Performance Challenges Encountered with Permeable Reactive Barriers

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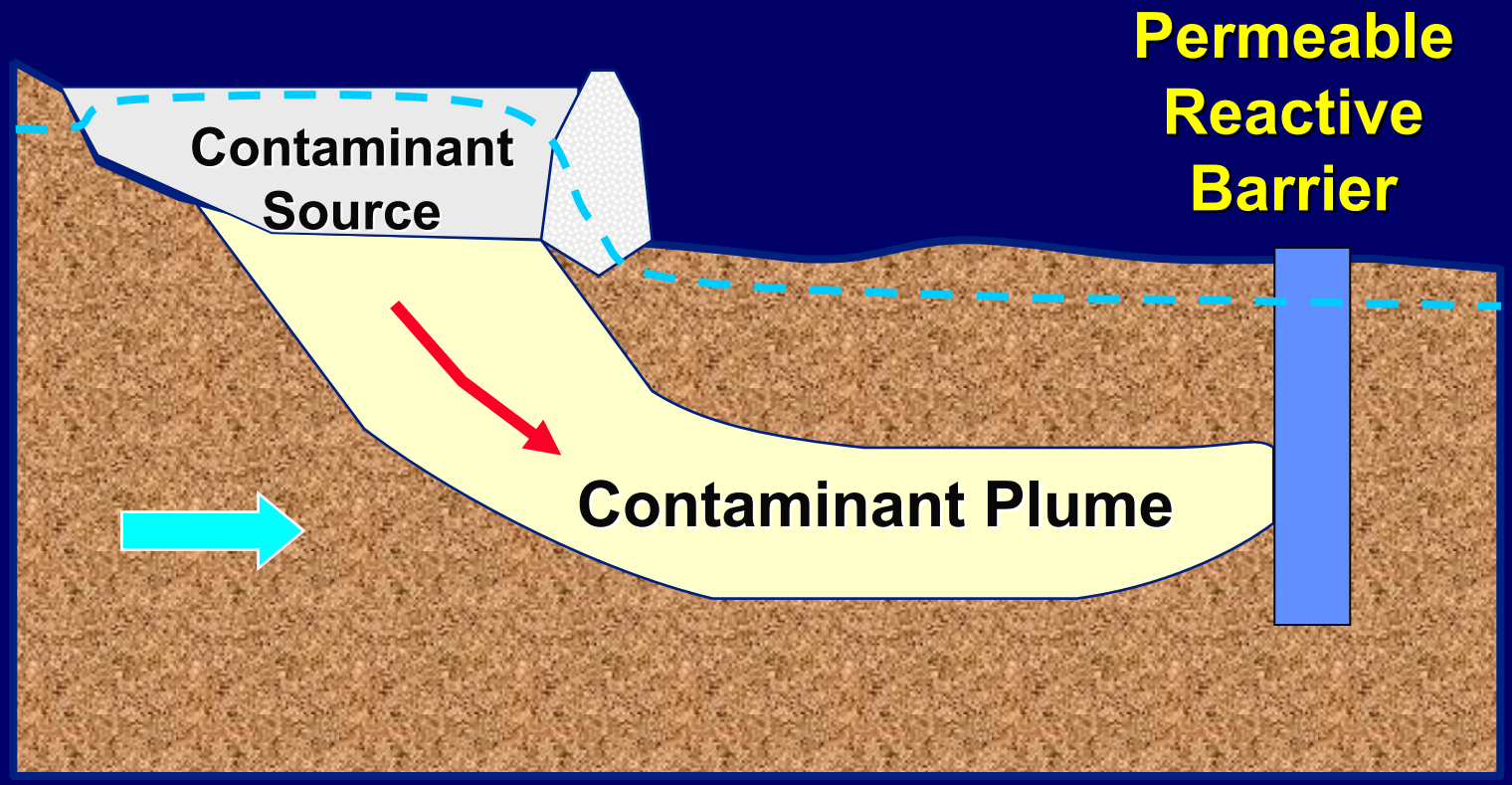
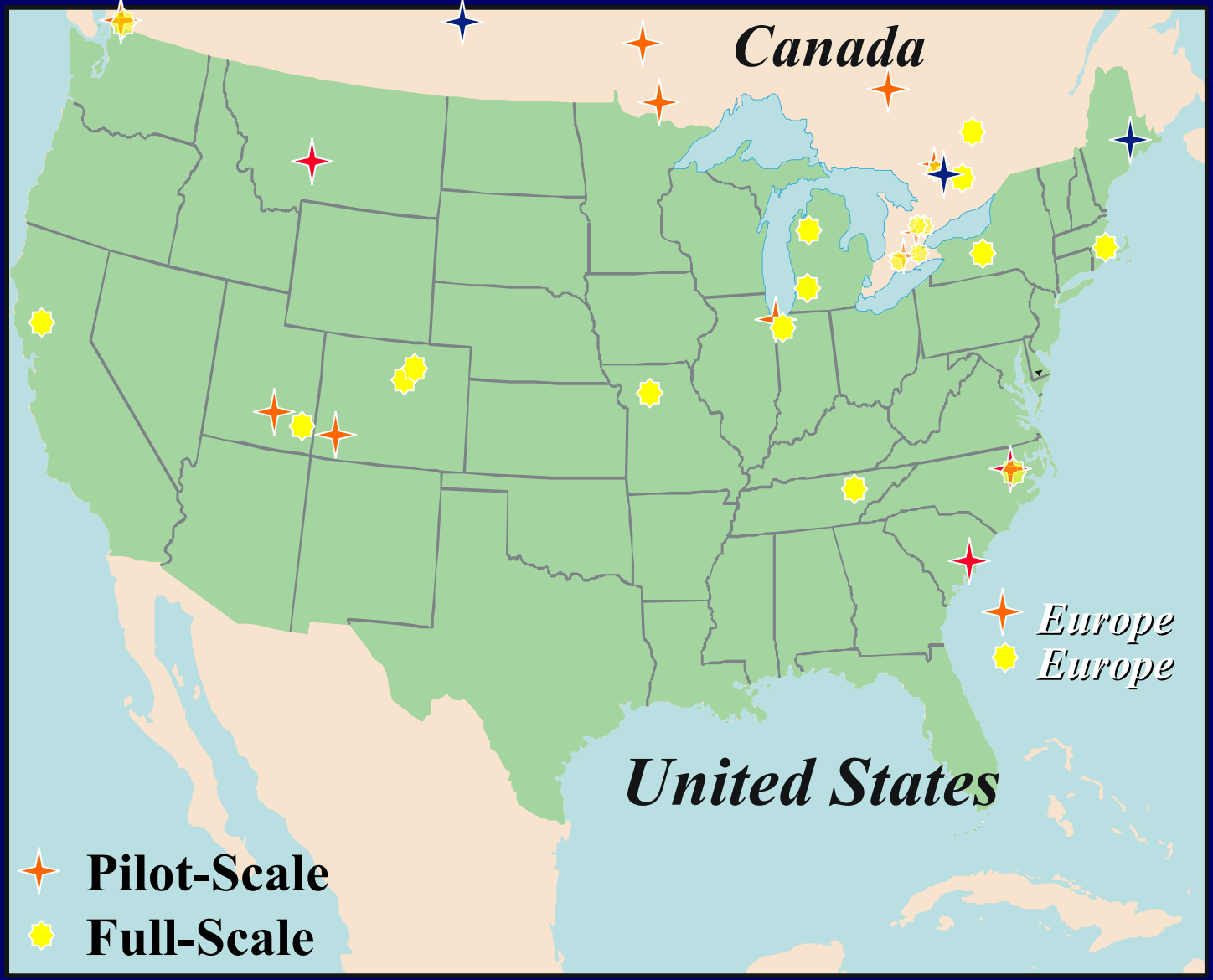
Permeable Reactive Barrier



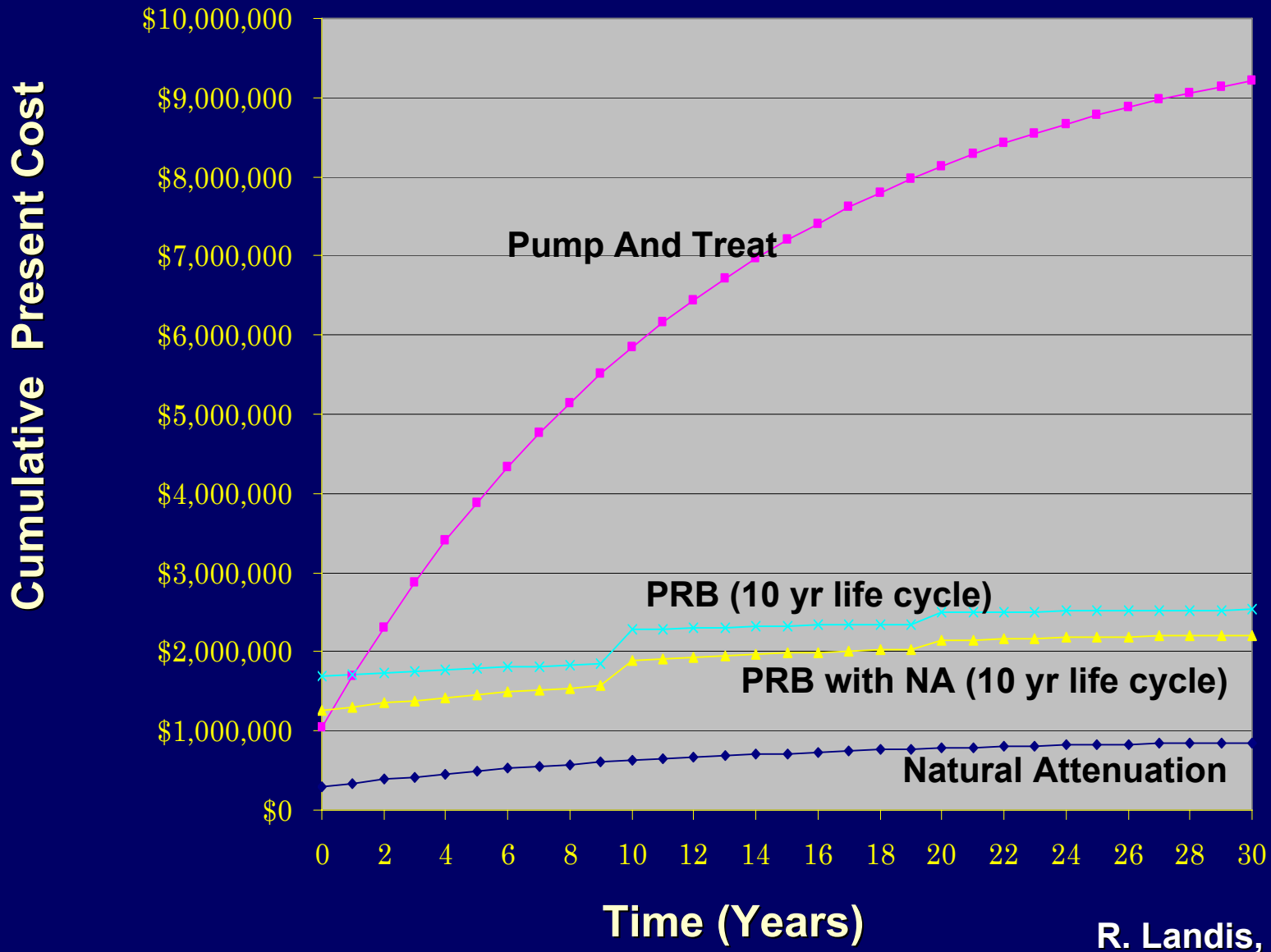
Reactive Barriers for Dissolved Metals and Inorganic Contaminants

- Designed to:
  - Change redox state of dissolved metal
  - Precipitate insoluble solids
  - Adsorb contaminants
- Objective:
  - Passive treatment consistent with the scale and duration of contamination problems
- Status:
  - Initial installations now in place for > 10 years

PRB for Treating Inorganic Contaminants

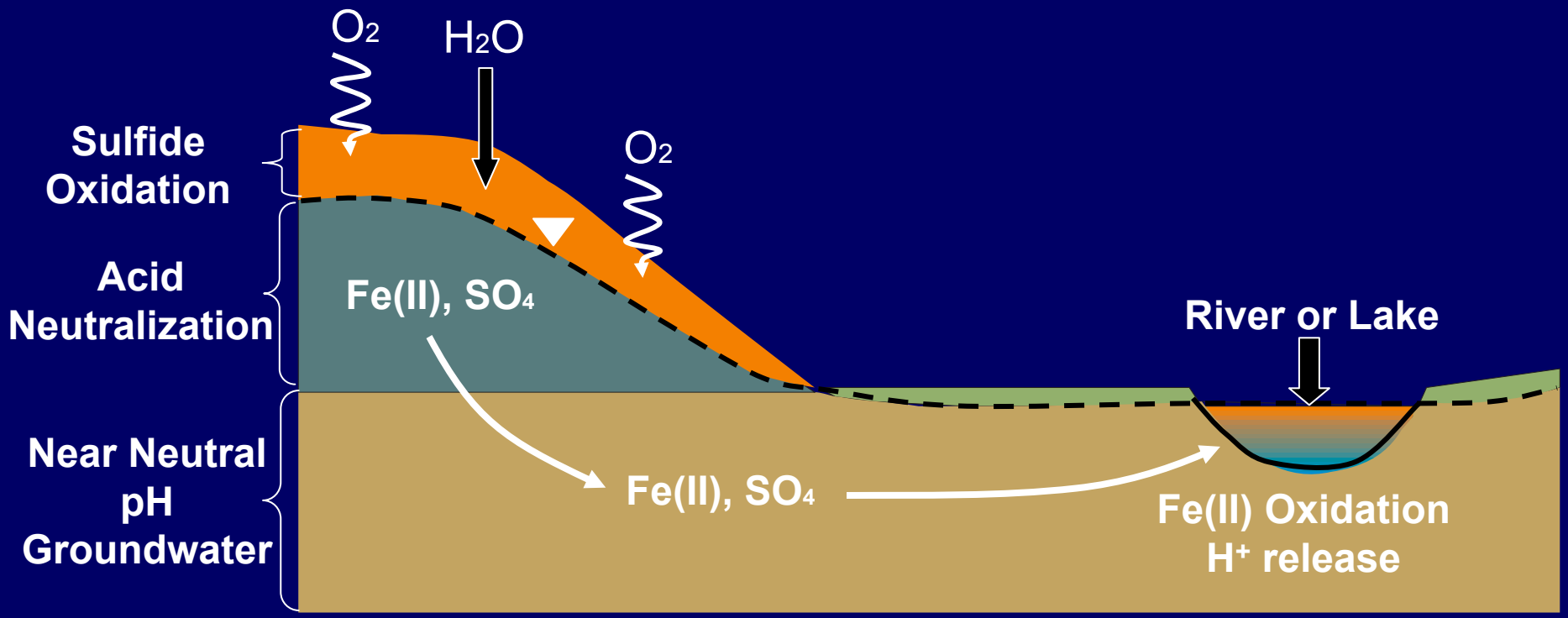


Typical Cost Comparison



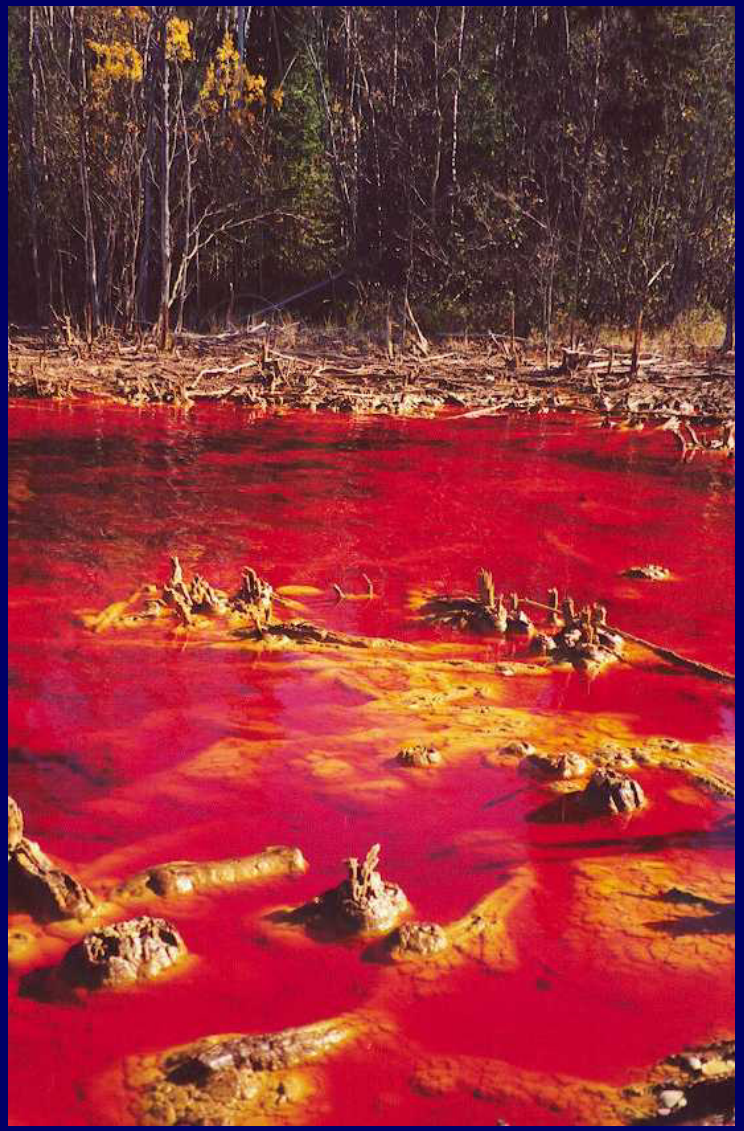
R. Landis, DuPont Inc.

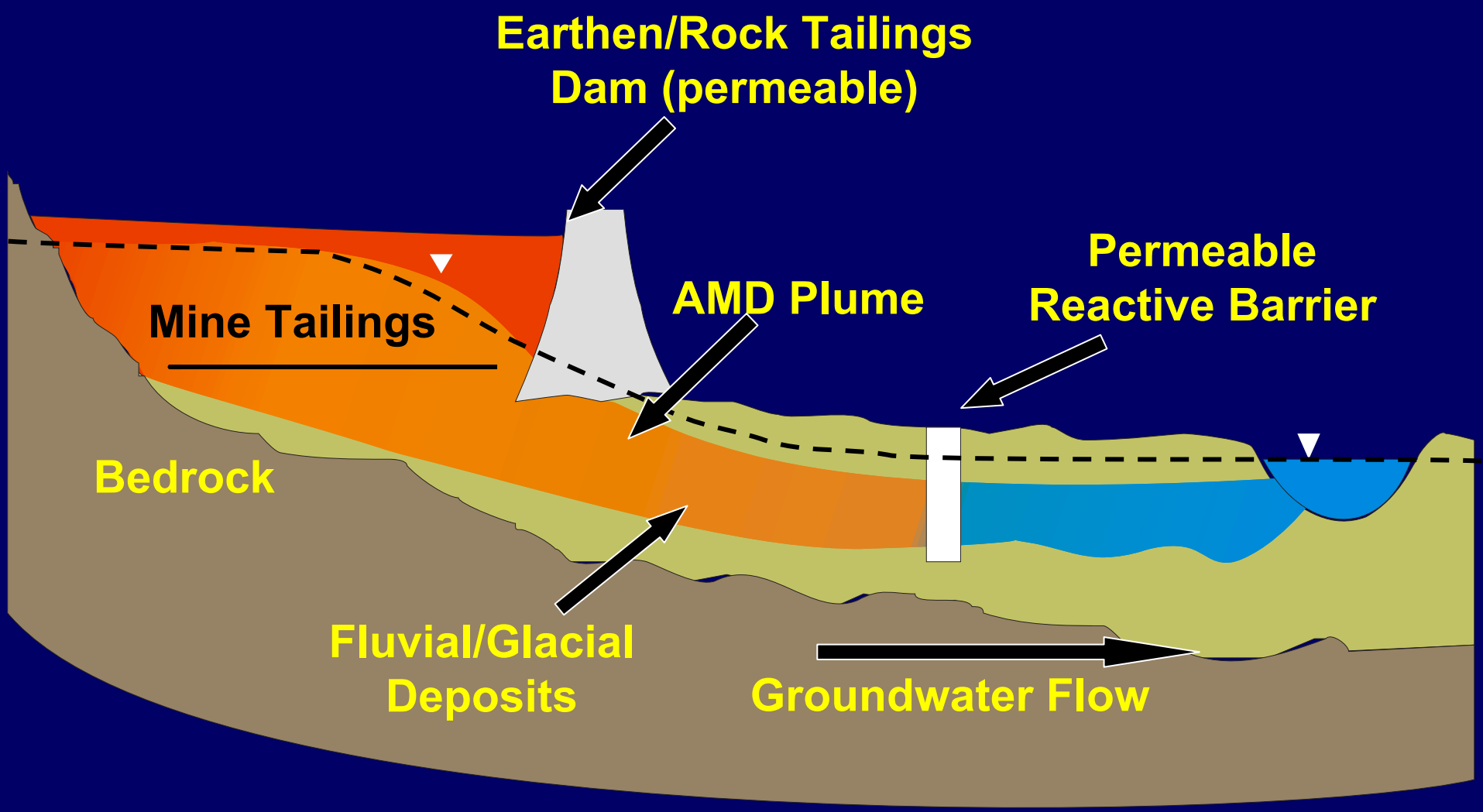
Mine Waste Sites



Sulfide Oxidation

Fe(II) Oxidation




Earthen/Rock Tailings
Dam (permeable)
Mine Tailings
AMD Plume
Permeable
Reactive Barrier
Bedrock
Fluvial/Glacial
Deposits
Groundwater Flow

Reactive Materials

Reduction and Precipitation

- Zero valent iron
- Organic carbon
- Mixtures

Adsorption

- Basic Oxygen Furnace (BOF) oxides and slags
- Zeolites

Construction Challenges

- Depth of plume
  - Most techniques limited to <100 m
- Infrastructure
  - Buildings, service corridors, utilities
- Regulatory approvals
- Land titles
- Cost

Implementation Challenges

- Inadequate site characterization
  - Poorly defined plume characteristics
    - Size, depth, concentration ranges
  - Insufficient characterization of aquifer properties
  - Incomplete data interpretation
- Unrealistic expectations
  - Overly pessimistic – high costs
  - Overly optimistic – incomplete treatment

Performance Challenges

Zero valent iron

- Residence time/high velocity
  - Exceed reaction rate limitations
- pH increase
- Excessive carbonate precipitation

  ⇒ Clogging

Contaminants Suitable for Treatment using Zero Valent Iron

- Chromium
- Selenium
- Arsenic
- Uranium
- Technetium
- Mercury
- Molybdenum
- Vanadium
- Other elements with lower solubilities in reduced forms

Treatment of Chromate-Contaminated Groundwater

Reduction:

$$8H^{+} + CrO_4^{2-} + Fe^{0}_{(s)} \Rightarrow Fe^{3+} + Cr^{3+} + 4H_2O$$

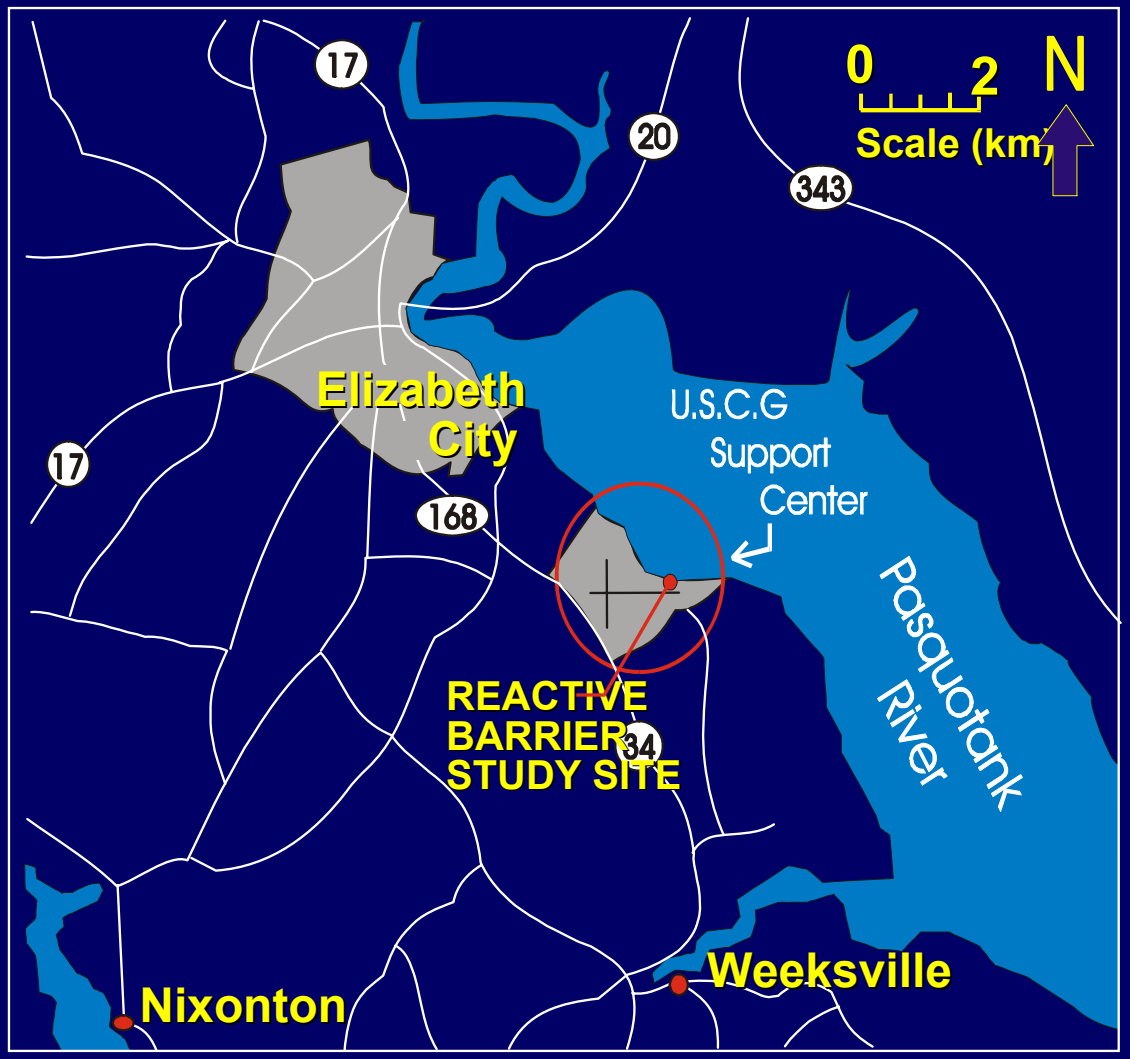
$$Fe^{0} + 2H_2O \Rightarrow Fe^{2+} + H_{2(g)} + 2OH^{-}$$

Precipitation:

$$Cr^{3+} + 3OH^{-} \Rightarrow Cr(OH)_{3\ (s)}$$

$$Cr^{3+} + Fe^{3+} + 3OH^{-} \Rightarrow (Fe,Cr)(OH)_{3(s)}$$

Elizabeth City Reactive Barrier

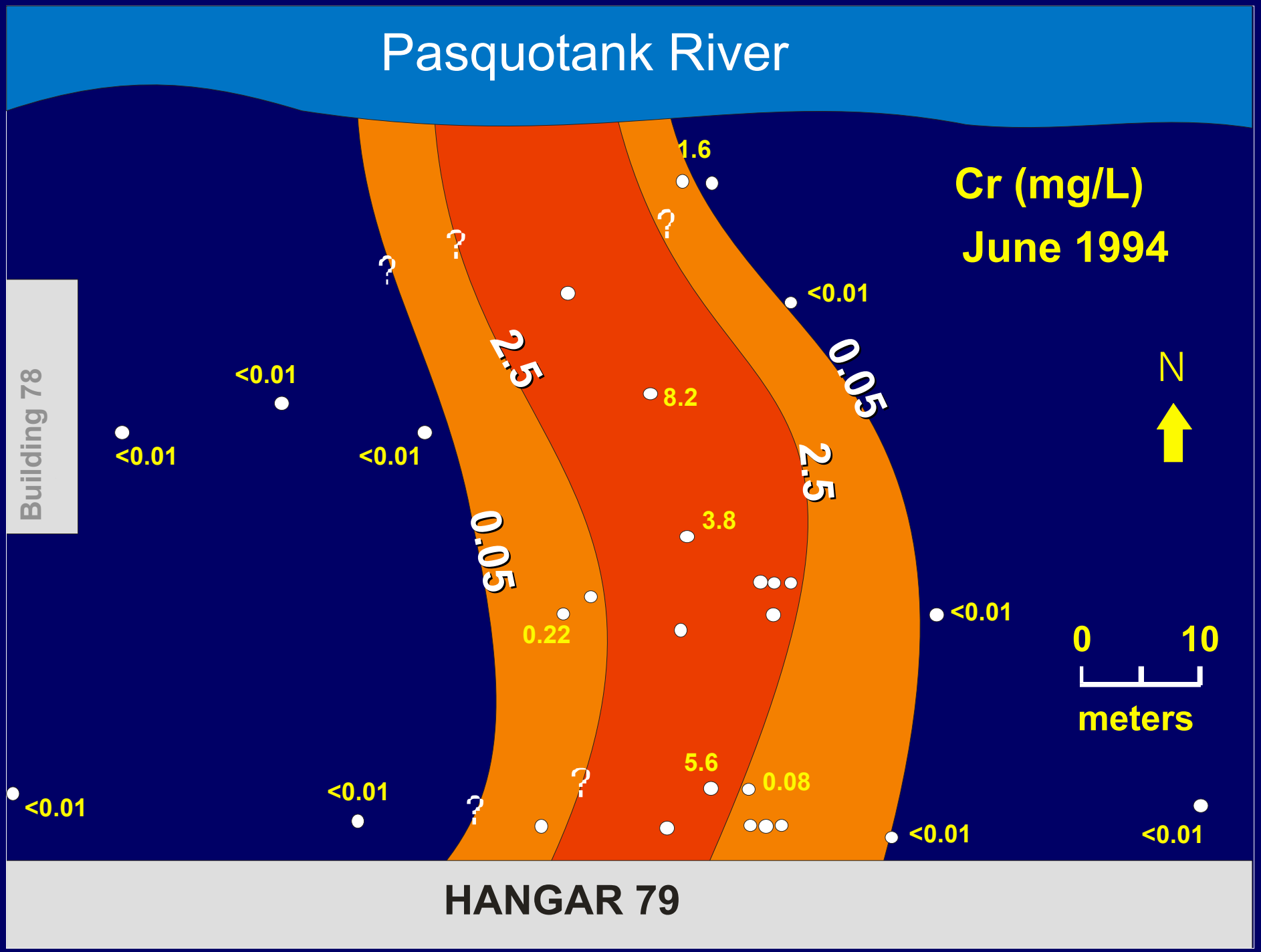


Installed: 1996

Collaborators

US EPA

US Coast Guard


Pasquotank River
Cr (mg/L)
June 1994
Building 78
HANGAR 79
N
0
10
meters
1.6
<0.01
<0.01
<0.01
<0.01
8.2
3.8
0.22
5.6
0.08
<0.01
<0.01
<0.01
<0.01
2.5
0.05
2.5
0.05
?
?
?
?
?
?

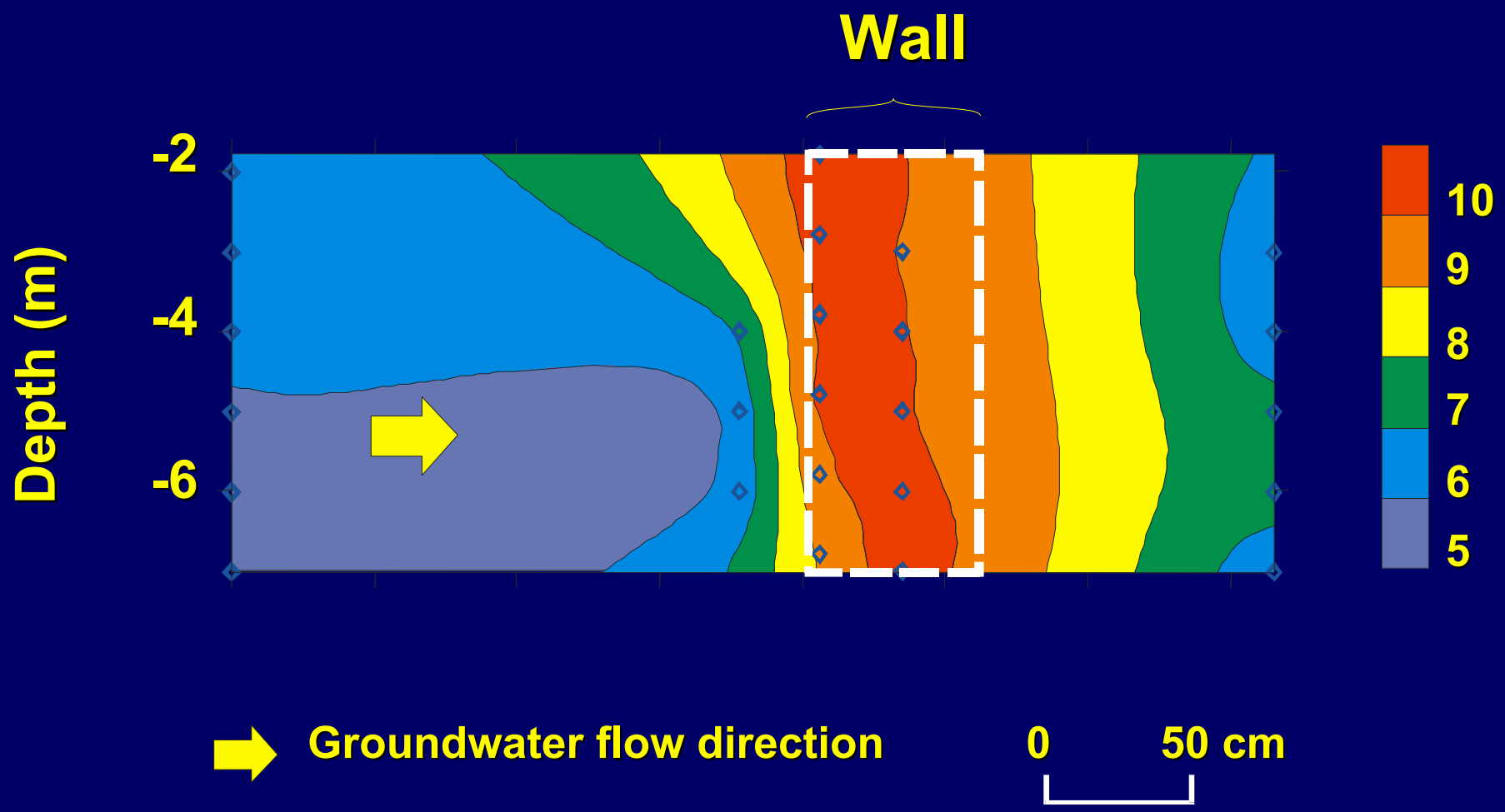
Reactive Material

- 150 m^3 zero valent iron (280 tons)
- 46 m long, 7.3 m deep and 0.6 m wide barrier

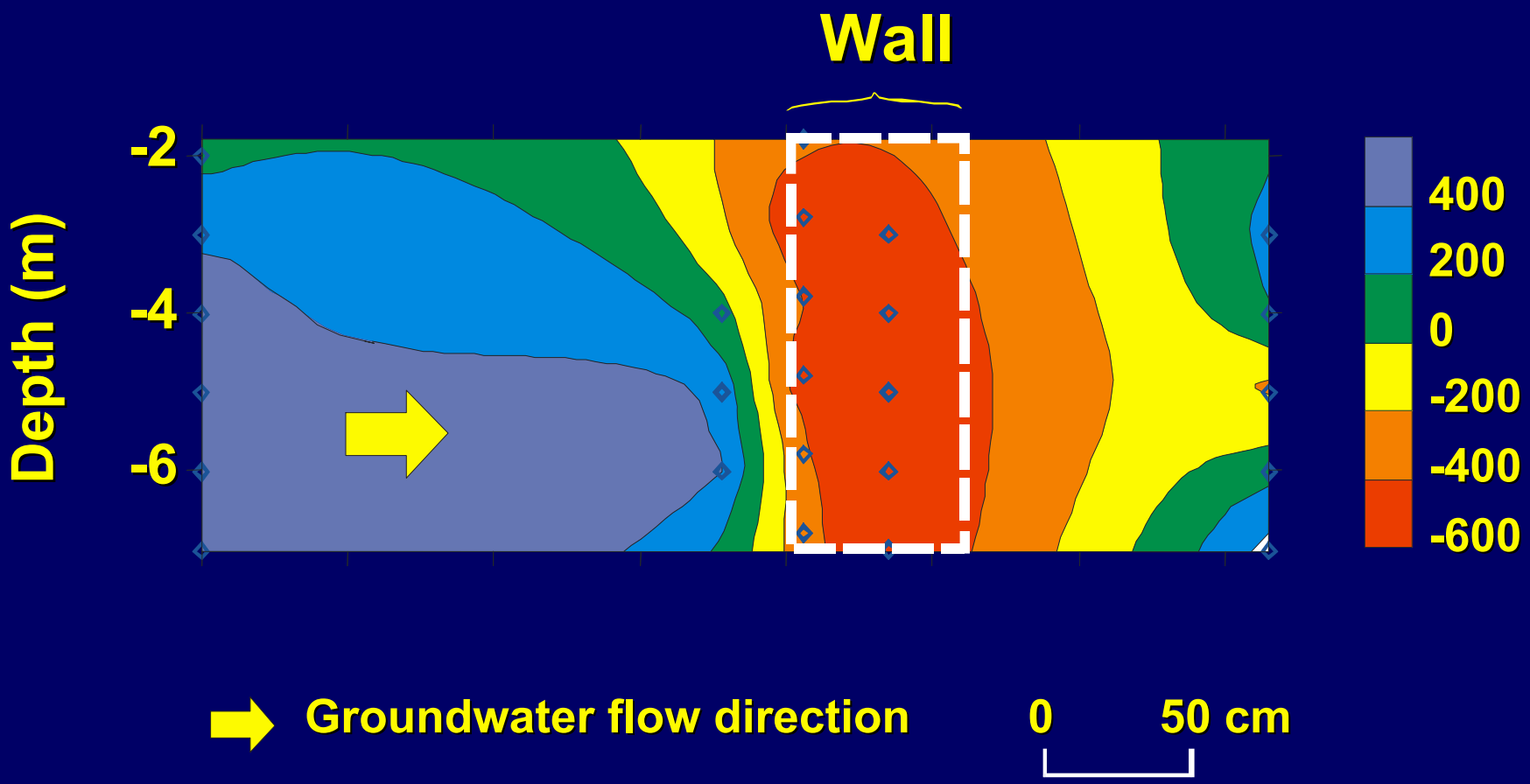
Continuous Trenching Machine

USCG Wall Installation

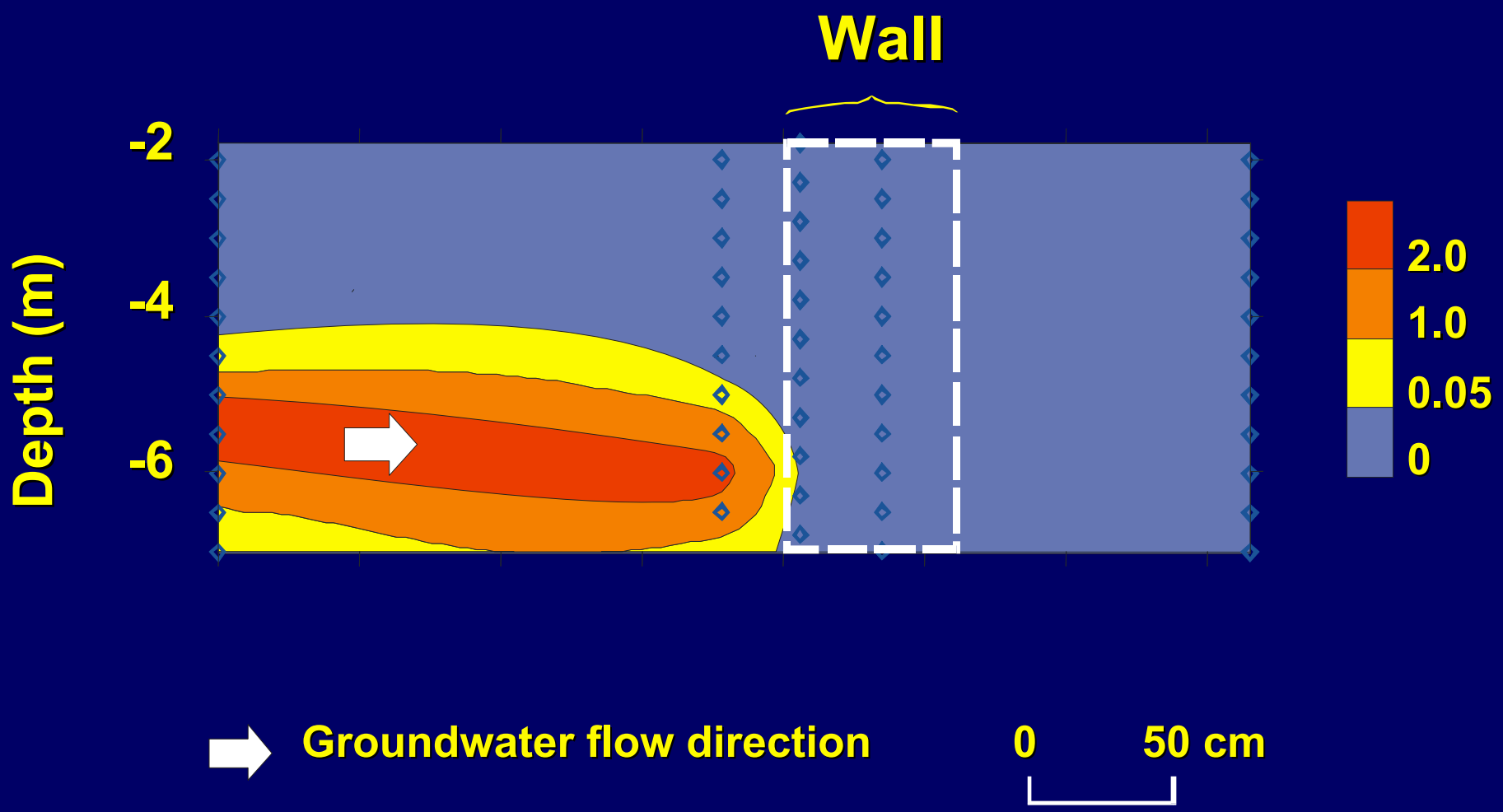
pH



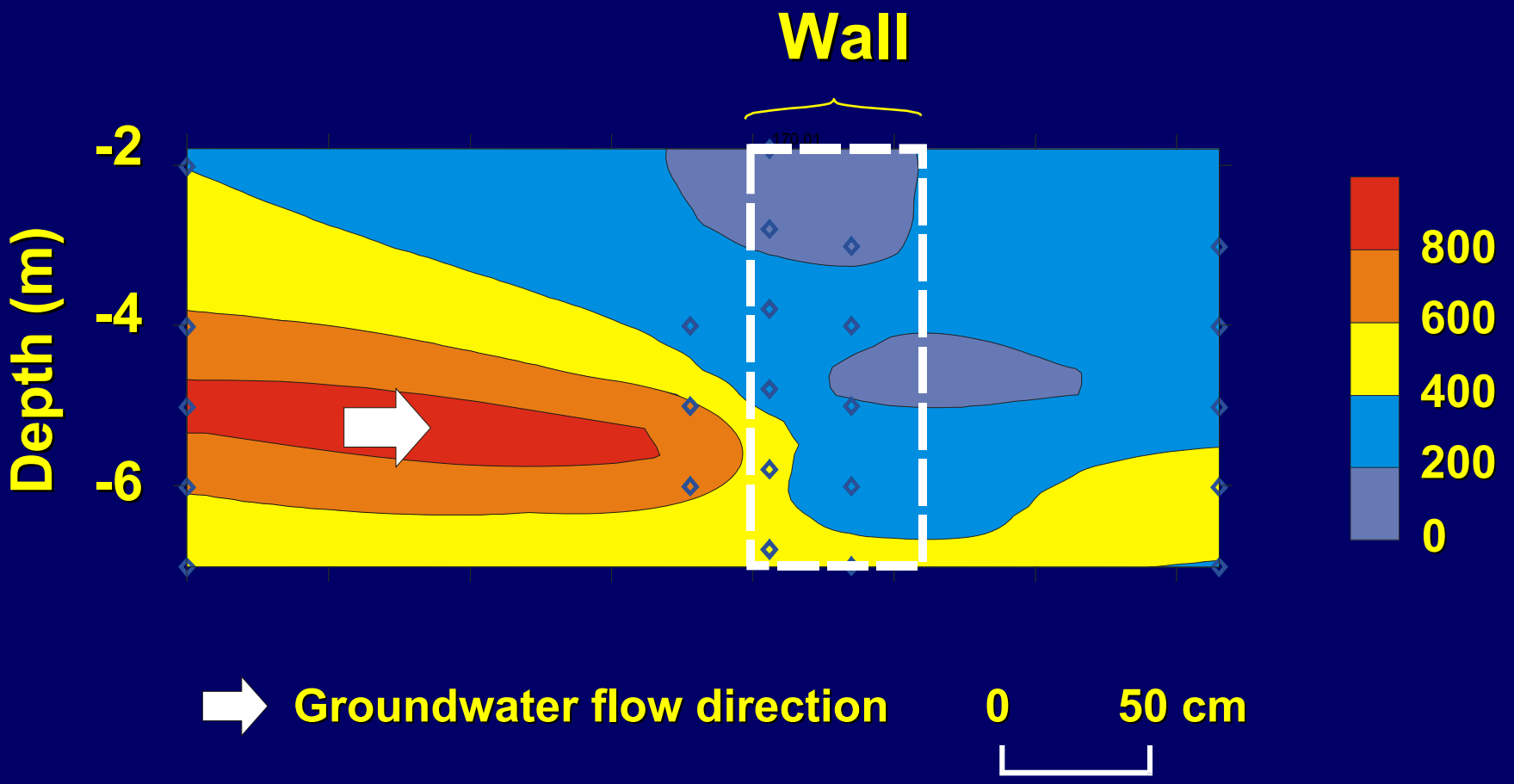
Eh (mV S.H.E.)


Wall
Depth (m)
-2
-4
-6
400
200
0
-200
-400
-600
Groundwater flow direction
0
50 cm

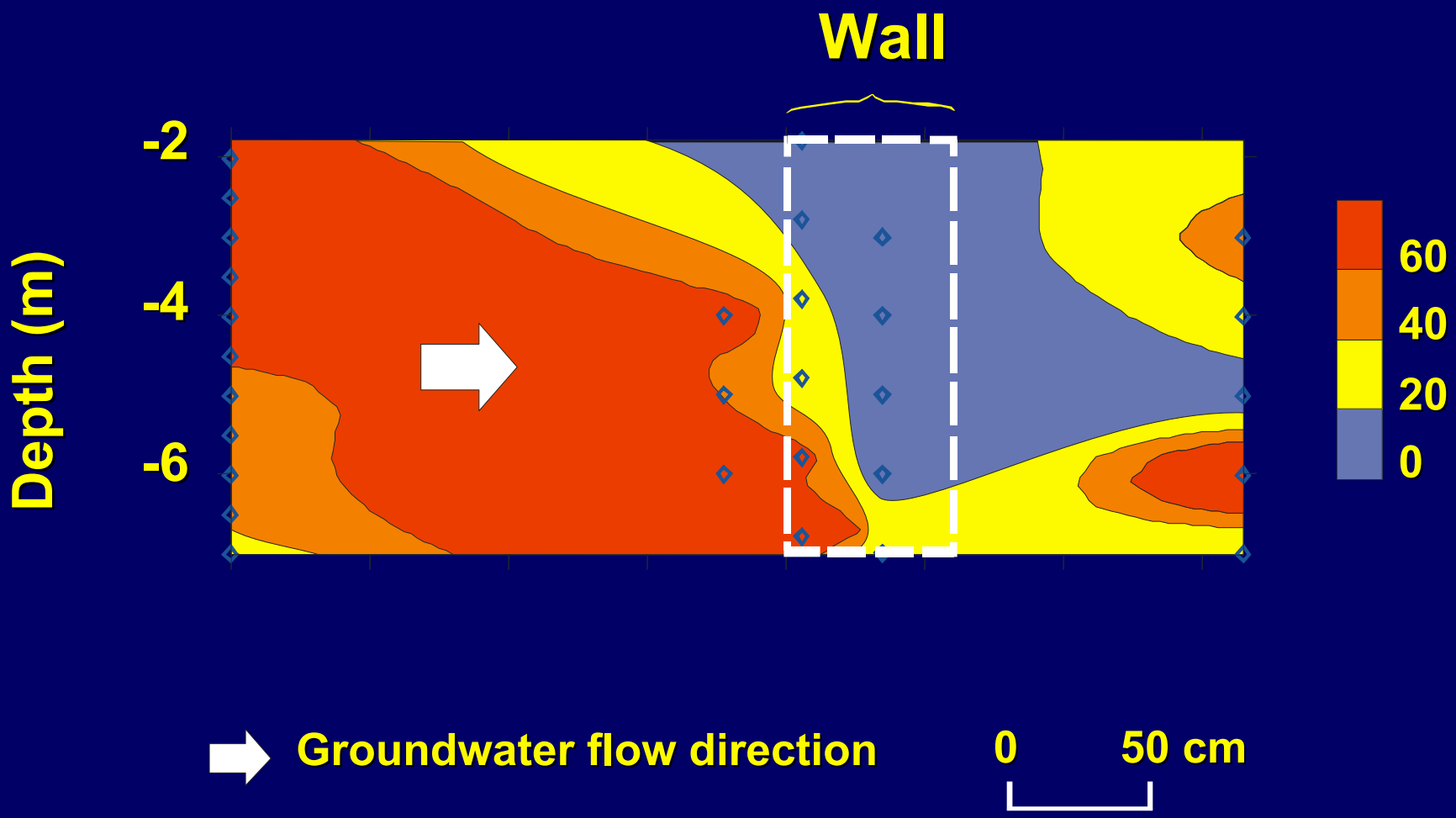
Cr(VI) (mg/L)


Wall
-2
-4
-6
Depth (m)
2.0
1.0
0.05
0
Groundwater flow direction
0
50 cm

Electrical Conductivity (µS/cm)

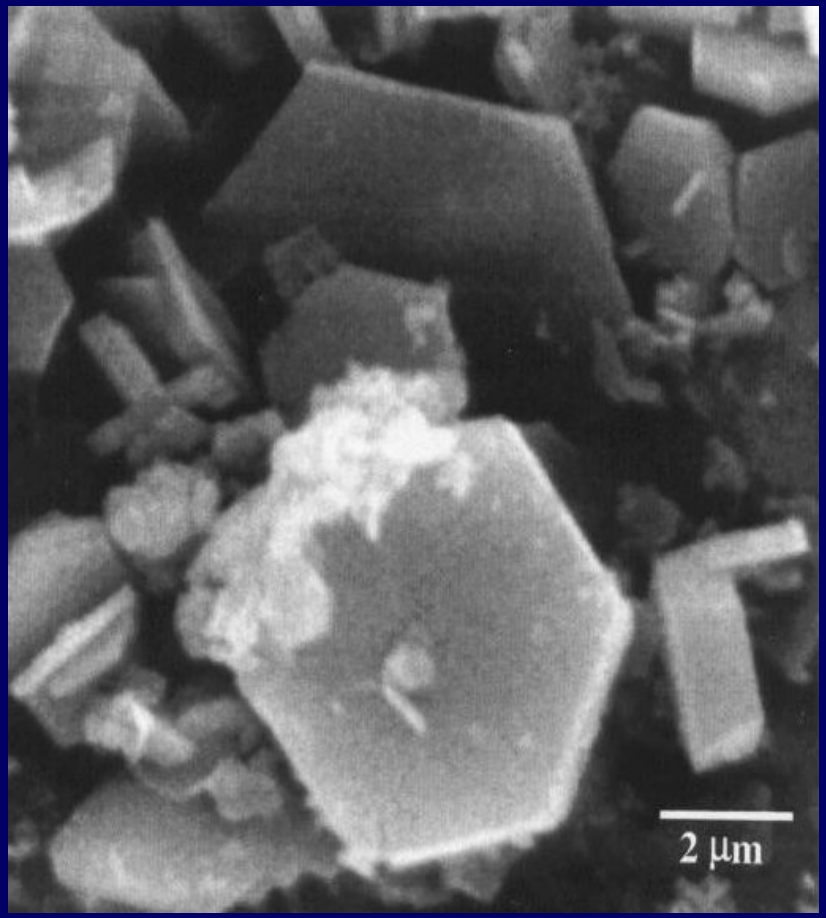


$CaCO_3$ (mg/L)



Mineralogical Characterization

- Increased solid-phase carbon
  - carbonate minerals isolated
  - $CaCO_3$
  - siderite ($FeCO_3$)
  - Fe Hydroxycarbonate
- Iron oxyhydroxides
  - goethite
  - ferrihydrite
  - green rust
- Iron Sulfides

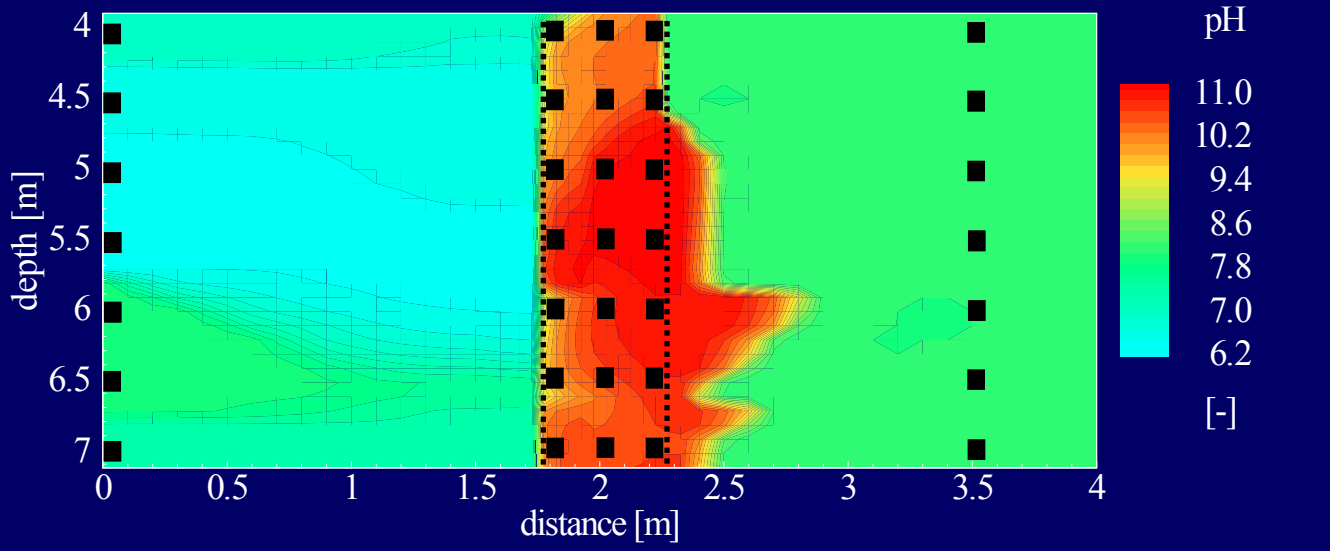


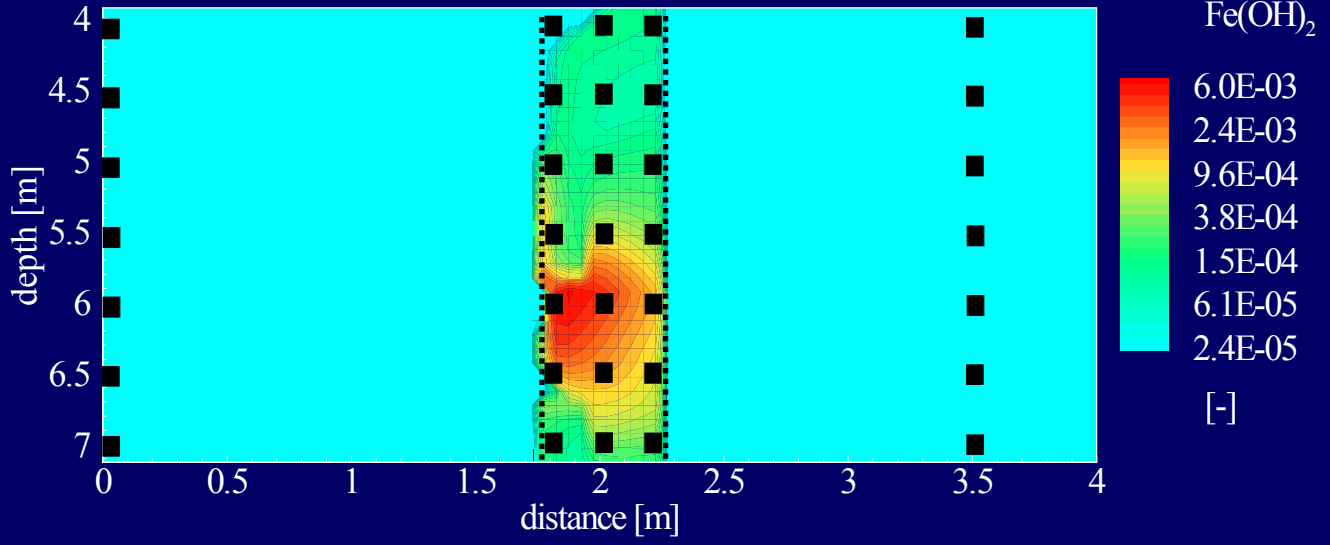
Modelling Barrier Performance

- Reactive transport model: MIN3P

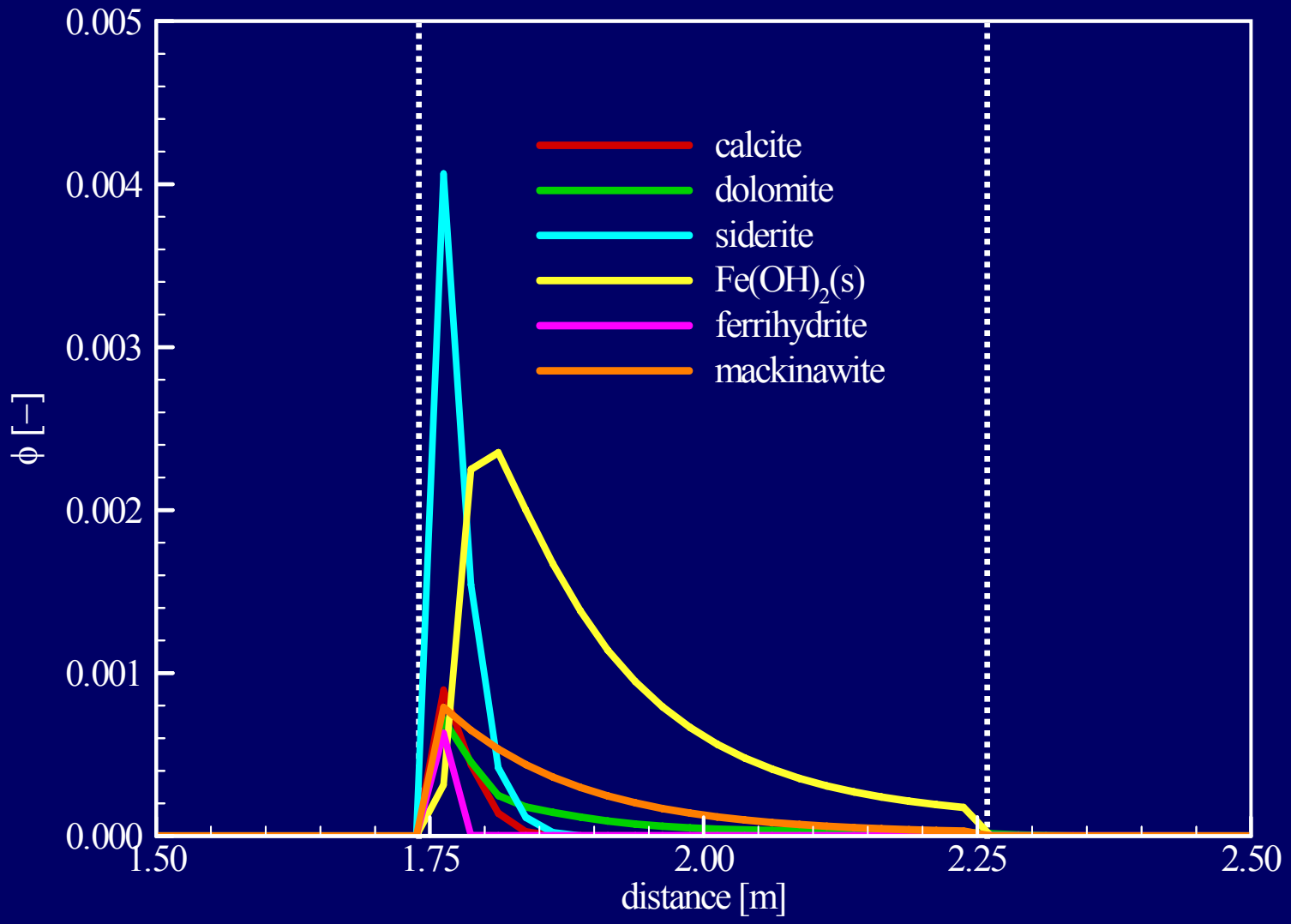
- Groundwater transport
  - Use site-specific data
- Reaction kinetics
  - Lab determined rate constant
  - Field observations

pH and $Fe(OH)_2$

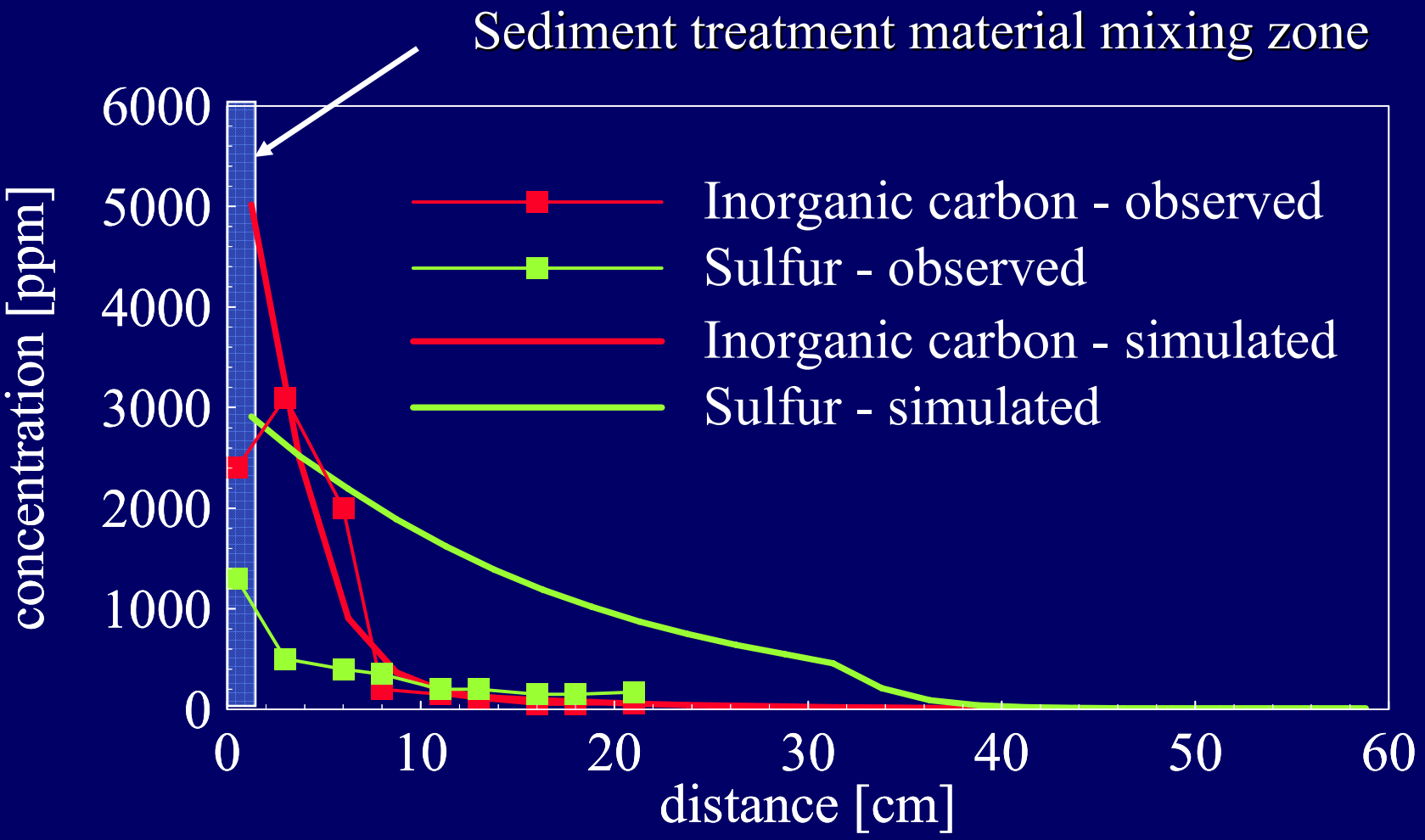

pH
11.0
10.2
9.4
8.6
7.8
7.0
6.2
[-]
depth [m]
4
4.5
5
5.5
6
6.5
7
0
0.5
1
1.5
2
2.5
3
3.5
4
distance [m]


Fe(OH)2
6.0E-03
2.4E-03
9.6E-04
3.8E-04
1.5E-04
6.1E-05
2.4E-05
[-]
depth [m]
4
4.5
5
5.5
6
6.5
7
0
0.5
1
1.5
2
2.5
3
3.5
4
distance [m]

Precipitation of Secondary Minerals

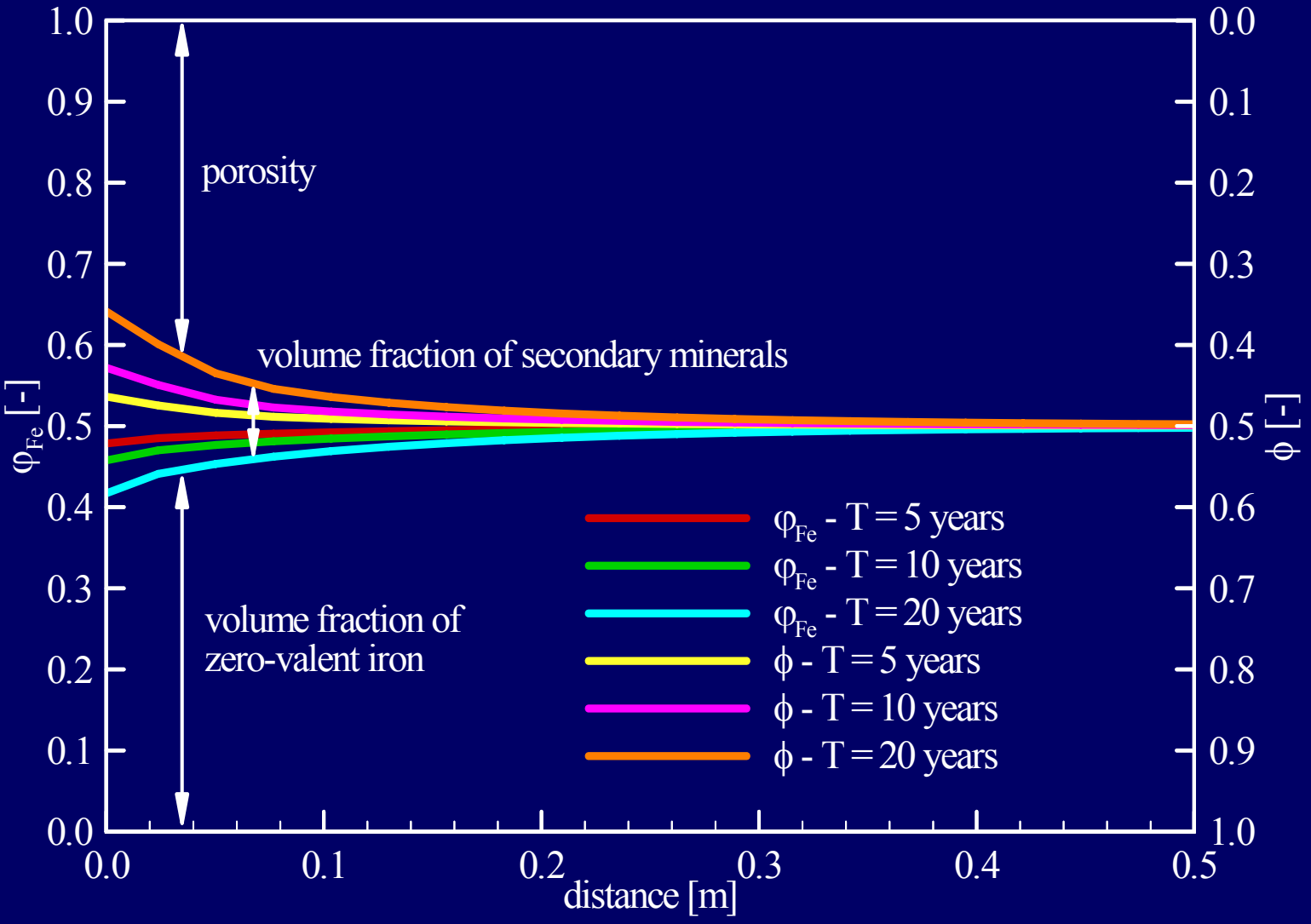


Inorganic Carbon and Sulfur

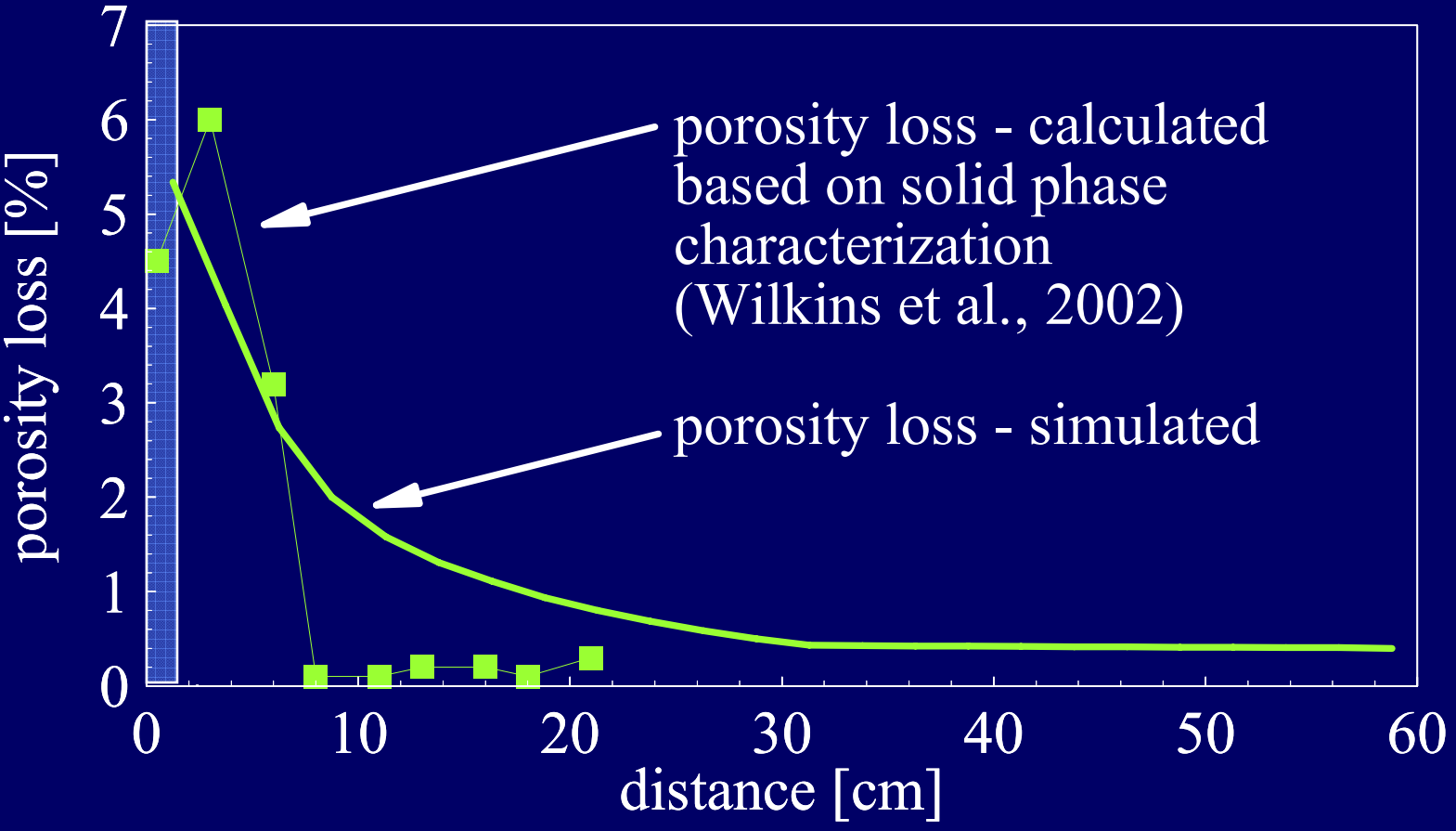


Data from Wilkins et al., 2002

Long-Term Efficiency



Porosity Changes



Monticello Canyon Reactive Barrier

Installed: 1998

Decline in permeability limits performance

Potential Solutions

Mix zero valent iron and organic carbon

$$CH_2O + \tfrac{1}{2}H_2O \rightarrow \tfrac{1}{2}CH_4(aq) + \tfrac{1}{2}CO_3^{2-} + H^+$$

$$CH_2O + \tfrac{1}{2}SO_4^{2-} \rightarrow HCO_3^- + \tfrac{1}{2}H_2S(aq) + H_2O$$

Reactions release H^+ and CO_2 and buffer pH

Avoid funnel & gate installations for high TDS water

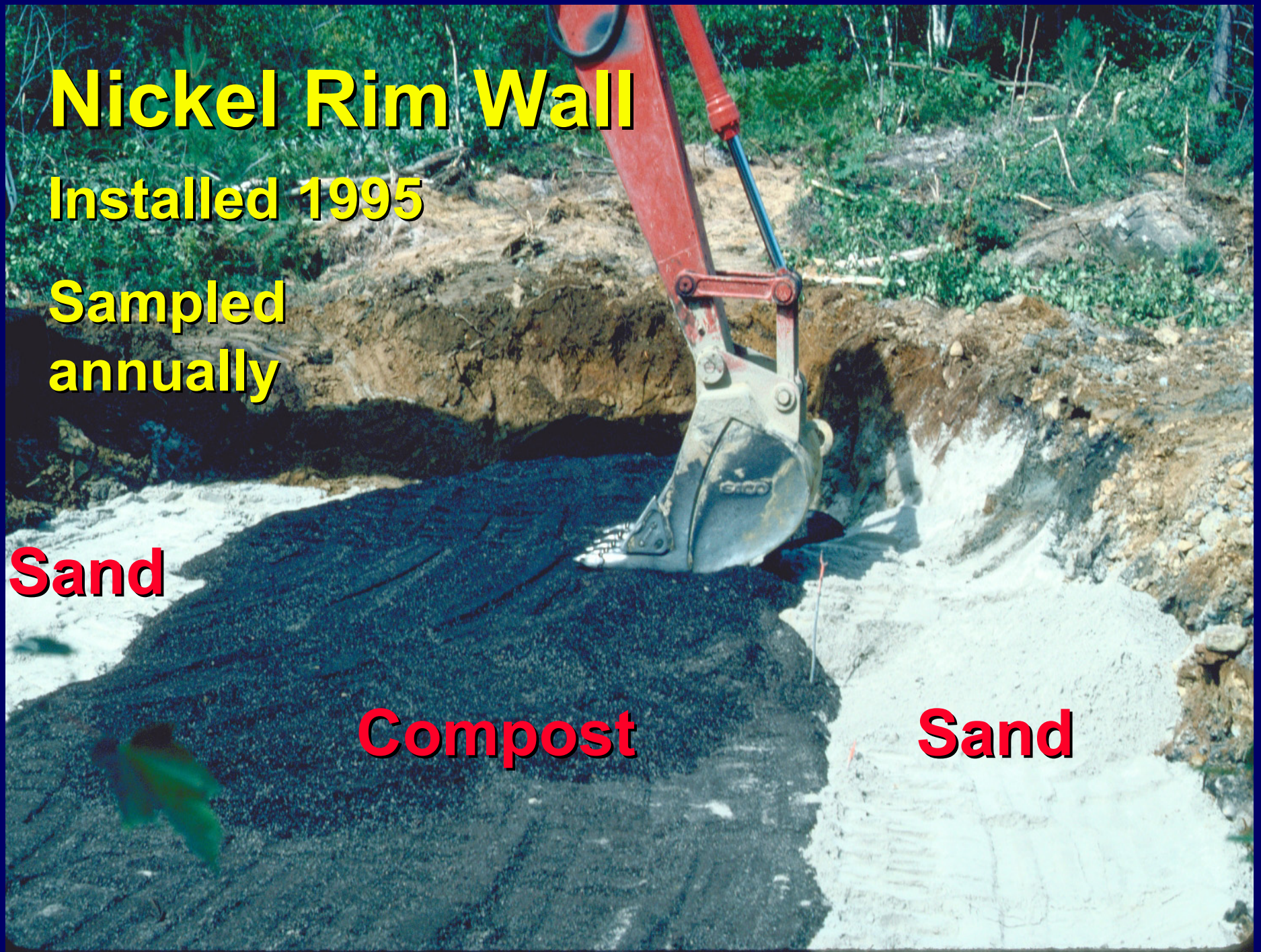
PRB's not suitable for some waters types

Challenges Encountered

Organic carbon

- Permeability variations in media
  - Insufficient preparation
- Decline in reactivity
- Temperature effects

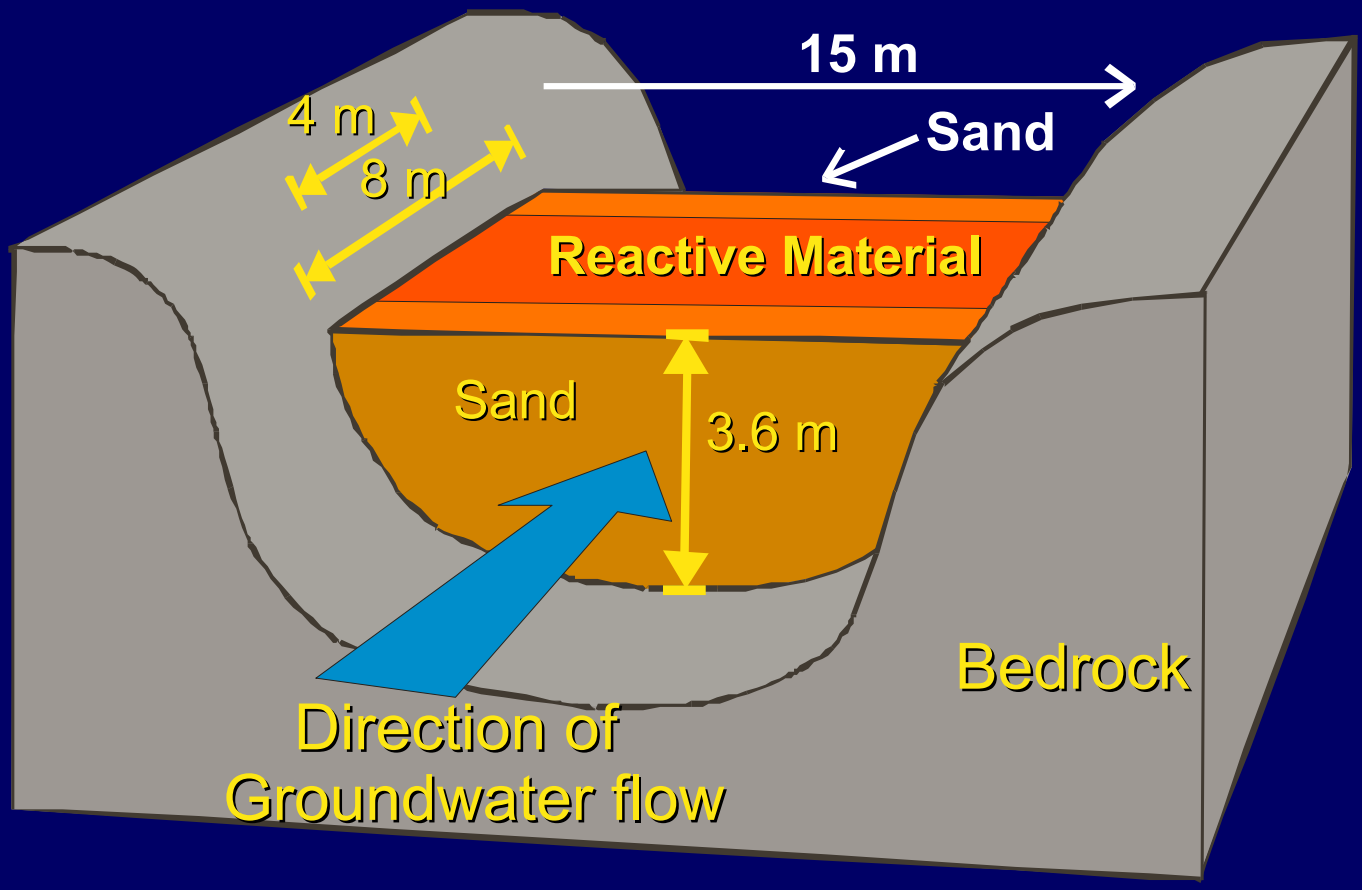
Nickel Rim Barrier Installation


Nickel Rim Wall
Installed 1995
Sampled annually
Sand
Compost
Sand

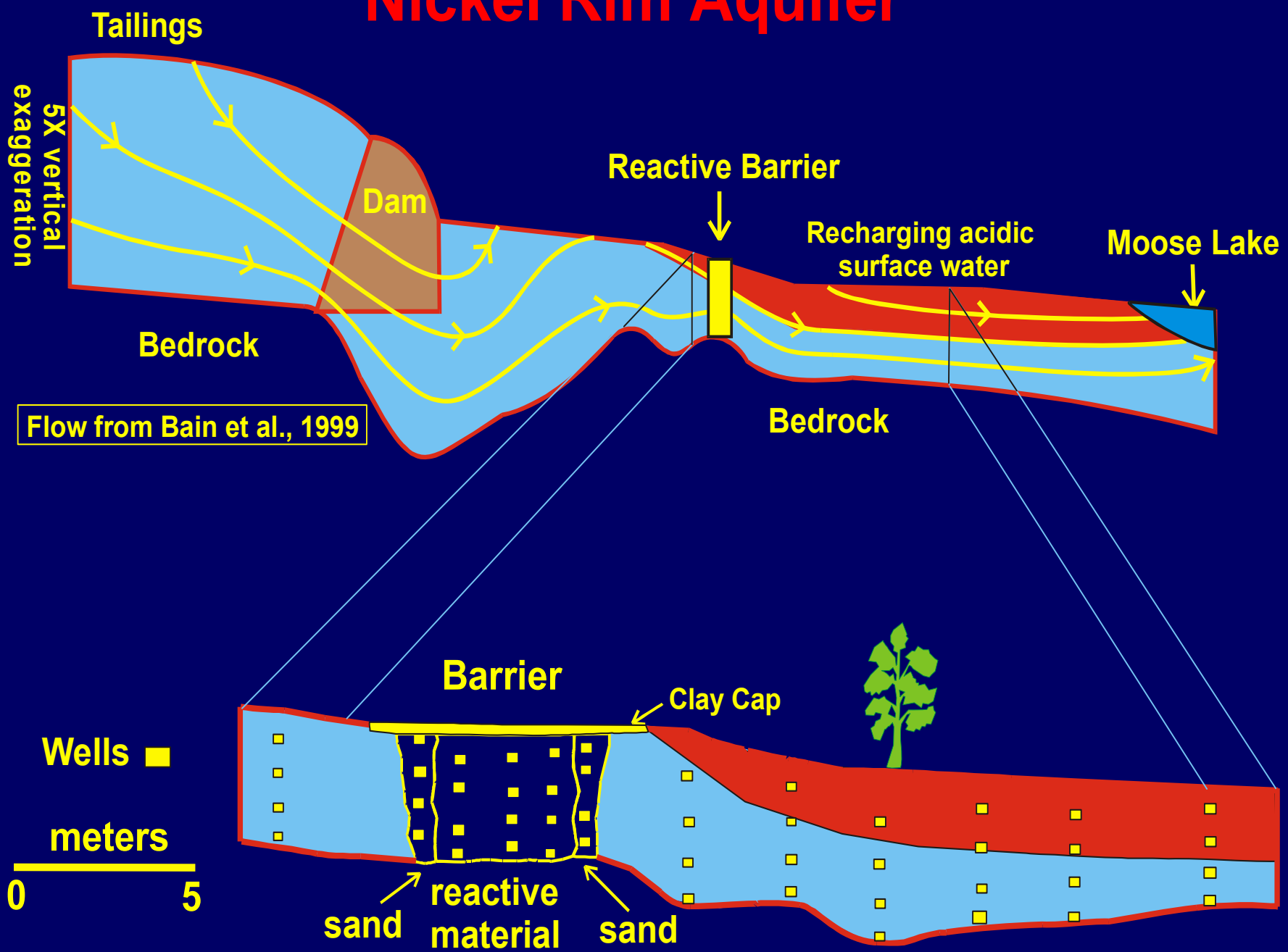
Nickel Rim Groundwater Plume

- Sulfate 2000- 4000 mg/L
- Iron 500-2000 mg/L
- pH slightly acidic (pH 6)
- Alkalinity 0-50 mg/L $CaCO_3$

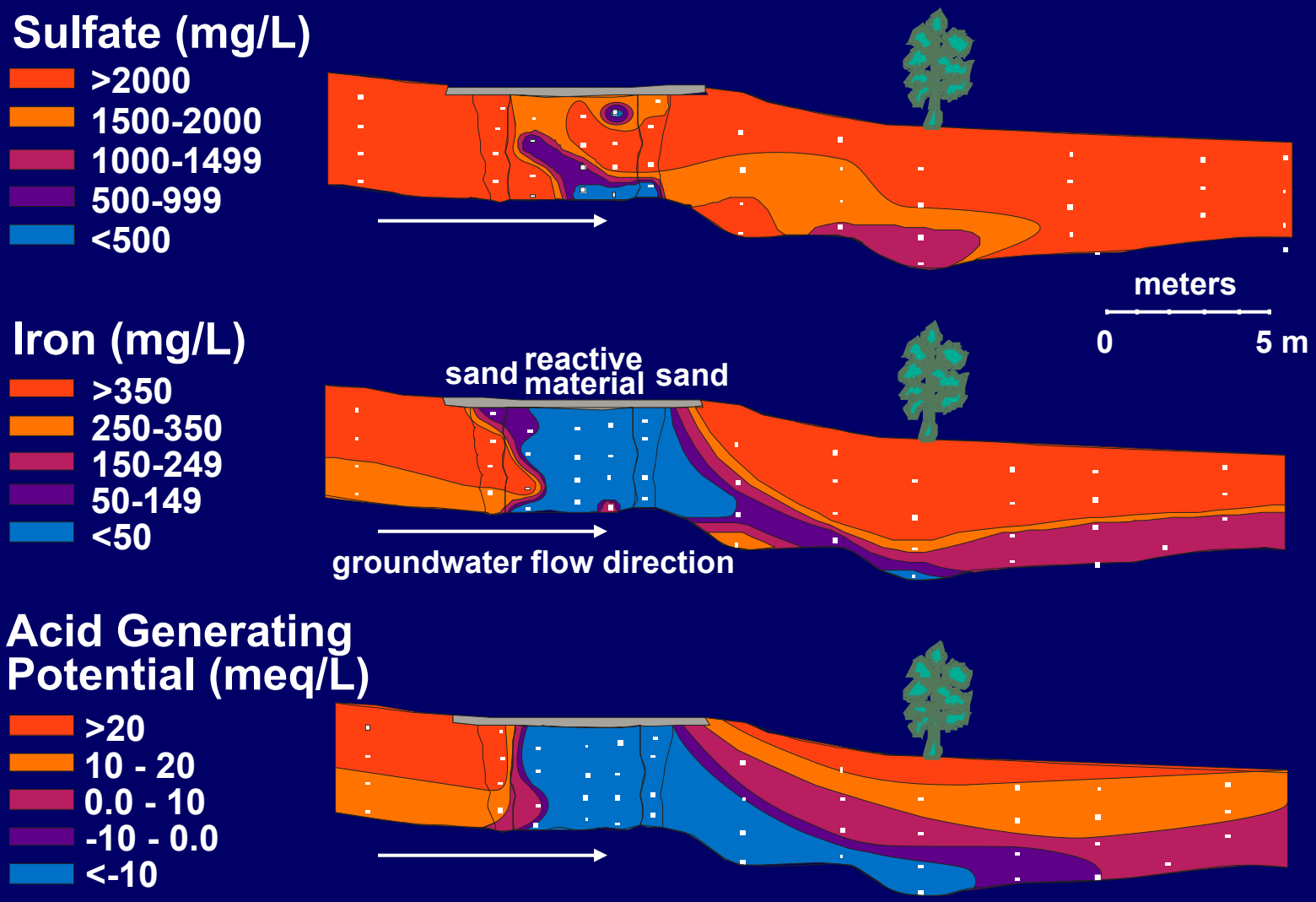
Permeable Reactive Barrier Installation



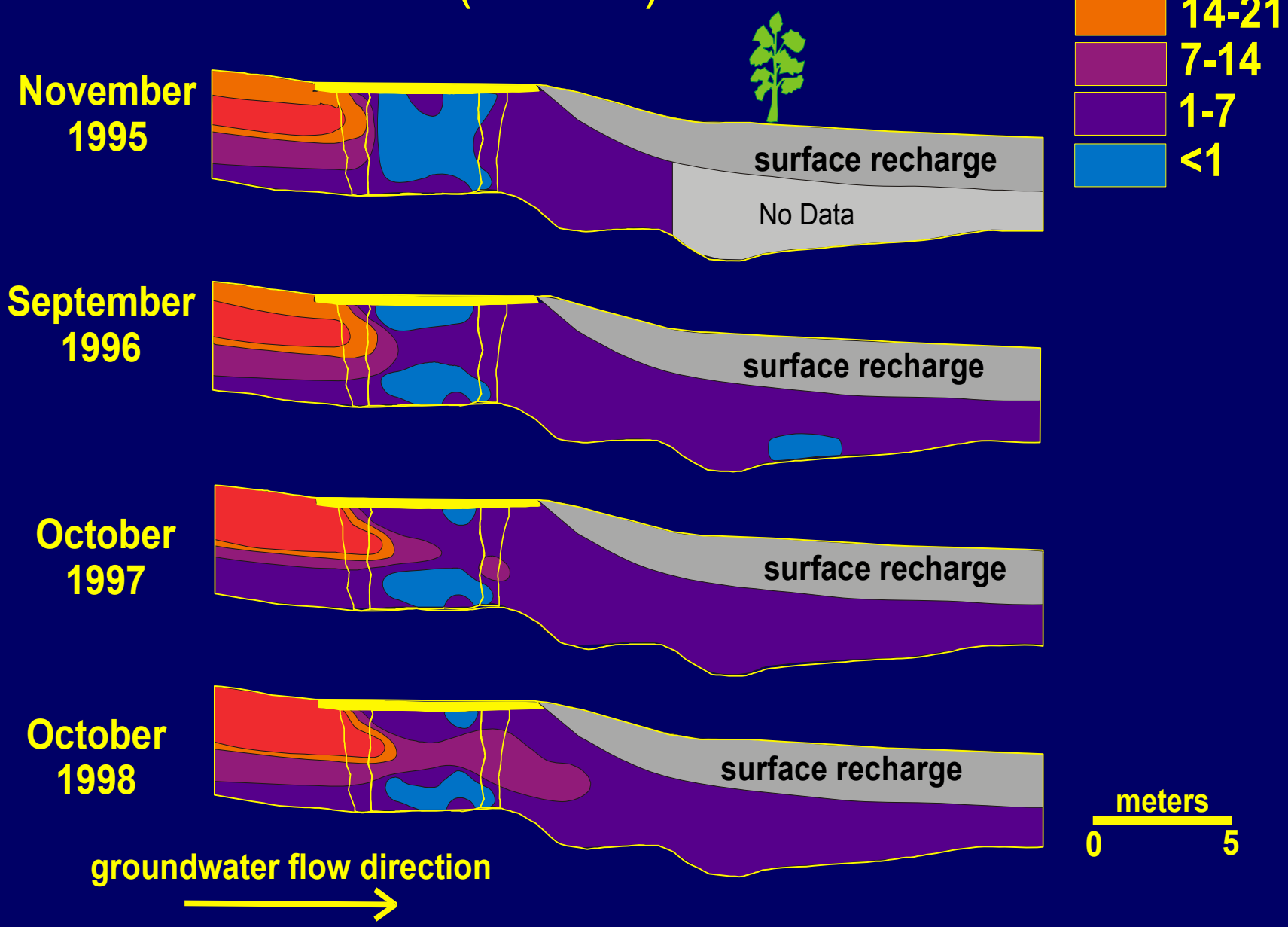
Nickel Rim Aquifer

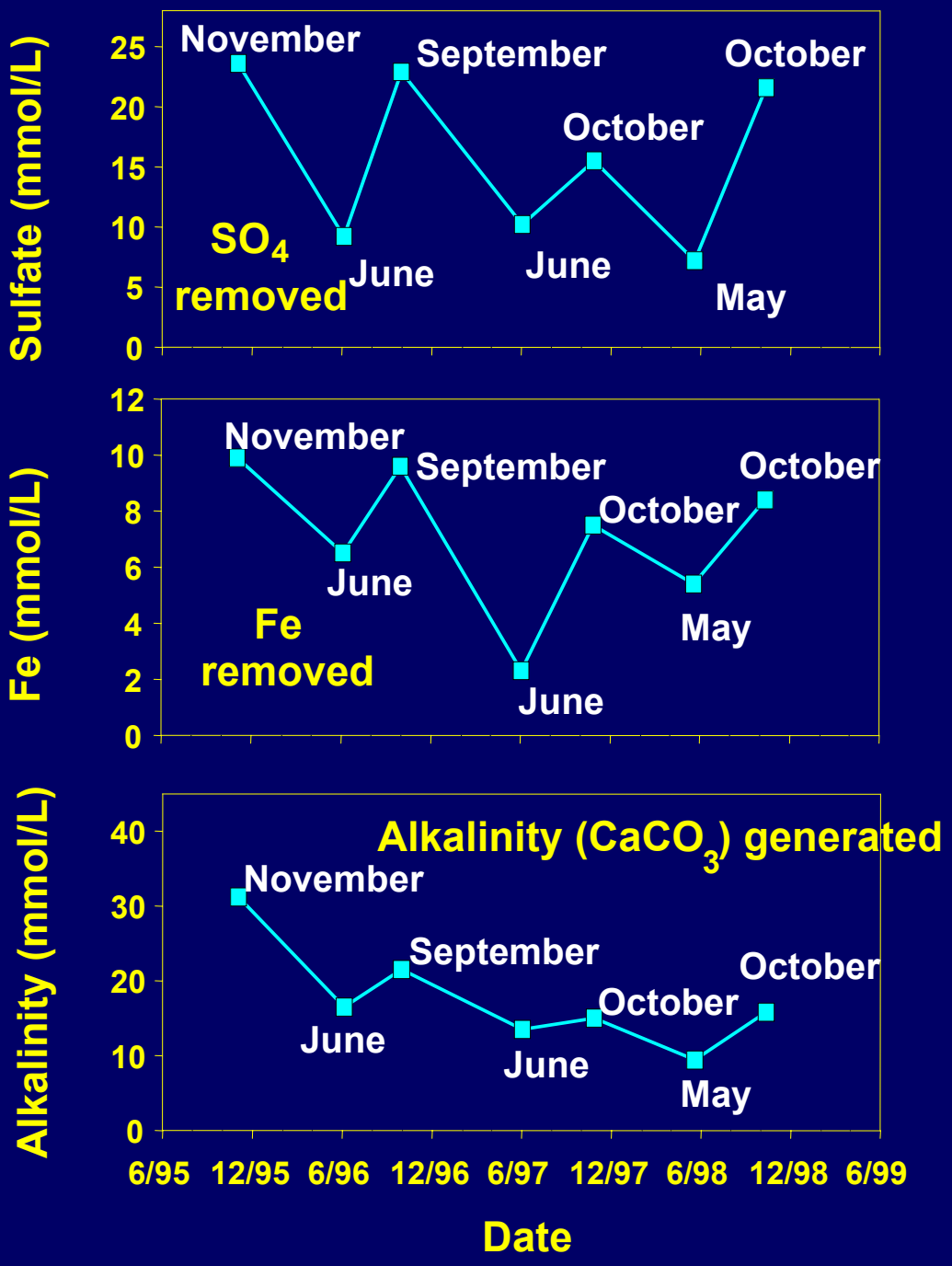


Treatment Results

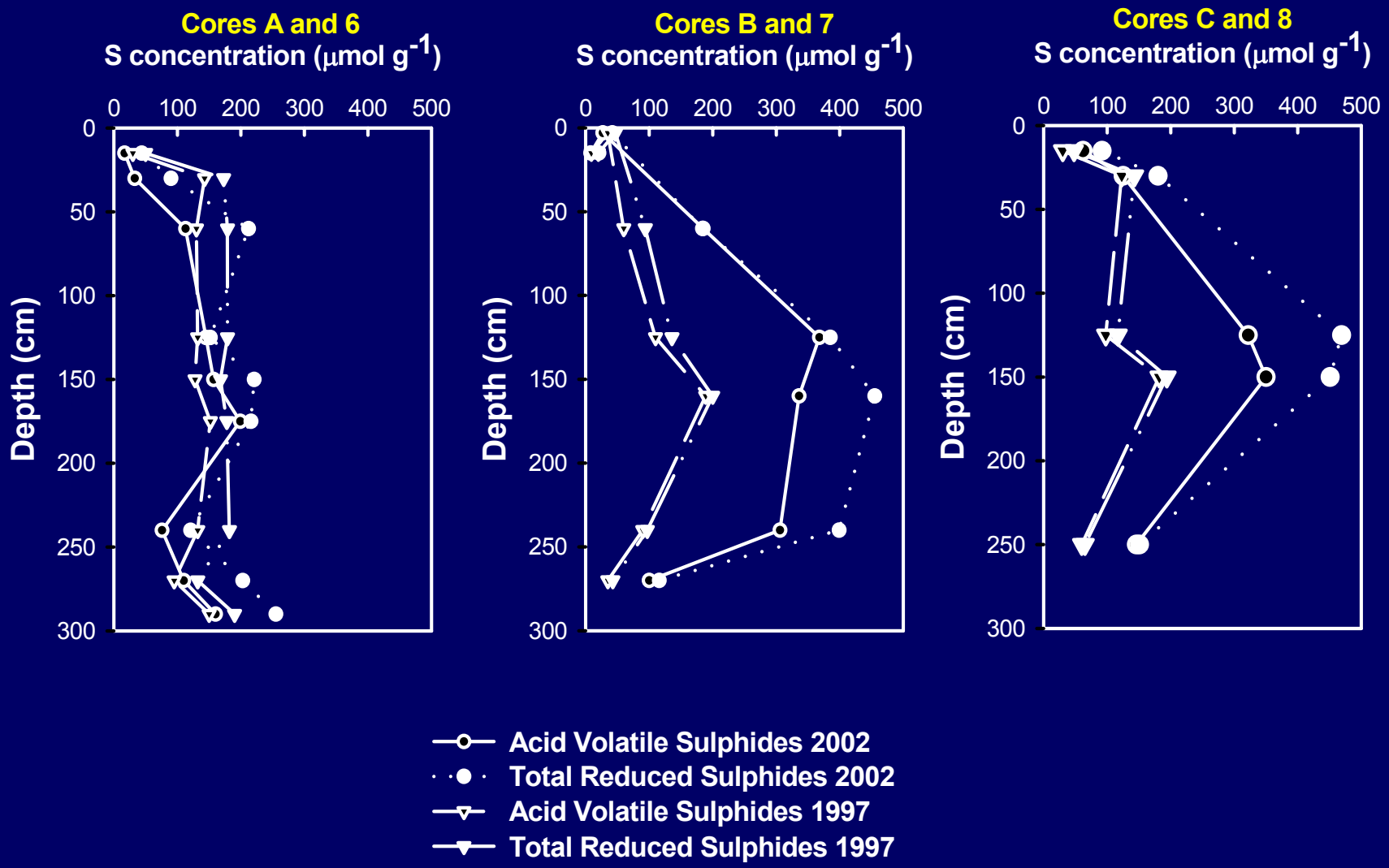


Fe Concentrations (mmol/L)

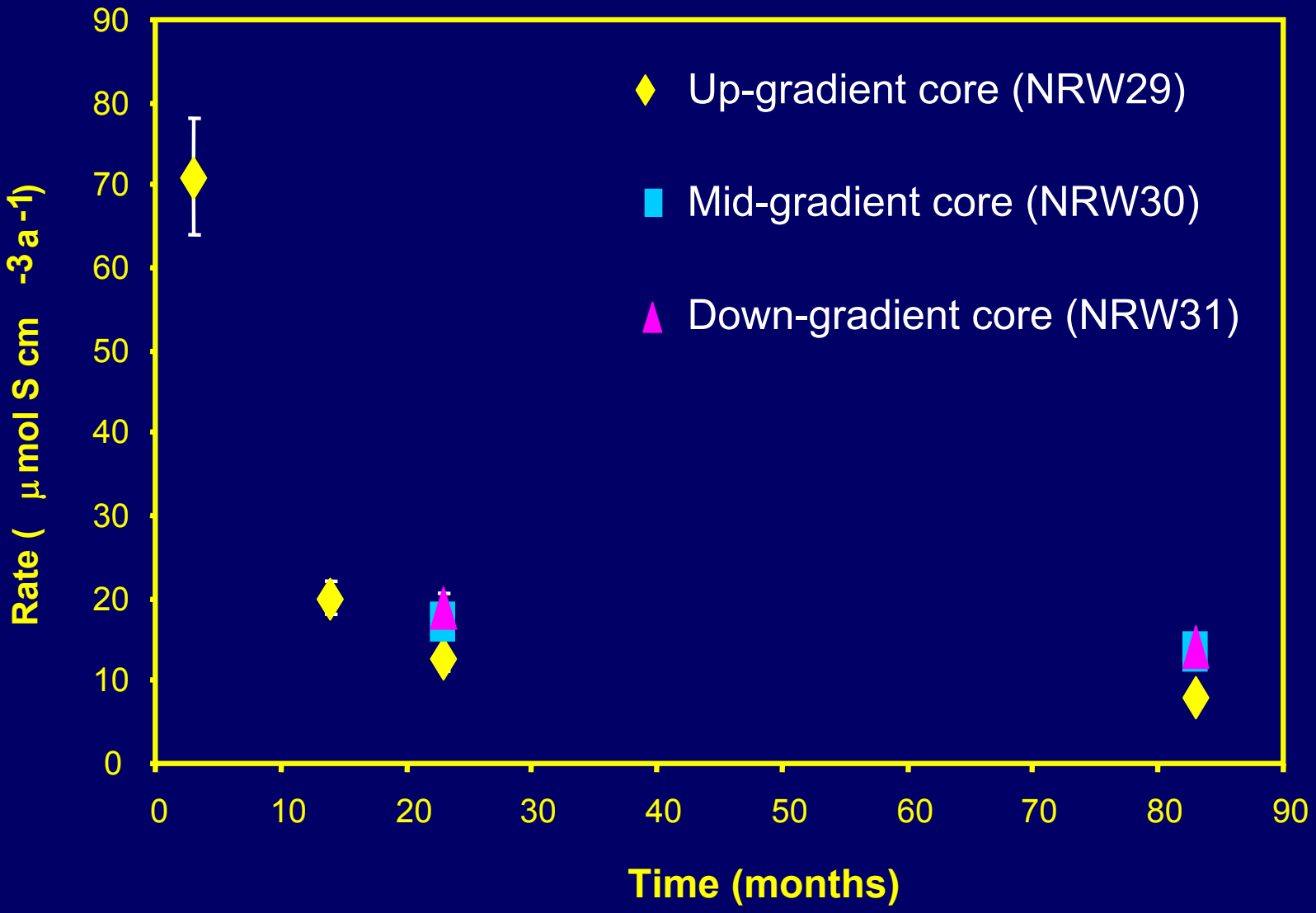



Sulfate (mmol/L)
25
20
15
10
5
0
November
September
October
October
SO_4 removed
June
June
May
Fe (mmol/L)
12
10
8
6
4
2
0
November
September
October
October
June
Fe removed
May
June
Alkalinity (mmol/L)
40
30
20
10
0
Alkalinity ($CaCO_3$) generated
November
September
October
October
June
June
May
6/95
12/95
6/96
12/96
6/97
12/97
6/98
12/98
6/99
Date

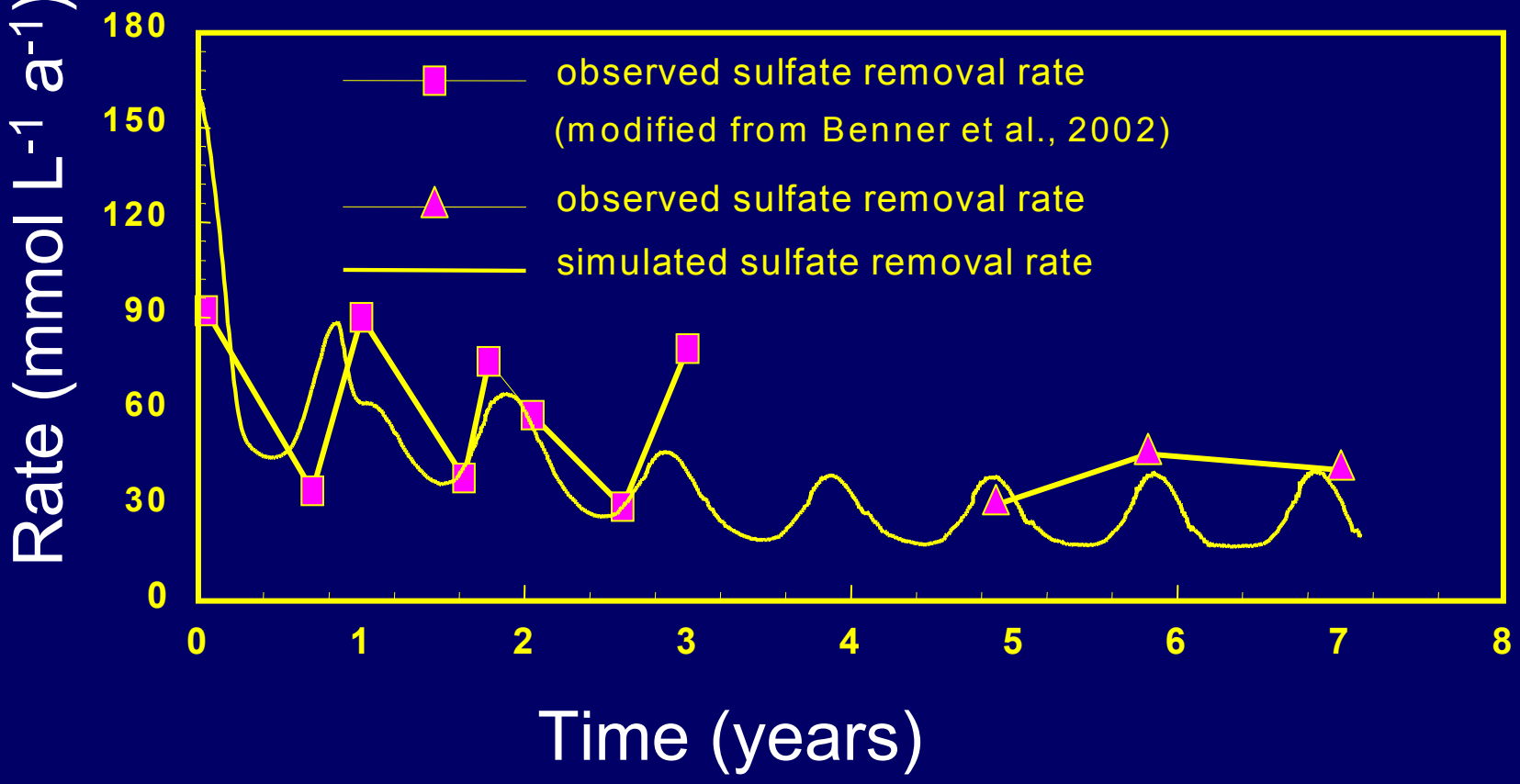
Results


Cores A and 6
S concentration (μmol g-1)
Cores B and 7
S concentration (μmol g-1)
Cores C and 8
S concentration (μmol g-1)
0
100
200
300
400
500
Depth (cm)
0
50
100
150
200
250
300
Acid Volatile Sulphides 2002
Total Reduced Sulphides 2002
Acid Volatile Sulphides 1997
Total Reduced Sulphides 1997

Sulfide Accumulation



Sulfate Removal Rates



Potential Solutions

- Design barriers for long-term sulfate reduction rates
- Increase barrier thickness to provide more complete treatment
- More attention to mixture preparation
- Add a small amount (5-1- vol.%) of ZVI to mixture

Dissolved Hydrogen Gas

- $H_{2(g)}$ is produced by iron corrosion

  $Fe^0 + 2H_2O \Rightarrow Fe^{2+} + H_{2(g)} + 2OH^-$

- $H_{2(g)}$ is an electron donor

  $2CH_2O + SO_4^{2-} \Rightarrow 2HCO_3^- + 2H^+ + S^{2-}$

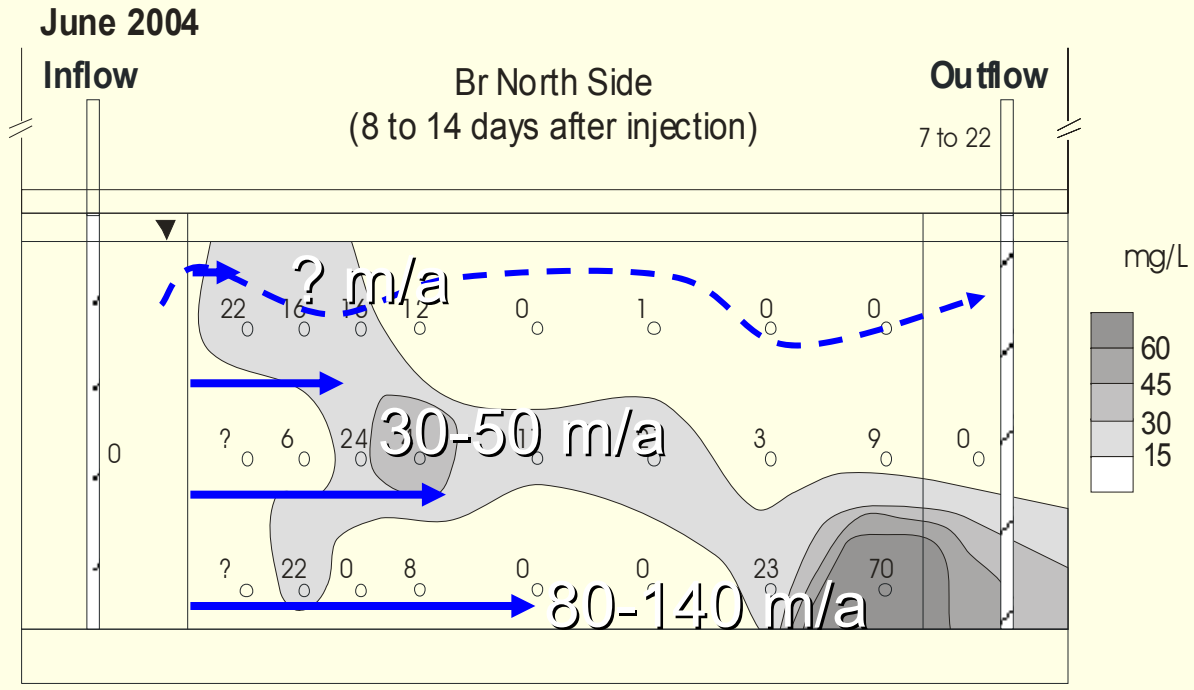
  $4H_{2(g)} + SO_4^{2-} \Rightarrow 4H_2O + S^{2-}$

- Two mechanisms supporting sulfate reduction

Test cell and pump shed

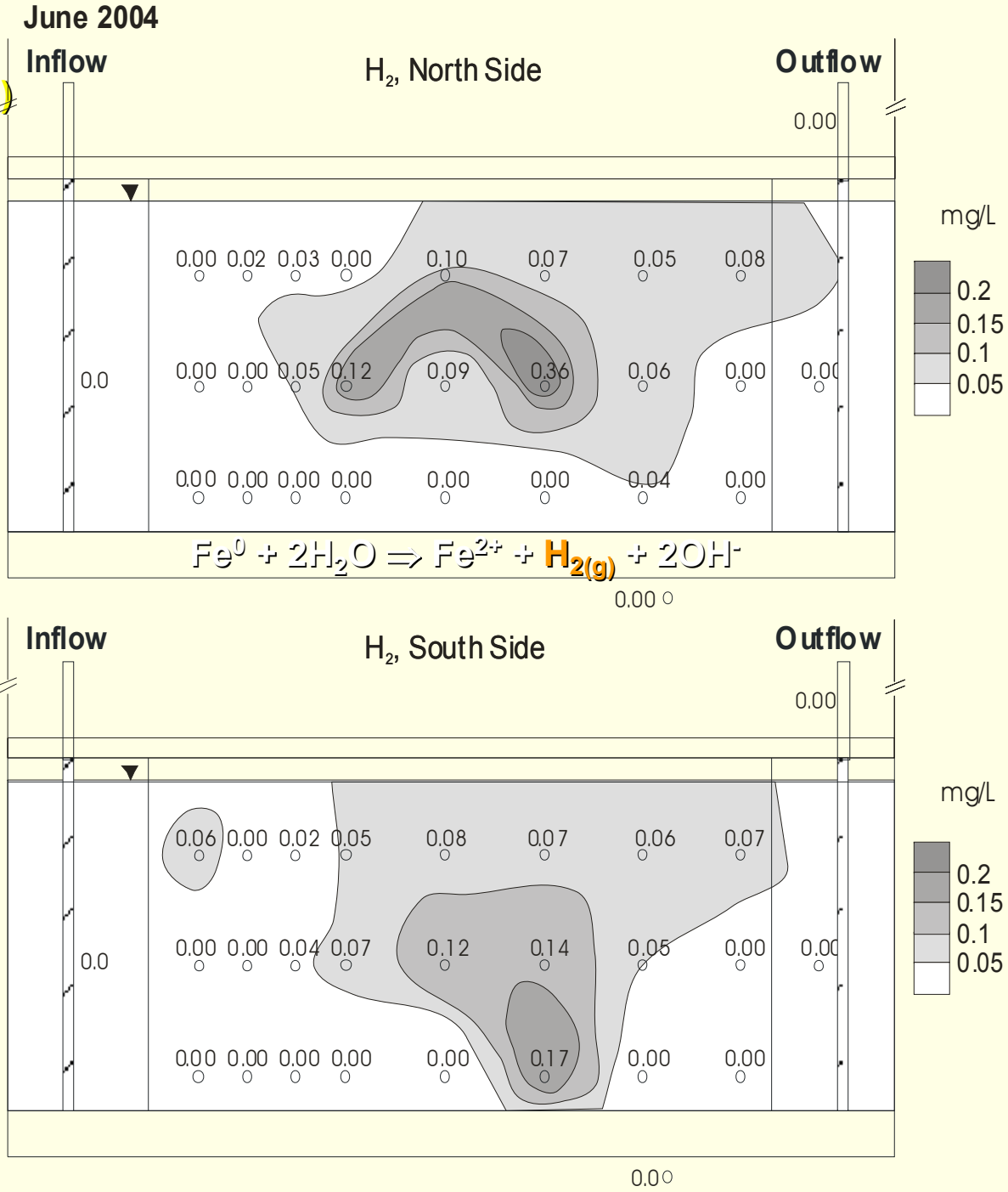
Experiment - Inject and Monitor Movement of Bromide Tracer

Particle path with fluctuating water table



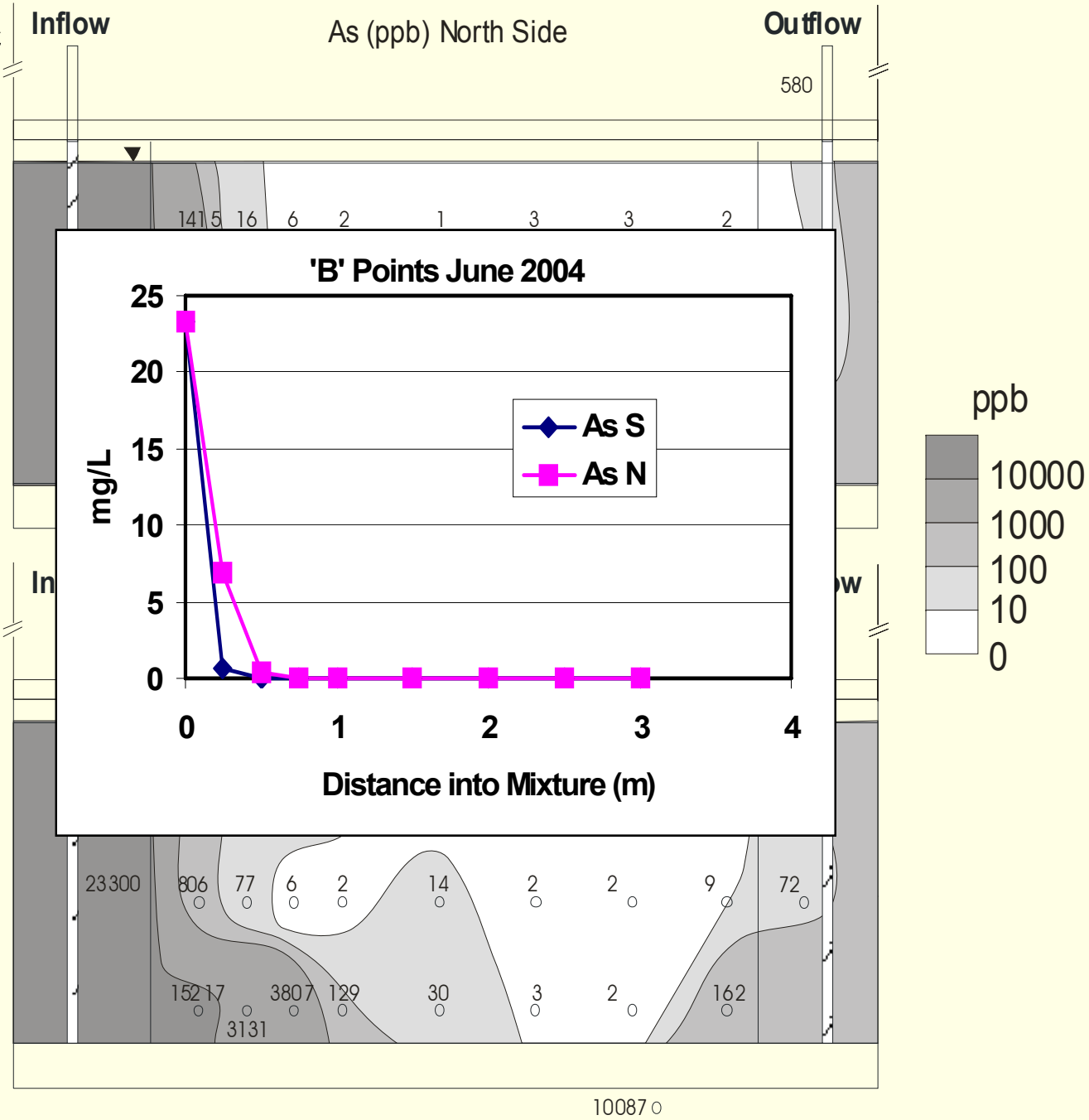
- Br tracer movement shows flow variability
- Improved understanding of As removal trends

Diss. $H_{2(g)}$


June 2004
Inflow
H_2, North Side
Outflow
0.00
0.00 0.02 0.03 0.00 0.10 0.07 0.05 0.08
0.0
0.00 0.00 0.05 0.12 0.09 0.36 0.06 0.00 0.00
0.00 0.00 0.00 0.00 0.00 0.00 0.04 0.00
mg/L
0.2
0.15
0.1
0.05
$Fe^0 + 2H_2O \Rightarrow Fe^{2+} + H_{2(g)} + 2OH^-$
0.00
Inflow
H_2, South Side
Outflow
0.00
0.06 0.00 0.02 0.05 0.08 0.07 0.06 0.07
0.0
0.00 0.00 0.04 0.07 0.12 0.14 0.05 0.00 0.00
0.00 0.00 0.00 0.00 0.00 0.17 0.00 0.00
mg/L
0.2
0.15
0.1
0.05
0.00

Arsenic

June 2004



Conclusions

- Long-term monitoring indicates continued treatment for > 10 years
- Treatment limitations:
  - Capacity of reactive materials
  - Permeability losses
- Alternative mixtures can alleviate some problems

Acknowledgements

Colleagues and Students

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