil/products/techtrans/bioremediation/downloads/DoverAFBBattellePaper04.pdf
10. SAFIRA Test Site, Bitterfeld, Germany. Hydrogen with Paladium Catalyst to treat Benzene, Chlorobenzene, Dichlorobenzene, TCE, DCE. Pilot Scale in 1999. http://www.rtdf.org/public/permbarr/prbsumms/default.cfm
11. East Garrington, Alberta, Canada. Oxygen to treat BTEX. Pilot Scale since 1995. http://www.rtdf.org/public/permbarr/prbsumms/default.cfm
12. ExxonMobil Bayway Refinery, Linden, New Jersey. Dissolved Oxygen to treat BTEX. Full Scale since 2002. Contact: Brent Archibald, Exxon Mobil 908-730-2404.
13. Offutt AFB Building 301, Nebraska. Sand & Wood Mulch to treat TCE. Full Scale since 2001. Contact: Philip E. Cork, Chief, Env. Restoration Element 402-297-7621.

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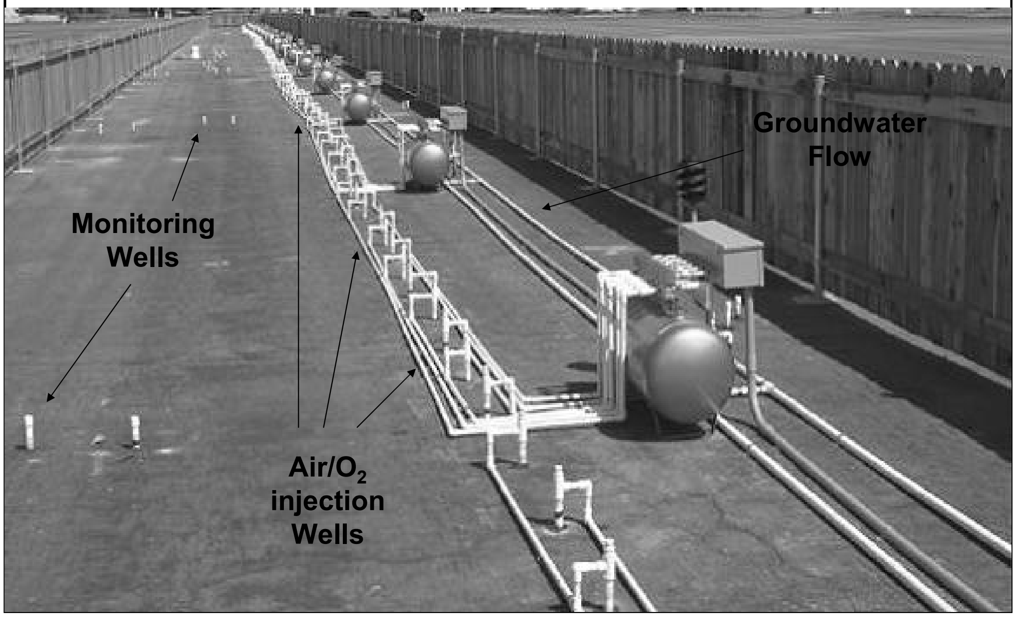
Example of Bio-Barrier Using Oxygen/Air Injection



This photo is an example of a bio-barrier site at Port Hueneme, CA (referenced below) where oxygen is injected to treat a gasoline plume containing MTBE and BTEX constituents.

Naval Base Ventura County Port Hueneme Naval Base, Ventura County California. Microbes and oxygen to treat MTBE & BTEX. Full Scale since 2000 – contact: Karen Miller, U.S. Department of the Navy, Naval Facilities Engineering Service Center, karen.miller@navy.mil, (805) 982-1010. Ref: Naval Facilities Engineering Service Center; Johnson, P.C., Bruce, C.L, Miller, K.D., June 2003, ESTCP Cost and Summary Report, In-Situ Bioremediation of MTBE in Groundwater, (ESTCP Project No. CU-0013), Technical Report TR-2216-ENV, pgs. 1-118.

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Typical Bio-Barrier Amendments

- Solid organic amendments
  - Wood chips
  - Leaf compost
- Liquid organic amendments
  - Lactate
  - Molasses
  - Cheese whey
  - Propylene glycol
  - Edible vegetable oils
- Gas amendments
  - Oxygen / air
  - Hydrogen
  - Oxygen / hydrogen release compound (ORC / HRC)
- Microbial cultures (bioaugmentation)

Three categories of “Amendments” (**see Table 2-2 and Section 2.5**):

1. Solid organic amendments (e.g., wood chips, compost, etc.)
   - Used to treat acid mine drainage and stabilize heavy metals
   - Decomposition uses oxygen, thereby eliminating acid generation and facilitating a rise in pH.

2. Liquid organic amendments, (e.g., lactate, molasses, glycol, etc.)
   - Used to stimulate anaerobic breakdown of pollutants
   - Many undergo fermentation reactions which produces hydrogen, which can then be used as an electron donor in the reductive dechlorination of chlorinated solvents like PCE, TCE, CTet, etc.

3. Gas amendments (e.g., air, oxygen, oxygen/hydrogen releasing compounds, etc.)
   - Oxygen stimulates aerobic degradation processes favored for treatment of petroleum hydrocarbon pollutants such as BTEX and fuel oxygenates like MTBE
   - Hydrogen stimulates anaerobic processes favored for treatment of chlorinated solvents.

4. Microbial cultures (e.g., addition of various cultures known to degrade specific contaminants - bioaugmentation).
   - Can occur in conjunction with the addition of other amendments
   - Typically used only if the contaminant-specific microbes are not plentiful at the site.

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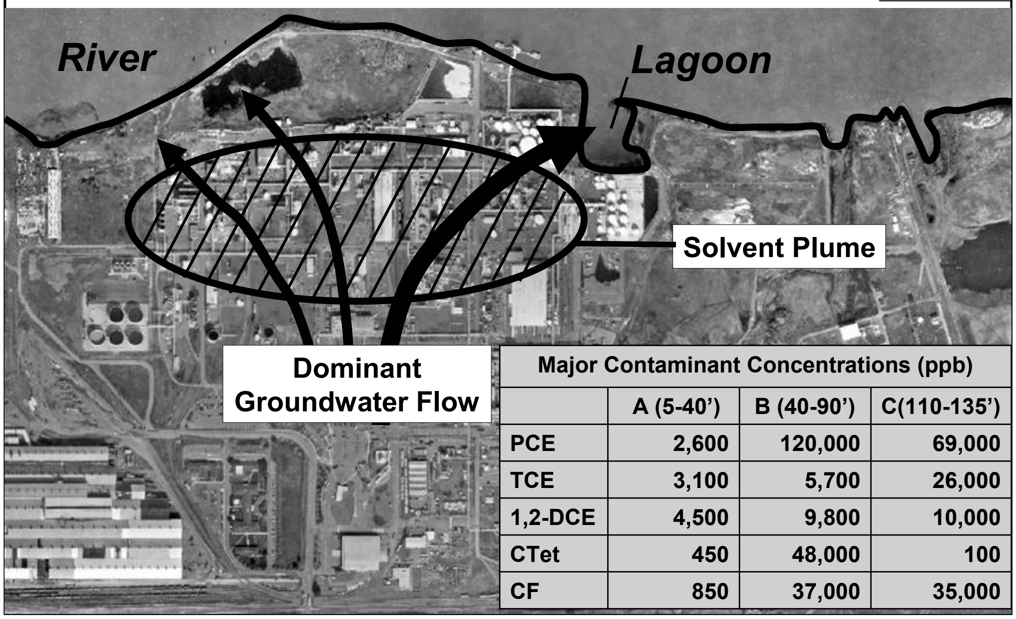
Case Example: Solvent Plume at Large Industrial Facility in California



Major Contaminant Concentrations (ppb)			
	A (5-40’)	B (40-90’)	C(110-135’)
PCE	2,600	120,000	69,000
TCE	3,100	5,700	26,000
1,2-DCE	4,500	9,800	10,000
CTet	450	48,000	100
CF	850	37,000	35,000

Case example of a large-scale bio-barrier system installed at an industrial facility in California

•Chlorinated solvent plume ~1000 feet wide

•Perchlorethylene (PCE) and Carbon Tetrachloride (CTet) parent products manufactured at site for many years

•Sources: historic spills, leaks, disposal activities

•Three depth zones characterized in upper 140 feet: A (shallow), B(mid-depth), C(deep)

•Groundwater flow northward across site toward river and lagoon

•Flow paths diverge as groundwater follows path of least resistance

•Dominant flow toward lagoon

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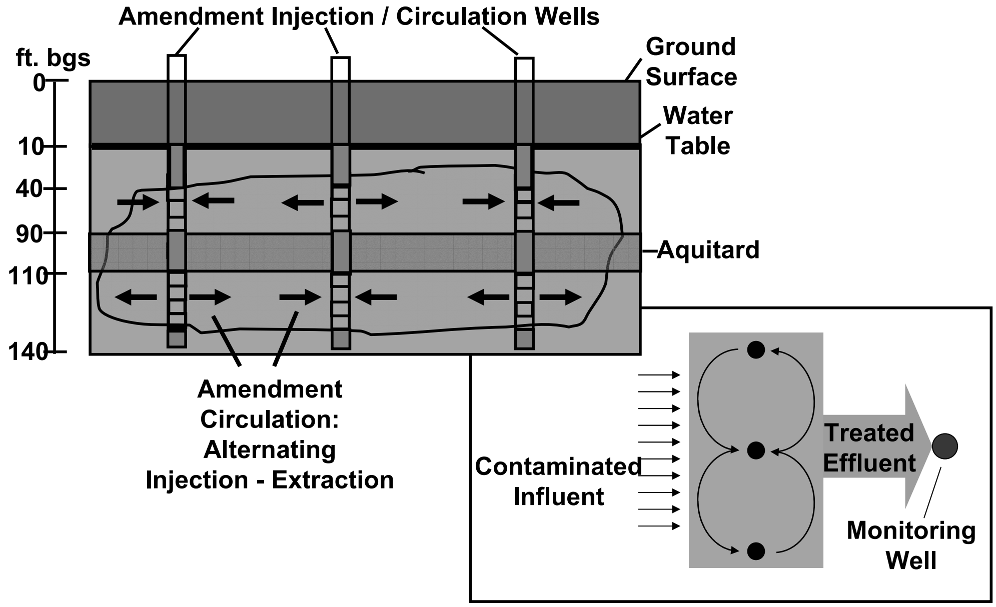
In-Situ Bioreactor Concept



A subsurface circulation system was selected based on distribution and depth of contaminants:

- Alternating patterns of extraction and injection (up-pumping and down-pumping) to circulate amendments
- Propylene Glycol added as carbon source to stimulate anaerobic conditions
- Fermentation releases hydrogen, which is electron donor for reductive dechlorination
- Continuous circulation of groundwater and amendments
- Batch injection of propylene gylcol (bi-weekly)
- Primary focus on capture and treatment of contaminants in mid-depth and deep zones

In-Situ Bioreactor Concept:

- Up-gradient groundwater captured by pumping inlets across 3-well segment
- Contaminated groundwater is mixed with injected amendments and circulated many times within segment capture zone (“Bioreactor”)
- Groundwater effluent monitored at down-gradient exit adjacent middle well; monitoring well screened over corresponding depth zone where exit occurs
- Circulation within bioreactor up to 25x prior to down-gradient escape

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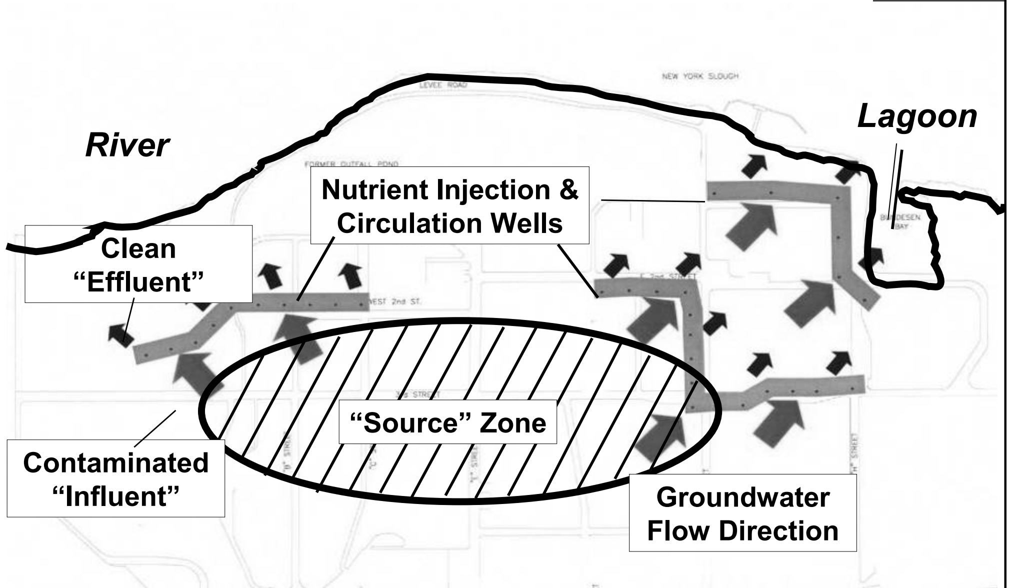
Bio-Barrier Layout



Three bio-barrier segments with 39 circulation wells in all (17 three-well segments):

- Pilot scale system from 2000 – 2001; full-scale since 2001
- 100 foot circulation well spacing
- One effluent monitoring well 20 feet down-gradient from each circulation well
- Goal is mass flux reduction migrating toward river and lagoon

References for In-Situ Bioremediation of Chlorinated Solvents:

- ITRC. 1999. *Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices*.
- ITRC. 1998. *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater*.
- USEPA. 1998. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*. ORD. EPA/600/R98/128.

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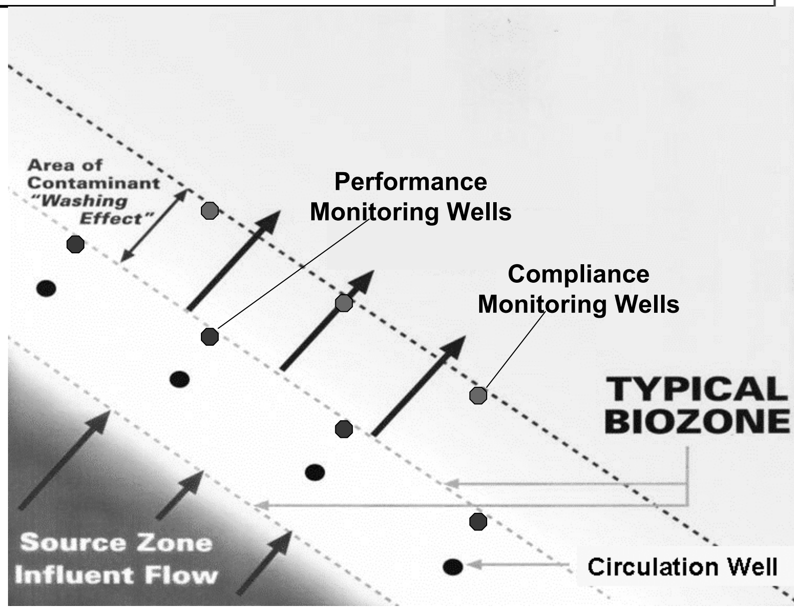
Evaluating Performance and Compliance: Conceptual Model



- Bio-barrier creates down-gradient "washing and flushing" zone similar to other PRBs
- Time needed for down-gradient residual to clean up
- Performance monitoring wells must be within "washing" zone
- Compliance monitoring wells needed further down-gradient to monitor growth of "washing" zone and evaluate compliance with long-term cleanup goals

See **Section 6** for overall PRB performance and compliance monitoring discussion

Compliance Monitoring

Measures downgradient effects on aquifer conditions and residual plume (~100-200 ft):

- Parent and daughter compounds
- To soon to see significant reductions since installed within down-gradient residual plume
- 5-year evaluation will determine need for:
    1. additional wells
    2. better well locations
    3. additional circulation segments

Performance Monitoring

Measures System Effluent directly downgradient of circulation wells (~20 ft)

1. Parent and daughter compounds:
2. Metabolic products (CO_2, hydrogen, ethene, methane)
3. Quantification of microbes
4. Contaminant mass reduction

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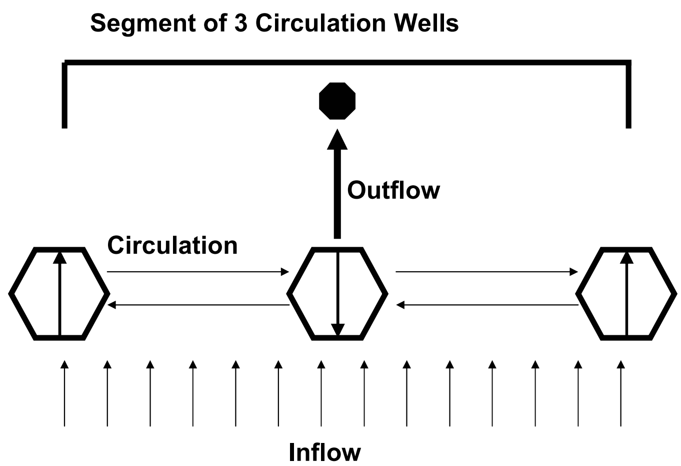
Performance Monitoring: Destruction Rate Efficiency



Destruction Rate Efficiency (DRE) is a measure of the reduction in total contaminant concentration (or mass) between the influent and effluent over one segment. As with the in-situ bioreactor approach, a segment consists of 3 circulation wells and one monitoring well located directly down-gradient from the middle center circulation well.

Monitoring the performance of the system includes:

1. Parent and daughter compounds:
2. Metabolic products (CO_2, hydrogen, ethene, methane)
3. Quantification of microbes
4. Contaminant mass reduction

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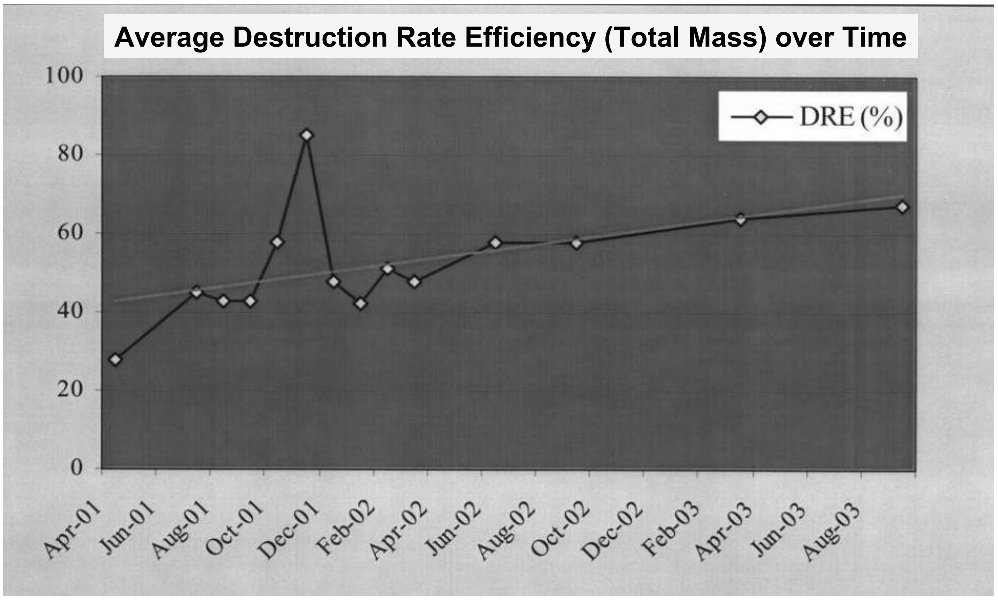
Overall System Performance



No associated notes.

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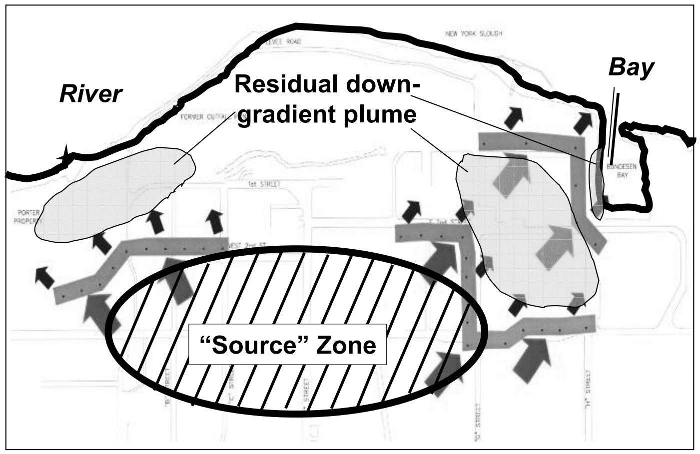
Regulatory Issues

- Concerns with injection of chemical amendments
- Takes time to “grow”; experiences growth and decay…incomplete treatment??
- Difficult to verify placement
- Installed within down-gradient plume residual
- How to evaluate performance and compliance?



Concern with injection of liquids into aquifers

•Mobilization of metals, toxic breakdown products (**see discussion in Section 6.3.2**)

•Installation within residual plume (**see discussion in Section 6.2.1.1**)

•Challenges with performance and compliance monitoring (**see discussion in Section 6.2**)

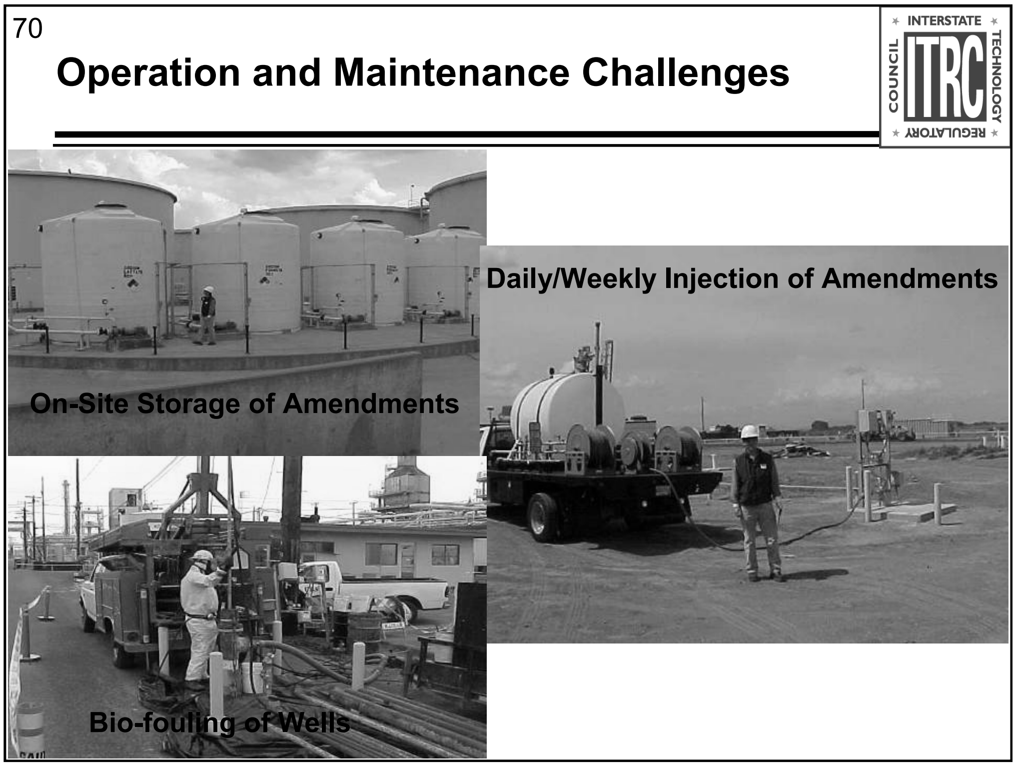
Clarification of RCRA Regulatory Issue:

•RCRA 3020(b) requires contaminated groundwater to be “treated to substantially reduce hazardous constituents prior to injection”. RCRA Section 261.3 requires that groundwater contaminated with a hazardous waste be treated as a hazardous waste (mixture rule).

•Prior to clarification, re-injecting contaminated groundwater with or without amendments added would not be allowed. Furthermore, any water used to carry the amendments into the aquifer, would have to be treated as a hazardous waste once injected per the mixture rule

•RCRA 3020 (b) was subsequently clarified as 1999, based on ITRC involvement, to allow the use of contaminated groundwater as the carrier for the injected amendments.

•This approach greatly reduces the accumulation of wastewater and the need for costly ex-situ groundwater treatment prior to reinjection.



O&M Challenges

1. Continual amendment injection…Facility has recently gone to above-ground skids for each well, which include above-ground plumbing and pump and individual amendment tanks.
2. Alternating circulation patterns
3. Bio-fouling

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Bio-Barriers Summary and Conclusions

- Bio-barriers function similar to PRBs
- Significant regulatory concerns and O&M challenges exist
- Monitoring program is key to demonstrate success:
  - Different performance vs. compliance well locations
  - Down-gradient residual can obscure results

For additional information on using oxygen as an amendment for a bio-barrier, see document section 2.5.3 (Oxygen for Fuel Sites).

Additional Bio-Barrier Sites:

Port Hueneme Naval Base (CA)[1]

Oxygen gas and air injection and augmentation with specialized microbial cultures for MTBE & BTEX degradation (www.estcp.org/projects/cleanup/200013o.cfm)

Vandenberg AFB (CA)[2]

Diffused oxygen for MTBE degradation

Zeneca/UC Richmond Field Station (CA)[3]

Compost wall augmented with sulfate-reducing bacteria to raise ph, precipitate metals (Hg, As, Cu, Zn) and stabilize Fe

Moss-American (WI)

Funnel and gate system with injection of air and nutrients for PAHs and BTEX

Abstracts of Remediation Case Studies, Vol. 8, Federal Remediation Technologies Roundtable, June 2004.

Altus AFB (OK)

Cotton gin compost, sand and shredded bark mulch for treatment of TCE and cis-1,2-DCE.

http://www.afcee.brooks.af.mil/ms/msp/center/spring2003/6.asp

http://www.afcee.brooks.af.mil/products/techtrans/bioremediation/downloads/AltusBiowallPaper-163PEHa.pdf

McGregor Naval Weapons Plant (TX)

Solid carbon substrate for perchlorate treatment

http://www.afcee.brooks.af.mil/products/techtrans/perchloratetreatment/permeablereactivebarriers.pdf

Private Site (TX)

Solid Carbon and ZVI for treatment of chlorinated VOCs

http://www.adventus.us/vocs_ehc.htm

Dover AFB (DE)

Edible soybean oil for treatment of chlorinated solvents

http://www.afcee.brooks.af.mil/products/techtrans/bioremediation/downloads/DoverAFBBattellePaper04.pdf

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Sulfate-Reduction PRBs

- Metals in sulfate-rich groundwater
  - Acid-mine drainage
  - Industrial and waste management sites
- Organic carbon in reactive mixtures
- Field-scale PRB installed at the Nickel Rim Mine, Sudbury, Canada in 1995

For additional information see document section 2.5.6 (Organic Carbon Media for Denitrification, Sulfate Reduction, and Perchlorate Destruction).

The primary document sections within Permeable Reactive Barriers: Lessons Learned and New Directions (PRB-4) that are discussed in this portion of the training course include:

2.5.6: Organic Carbon Media for Denitrification, Sulfate Reduction, and Perchlorate Destruction

4.2: PRB Construction

6.2: Monitoring

11: Conclusions and Recommendations

Appendix E: Case Study 34

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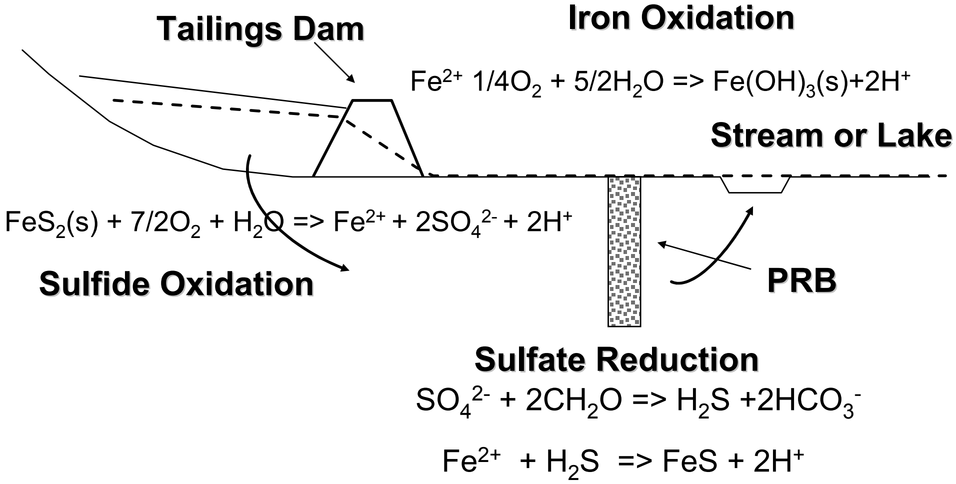
Acid-Mine Drainage Generation and PRB Treatment



Acid-mine drainage generation:

- Oxidation of sulfide minerals in mine wastes or workings; requires exposure to oxygen, and occurs primarily in zone above the water table.
- Generates elevated concentrations of dissolved sulfate, iron and metals/metalloids in water
- Low pH conditions
- Plume of acid-mine drainage impacted groundwater; some capacity in subsurface for pH neutralization reactions as groundwater moves downward and laterally below the water table, but capacity may be exceeded with time.
- Discharge of plume to surface water: oxidation of iron, lower pH of water.
- PRB intercepts and treats plume before discharge to surface water.

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Remedial Objectives for Acid-Mine Drainage in Groundwater

- Removal of sulfate and iron
  - Acid-generating potential of ferrous iron if discharged to surface water
- Removal of metals and metalloids
- Generation of alkalinity; acid consuming characteristics

Objectives of PRB:

- Passive interception and treatment of groundwater
- Promote sulfate reduction by providing carbon for sulfate-reducing bacteria.
- Reduce or remove metals as metal sulfides
- Sulfate reduction generates alkalinity, acid neutralization

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Sulfate-Reduction Process

- Carbon provides energy for sulfate-reducing bacteria (SRBs)
- Reduction of sulfate to H_2S
- H_2S combines with metals
- Precipitation of metal sulfide minerals
- Decreases concentrations of sulfate and dissolved metals
- Increased alkalinity and pH

Sulfate-reduction process:

- Microbially mediated process; organic carbon consumed.
- Kinetic (rate) limitations.
- Days to tens of days residence time for high concentration plumes.
- Rate of sulfate reduction decreases with decreasing temperature.
- Metal-sulfide precipitates are stable and sparingly soluble in settings below the water table.

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Nickel Rim Mine, Sudbury, Ontario

- Field installation (1995) following laboratory batch and column studies
- Acid-Mine Drainage (AMD)-impacted plume from tailings
- Shallow aquifer in bedrock-bounded valley
- pH ~ 6; 1,000-7,000 mg/L SO_4; 500-2,000 mg/L Fe
- Plume advancing so sulfate and iron concentrations increasing with time
- Water table very close to ground surface
- Groundwater temperature fluctuations (winter and summer influences)
- Tailings-impacted material in surficial sediments

Nickel Rim Mine PRB, Sudbury (Ontario, Canada)

The Nickel Rim Mine is located in the northern part of the Sudbury Basin. It is approximately 500 km northwest of Toronto, and lies to the north of Lake Huron.

The design and installation of the PRB are described in series of papers by Shawn Benner.

Benner, S.G., Blowes, D.W. and Ptacek, C.J. 1997. A full-scale porous reactive wall for prevention of acid mine drainage. *Ground Water Monitoring and Remediation, 17(4), 99-107.*

Benner, S.G., Blowes, D.W., Gould, W.D., Herbert Jr., R.B., and Ptacek, C.J., 1999. Geochemistry of a reactive barrier for metals and acid mine drainage. *Environmental Science and Technology, 33, 2793-2799*.

Benner, S.G., Blowes, D.W., Ptacek, C.J. and Mayer, K.U., 2002. Rates of sulfate reduction and metal sulfide precipitation in a permeable reactive barrier. *Applied Geochemistry 17, 301-320.*

The shallow aquifer is a silty fine sand. Bedrock is competent Precambrian metamorphic rock that transmits little groundwater flow in comparison to the shallow aquifer. Groundwater temperature ranges from 2 ^{o}C in late winter and following spring recharge to 15 ^{o}C in late summer and early fall.

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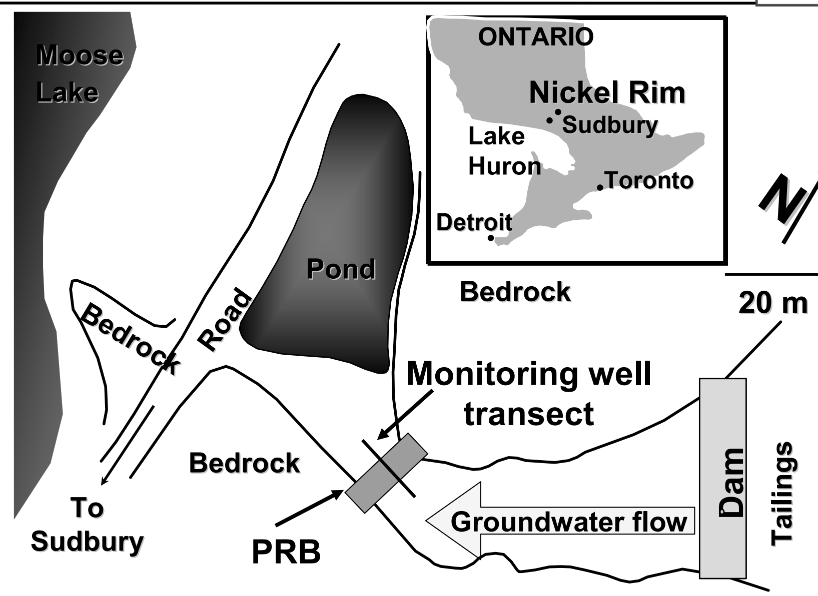
Site Plan for PRB at Nickel Rim Mine



PRB location and setting:

- Nickel Rim Mine near Sudbury, Ontario
- acid-mine drainage plume migrating through subsurface from tailings
- Silty fine sand aquifer in shallow bedrock valley
- PRB mid-way between mine tailings and receiving surface water
- PRB installed across narrowest part of valley (~15 m)

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PRB Construction

- Backfilled trench; unsupported excavation
- Reactive materials (40 % municipal plant compost, 40 % leaf mulch, 19 % wood chips, 1% limestone) mixed 1:1 with gravel
- 15 m long, 4 m deep and 8 m thick including sand zones
- Cost for materials and installation approximately $35 K (US) in 1995
- Benner et al., 1997; 1999; 2002

Construction of PRB:

- Unsupported backfilled trench
- Track-mounted excavator for construction and placement of materials
- Reactive material bounded up- and down-gradient by sand
- Reactive mixture (compost, leaf mulch, wood chips and limestone mixed with gravel (1:1 by volume)

For additional information on PRB construction see document section 4.2.

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Installation of Nickel Rim PRB

Picture of installation

View from base of tailings dam towards lake. Groundwater flow is from left corner of slide towards lake. Slide shows backfilling of trench with reactive materials and sand. The trench extended to the bedrock surface. Evidence of tailings material and oxidized iron in sediments down-gradient of PRB. Water table in vicinity of PRB is very close to ground surface.

Picture provided by S. Benner.

For additional information on PRB construction see document section 4.2.

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Nickel Rim PRB

Picture of installation

Backfilling of PRB trench is almost complete. Picture shows reactive mixture (organic carbon and gravel) bounded by sand zones. Sand zones are approximately 2 m in thickness. Reactive-mixture zone approximately 4 m in thickness.

Picture provided by S. Benner.

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Nickel Rim PRB

Picture of installation

Installation of PRB is almost complete. The picture shows placement of clay cap on top of reactive materials to minimize infiltration of precipitation. As moisture content of clay cap increases, the cap also serves as a barrier to the diffusion of oxygen into the reactive mixture. Sulfate reduction requires oxygen free conditions.

Picture provided by S. Benner.

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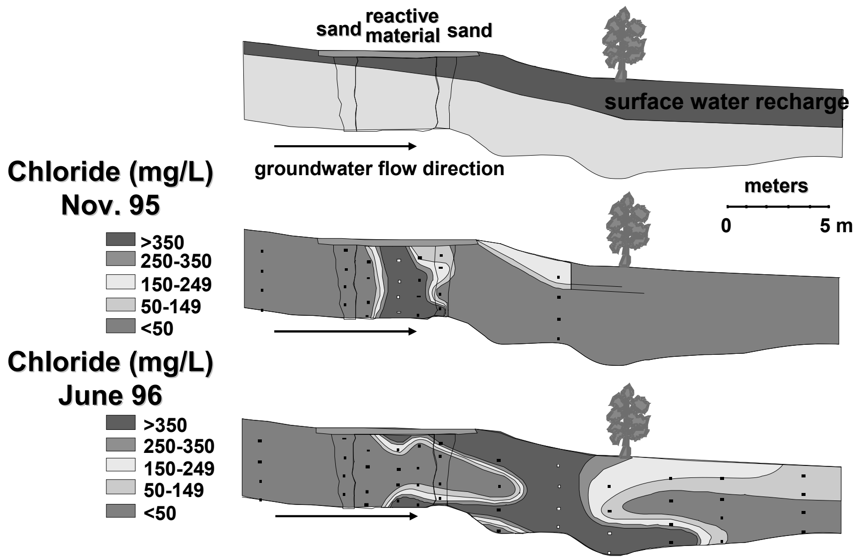
Groundwater Flow



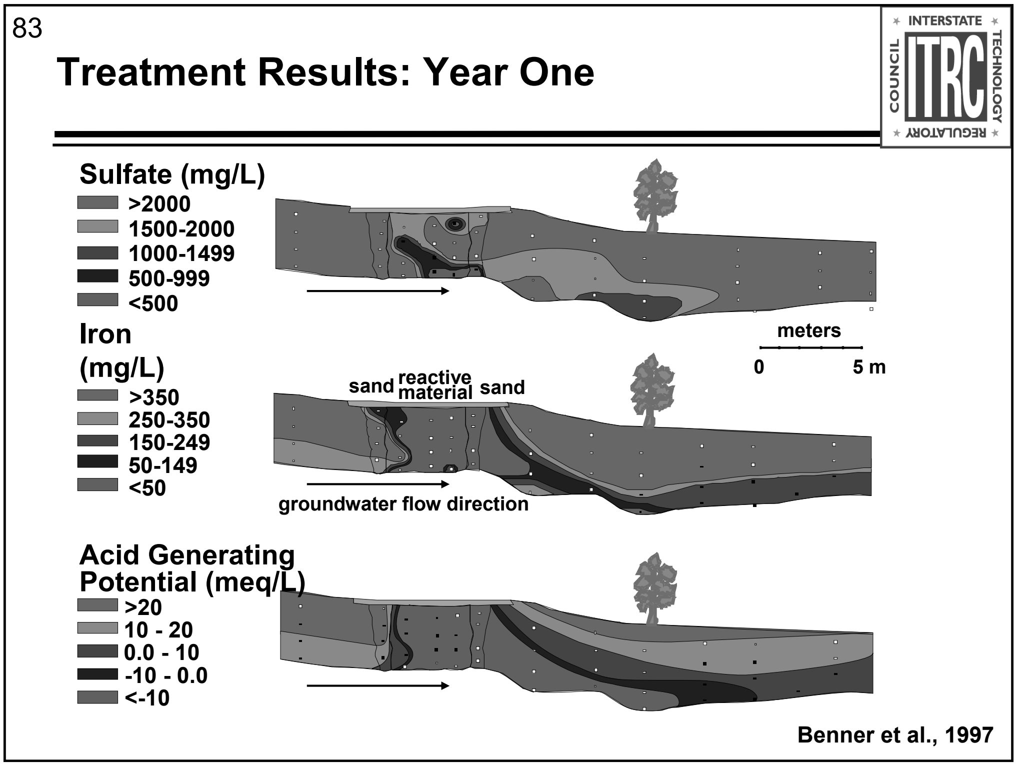
Benner et al., 1997

Monitoring of PRB performance

Three transects of multi-level monitors up-gradient, within and down-gradient were used for groundwater sampling purposes.

The acid-mine drainage-impacted plume contained low concentrations of chloride. The dissolution of chloride from organic carbon mixture in PRB during initial year of monitoring provides acted as a tracer for groundwater flow. Groundwater velocity estimated to be ~16 m per year. Minimum residence time in PRB estimated to be approximately 60 days. The preferential removal of chloride from the central zone indicated that groundwater flow was higher, and the residence time of groundwater lower, in this portion of the PRB.

Down-gradient of the PRB, evidence for low-chloride recharge water from the ground surface is shown. Acid-mine drainage impacts of overland surface water flow and of precipitation from shallow aquifer sediments continues to influence shallow groundwater quality.



Treatment results approximately one year after installation of PRB

Distribution of sulfate and iron within and in the vicinity of the PRB after one year of performance.

Removal of as much as 2,000 mg/L sulfate and more than 300 mg/L iron.

Addition of alkalinity (sulfate-reduction process, carbonate in sand and gravel) and removal of Fe^{2+} causes plume groundwater to be acid-consuming rather than acid-generating. Down-gradient flushing of existing contamination is long-term process. The PRB was installed within the limits of an existing plume. To achieve impacts on the quality of groundwater discharge to surface water, a PRB location in proximity to the surface water would have been necessary.

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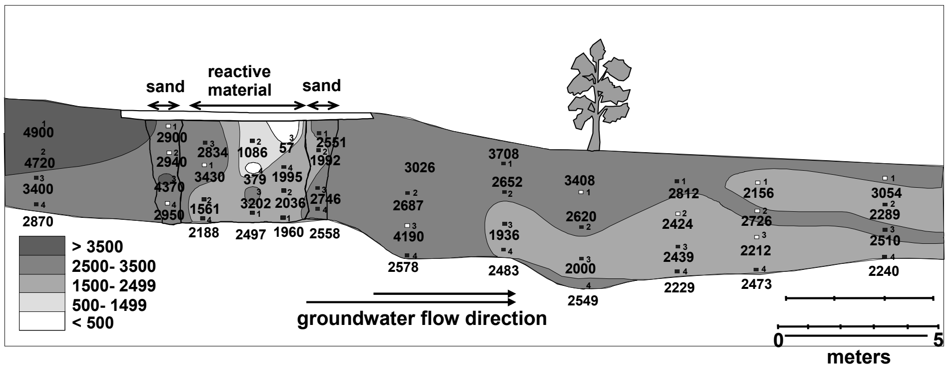
Treatment Results: Year Six

Sulfate (mg/L)
August 2001



Treatment performance after six years of operation

Sulfate removal of as much as 2,000 mg/L continues to occur six years after PRB installation. The concentration of sulfate entering the PRB has increased since installation as the plume of acid-mine drainage-impacted groundwater advances from beneath the tailings. The magnitude of sulfate removal characteristics has not changed significantly between the first and six year monitoring events.

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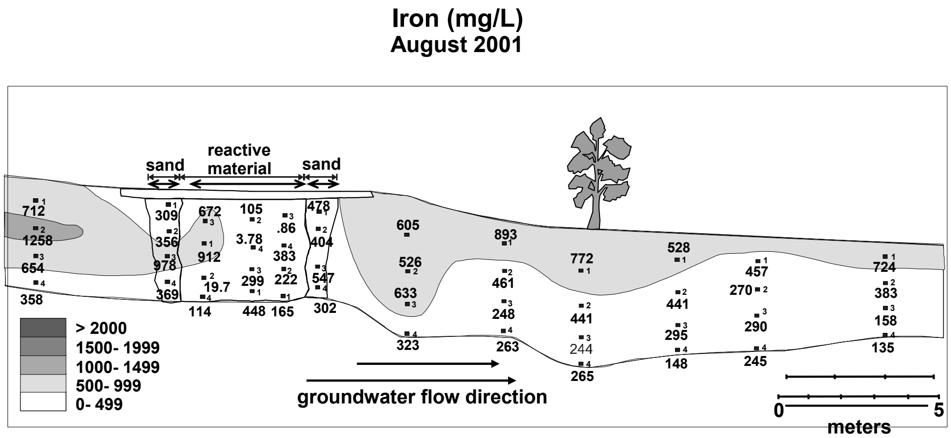
Treatment Results: Year Six



Treatment performance after six years of operation

Several hundred milligrams per liter of iron continues to be removed by PRB six years after installation. As plume of acid-mine drainage-impacted groundwater advances from the tailings, the concentrations of iron entering the PRB have Increased. The removal of iron continues to attenuate the acid-generating characteristics of the plume. Also, complete removal of iron feasible with thicker (longer residence time) PRB.

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Evidence for Sulfate Reduction in PRB

- Decreasing sulfate concentrations
  - >1,000 mg/L
  - >15 mg/L per day
- Enumeration of sulfate-reducing bacteria
- Dissolved sulfide present in groundwater
- Isotopic enrichment of ^{34}S in remnant sulfate
- Iron monosulfides identified in cores
- Continued accumulation of sulfides reflects sustained reactivity of the PRB over time
  - 1995-1997: 100 mmol/g per year
  - 1997-2001: ~100 mmol/g per year

Evidence for sulfate reduction

Loss of more than 1,000 mg/L in 60 day residence time; loss of more than 15 mg/L per day.

Sulfate-reducing bacteria populations have increased significantly within PRB relative to up-gradient and down-gradient locations.

Cores of solid materials contain iron monosulfide precipitates. The initial precipitates tend to have an amorphous crystalline form.

Herbert, Jr., R.B., Benner, S.G. and Blowes, D.W., 2000. Solid phase iron-sulfur geochemistry of a reactive barrier for treatment of acid mine drainage. *Applied Geochem.,* 15: 1331-1343.

Herbert, R., Benner, S.G., Pratt, A.R. and Blowes, D.W., 1998. Surface Chemistry and morphology of poorly crystalline iron sulfides precipitated in media containing sulfate-reducing bacteria. *Chem. Geol.,* 144: 87-97.

The rate of accumulation of iron monosulfides does not decrease appreciably over a six-year period.

Daignault, E., Blowes, D., and Jambor, J., 2003. The solid-phase sulfur speciation of metal sulfides in a permeable reactive barrier, Nickel Rim Mine, Sudbury, Ontario. In Proceedings of *Sudbury 2003: Mining and the Environment*, Sudbury, Ontario, May 25-28, Abstract (Session 3C).

Reactivity persists in PRB. Reactivity is related to ability of materials to continue to release organic carbon for sulfate reducing bacteria. Remedial reactions are unlikely to plug PRB because precipitates will tend to be higher density (smaller volume) than the organic carbon compounds being consumed or replaced.

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Summary of Nickel Rim PRB

- The reactive wall has removed significant portion of the dissolved iron from the plume; full treatment would have required thicker PRB with longer residence time
- PRB has reduced flux of contaminants in groundwater; reduced acid-generating potential of groundwater in receiving surface water
- Significant contaminant removal continues
- Heterogeneities: high groundwater velocity zone with shorter residence time
- Influence on carbon release from reactive materials
- Reactivity of other carbon sources
- Influence of temperature

PRB has achieved very significant treatment of concentrated acid-mine drainage-impacted groundwater. Sulfate reduction and the precipitation of iron sulfide minerals are the key remedial mechanisms. Sulfate reduction can be used to remove other metals and metalloids such as arsenic from groundwater.

Although a very significant reduction in contaminant load and acid-generating potential of the plume has been achieved, a thicker PRB creating longer residence time of groundwater within reactive zone would have enabled complete removal of iron to be achieved.

Significant remedial reactions continue almost a decade after installation.

This application of the technology has indicated that heterogeneities within the reactive mixture can contribute to the development of preferential flow zones. Preferential consumption of reactive carbon material can be expected to occur in these zones. More consistent hydraulic characteristics could be achieved with higher gravel content.

The continued release of organic carbon for sulfate reducing bacteria influences long-term performance of the PRB. A combination of reactive materials is likely to provide short-term release of dissolved organic compounds to stimulate initial sulfate reduction activity and slow-release of organic compound to support sulfate reduction in the longer term.

The rate of sulfate reduction is temperature dependent. In settings such as Sudbury, where groundwater temperature fluctuates between 2 and 15 ^{o}C, sulfate reduction can support sufficient removal of contaminants from groundwater to achieve remedial objectives. Groundwater temperature will influence the design thickness (residence time) for a PRB system to achieve treatment .

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Summary and Conclusions

- Complete and accurate site characterization is necessary for successful deployment of a PRB
- Performance assessment should include hydraulic, geochemical, and microbiological evaluation
- PRBs have been deployed at over 200 sites
- Other reactive materials such as zeolite, limestone, carbon sources, and phosphates have been deployed for use in PRBs and show promising results
- PRBs have been shown to be cost effective in relation to conventional technologies

Additional Summary Points

Seasonal variations in groundwater flow and temperatures can affect the performance of the PRB and need to be accounted for in the design.

In addition to recognizing the need for detailed hydrogeologic characterization, lessons learned from previous applications need to be incorporated into the design and construction of PRBs. These lessons include preventing zones of reduced permeability during construction and minimizing the variability in packing of the reactive material. Zones of reduced permeability or deflected flow can result from the use of sheet piling in incompatible geologic conditions, improper maintenance of biopolymer, and improper placement of reactive material through the biopolymer.

Deployment of PRBs has been enhanced in recent years through the installation techniques utilizing bioslurry and vertical hydraulic fracturing. This innovation has resulted in the installation of PRBs that are longer, thinner, and deeper. By using biopolymer for trench support, PRBs can be installed to depths of 90 feet and thickness exceeding 10 feet. Vertical hydraulic fracturing has been used to install PRBs to depths as great as 117 feet.

Research has shown that zero-valent iron PRBs can be expected to last an estimated 10–30 years depending on the rate of flow through the system and the levels of total dissolved solids.

Areas where additional research or development is needed

Monitoring of the performance of the PRB is difficult where the downgradient plume is contaminated with residual contamination when the PRB is installed. Better monitoring techniques are necessary for monitoring performance in this situation. A better understanding of estimating the time necessary for desorption and flushing of the downgradient residual contamination is needed.

Better means of identifying hydraulic performance of a PRB is needed due the current limitations with measuring groundwater head measurements over the short distance of a PRB system.

Research on the regeneration or replenishment of reactive media is necessary. Replenishment of media has the potential to further reduce the long-term operation and maintenance associated with this technology.

Research and development is needed on source zone treatment using iron as a reactive media.

Additional summary and conclusion data can be found in section 11 of the document.

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Thank You for Participating

- **Links to additional resources**
  - **http://www.clu-in.org/conf/itrc/prbll/resource.cfm**
- **2nd question and answer session**

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For more information on ITRC training opportunities and to provide feedback visit: **www.itrcweb.org**

Links to additional resources

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http://www.clu-in.org/conf/itrc/prbll/

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