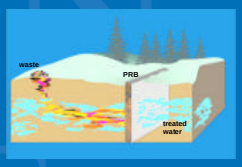
Permeable Reactive Zones for Groundwater Remediation

Richard T. Wilkin, Ph.D.



Office of Research and Development
National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, Ada, OK

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NARPM

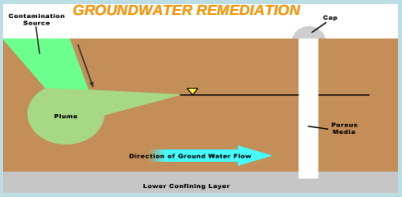
Outline of Topics

- Technology Background
- Field Case Examples – focus on COCs
  - Zerovalent Iron (Cr, TCE, As)
  - Organic Carbon (NO_3, Pb, pH)
  - Mechanisms
- Summary Remarks

1

Permeable Reactive Zones

Zerovalent Iron: Solvents, Inorganics



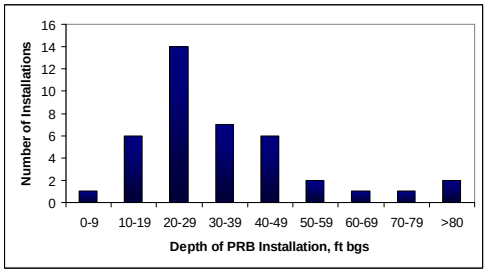
Advantages

- Subsurface Treatment
- Plume capture complete
- Passive treatment
- Lower costs/P&T
- Adaptable
- Focused monitoring

Limitations

- Greater capital investment
- Longevity concerns
  - Treatment performance
  - Hydraulic performance
    - ✓Cr, TCE
    - ✓As?

Depth of PRZ Installations



3

PRB Research at EPA

- **Long-term performance evaluations at full-scale zero-valent iron and organic carbon-based reactive barriers**
  - Geochemical-Hydrologic-Microbiological -
- **Pilot demonstrations to examine new applications of the technology (*e.g.*, Arsenic, Lead)**
- **Laboratory studies that explore fundamental geochemical processes important in PRBs**
- **Technical Assistance**

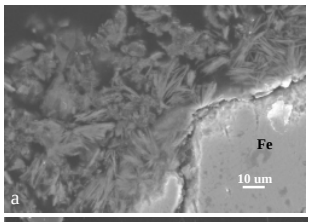
4

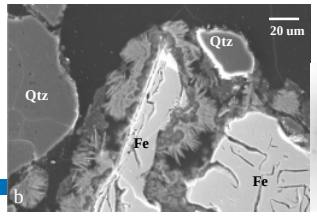
Iron/Water/Contaminant Interactions

- **Increase in pH (~10), Decrease in Eh (<-400 mV), Increase in H_2**

- Dissolved O_2 scrubbed => FeOOH, adsorption
- Precipitate metal hydroxides
- Metal plating reactions (Hg)
- Precipitate Ca and Fe carbonates
- Microbiology: Sulfate-reducers
Precipitate Fe sulfides, Me sulfides
- Fe^0 => Green Rust => Magnetite

5



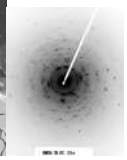


Role of Secondary Precipitates

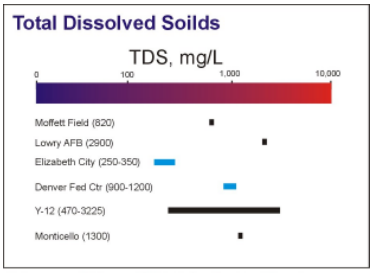
Pore infilling – hydraulics
Coat ZVI surfaces – reactivity
Creates secondary reactivity

Govern long-term performance
Control degradation mechanisms

Can be predicted!

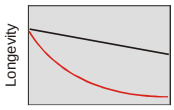


SEM/TEM



Data source: Tri-Agency PRB Initiative, Combined Report

Total Dissolved Solids



ZVI Examples

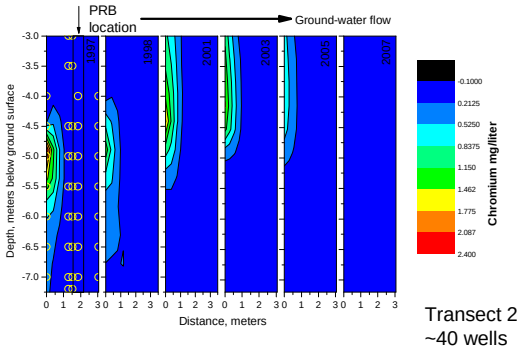
Elizabeth City, NC

Cr and TCE
Full scale installed in 1996
150 ft length, 2 ft wide, 25 ft deep
Trencher

East Helana, MT

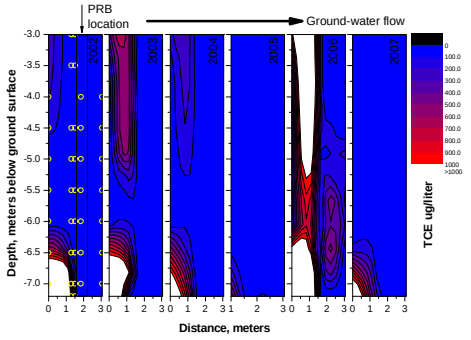
As
pilot-scale installed 2005
30 ft length, 6 ft wide,
45 ft deep
Long-arm excavator

Chromium – Elizabeth City

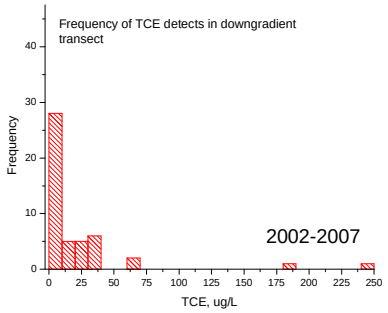


Transect 2
~40 wells

TCE – Elizabeth City

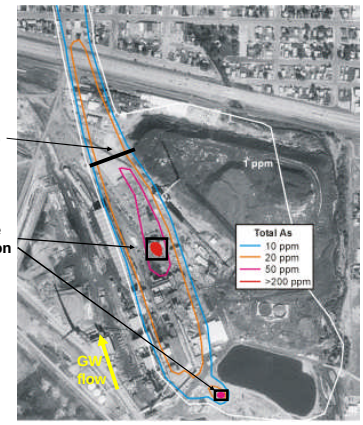


TCE – Downgradient of PRB



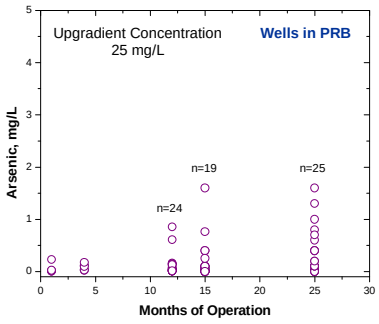
East Helena SF site

12



13

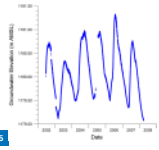
Arsenic Concentrations

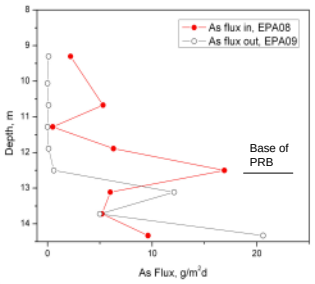


14

Arsenic Flux

- Discrete interval sampling, concentrations
- Discrete interval hydraulic conductivity determinations
- Continuous water levels/gradient, 3-point problem





15

East Helena Conclusions

- Zerovalent iron is effective for arsenic
- Arsenic removal mechanisms are complex
- Finite uptake capacity requires detailed site assessments
- Source control measures are desirable to reduce subsurface arsenic flux and maximize PRB lifetime

16

PRB Research: Carbon-Based Reactive Media

- **Arsenic: Columbia Nitrogen Superfund Site, Charleston, SC (Compost + Limestone + Iron)**
- **Lead: Delatte Superfund Site, Ponchatoula, LA (Cow Manure; Wood Chips, Limestone)**
- **Nitrate: Cimarron Pork hog farm, Stillwater, OK (Haystraw)**
- **TCE: Altus AFB, OK (Cotton Burr)**

17

Mechanisms in Carbon Systems

Media options
(Cost vs. Longevity vs. Reversibility)

- **Metals:**
  - **Sulfate reduction**
  - **Precipitation of CdS, ZnS, and PbS**
  - **Co-ppt/adsorption with FeS**
  - **Interactions with OC**
- **Degradation of nitrate/perchlorate**
- **Organics:**
  - **Abiotic pathways, iron sulfides**
  - **Biotic pathways**

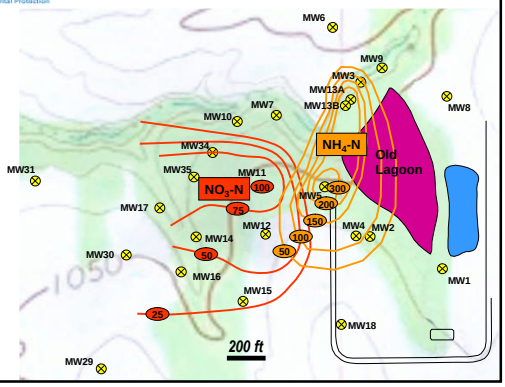
18

Background - Cimarron Pork

- *Concentrated Animal Feeding Operation site located in OK*
- *Facility in operation for approx. 7 y, closed in 1999; ground-water impact from leaking lagoon*
- *Ground water remediation strategy developed for separate ammonia and nitrate plumes*
- *Remedies implemented in late 2002 (site owner, OK Dept. Agriculture, EPA Region 6)*
- *EPA ORD began monitoring of Nitrate PRB in 2003*
  - *Performance evaluation*
  - *Longevity issues*

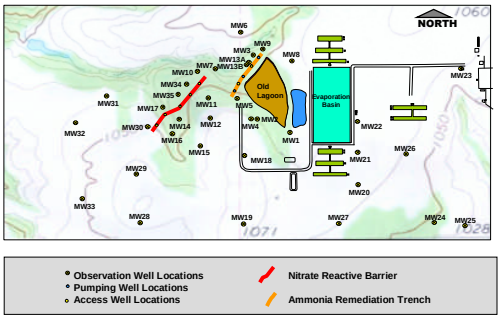
19

Contaminant Plumes



20

Site Remediation Plan

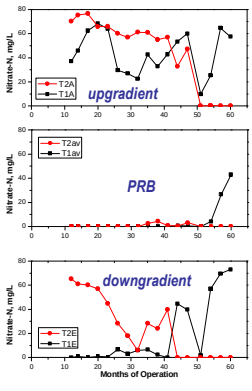


21

PRB Installation

22

Nitrate



- *Average % removal ranges from 10 (T1) to 91 (T2), based on influent & effluent*
- *Nitrate removal within PRB is 92 – 100%*
- *Transect 1 PRB wells show subtle increases in nitrate starting at 35 months; failure ~55 months*
- *Declining source term?*

23

Denitrification

$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2$

$2NO_3^-$	$2NO_2^-$	$2NO$	N_2O	N_2
Nitrate ions (+5)	Nitrite ions (+3)	Nitric oxide (+2)	Nitrous oxide (+1)	Dinitrogen gas (0)

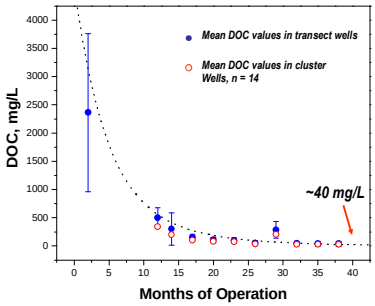
Dissimilatory Nitrate reduction to ammonia (under low electron acceptor conditions, i.e., C>>>NO_3^-)

$2NH_4^+$

24

Heterotrophic Denitrification

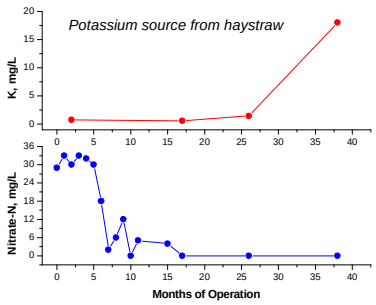
$5CH_2O + 4NO_3^- = CO_2 + 2N_2 + 3H_2O + 4HCO_3^-$



Decrease in capacity from ~2200 to 38 mg/L Nitrate-N To N_2 based on reaction stoichiometry

25

Downgradient Response MW34 – center location

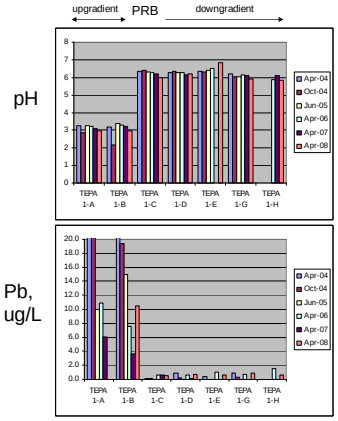


56 ft travel in 510 days

~ 0.11 ft/day Seepage velocity

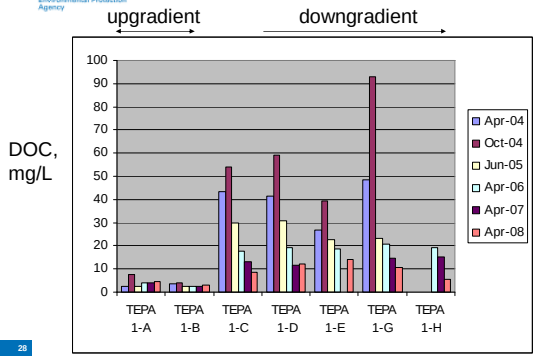
26

Delatte Metals PRB



27

Dissolved Organic Carbon - Performance



28

Summary Remarks

- Many case studies show consistent degradation of contaminants over years
- Need for coupling PRZs with source control measures
- Design for highest concentrations – flux based evaluations
- Site Characterization!
  - ZVI (ground water chemistry/hydrology)
  - Organic Carbon (DOC concentrations)
  - Flux based
- More information: wilkin.rick@epa.gov
  - (http://www.epa.gov/ada/publications/html)

29

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- **Dr. David S. Burden, Director(burden.david@epa.gov) 580-436-8606**

QUESTIONS ????