Metals Removal from Groundwater Using Permeable Reactive Barriers (PRBs)

David J.A. Smyth[1], David W. Blowes[1], Carol J. Ptacek[1], Jeff G. Bain[1]

Department of Earth Sciences, University of Waterloo

Waterloo, ON, N2L 3G1, Canada

BC MLARD Workshop, December 2002

© University of Waterloo 2002

PRBs for Removal of Inorganic Contaminants from Groundwater

- University of Waterloo experience
- Blowes, Ptacek and Robertson
- Metals, nutrients and water-borne pathogens
- Plume remediation or control
- U.S. Patents 5,362,394 5,514,279 5,876,606

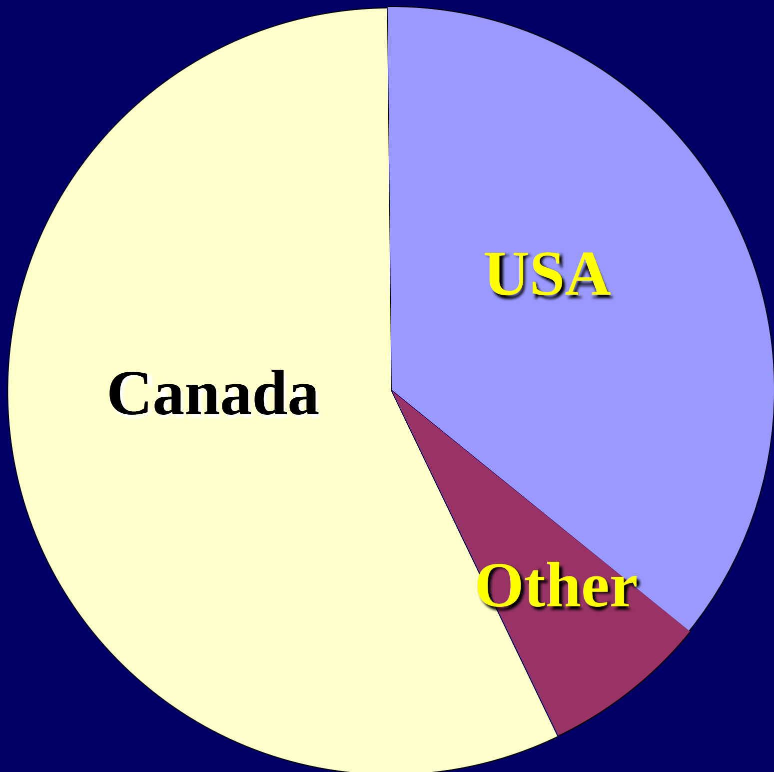
© University of Waterloo 2002

Geochemical Barriers for Metals

- Zero-valent iron: reductive precipitation on grain surfaces
- Organic carbon: sulfate reduction, denitrification
- BOF Slag: sorption and co-precipitation phosphate and arsenic
- U.S. Patents 5,362,394 5,514,279 5,876,606
- Activated carbon
- Limestone (neutralization)

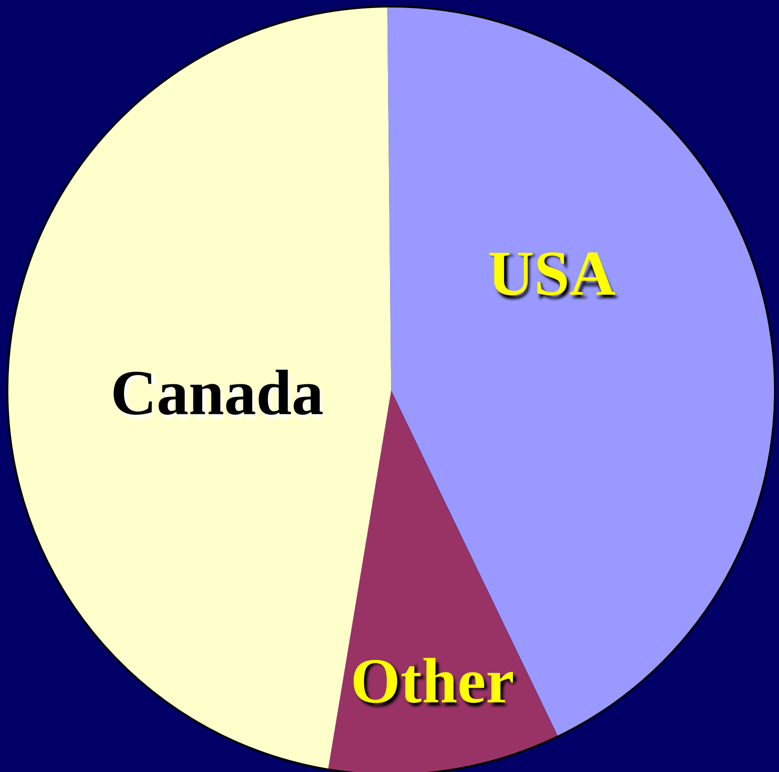
PRBs for Inorganic Contaminants

Pilot Scale Installations



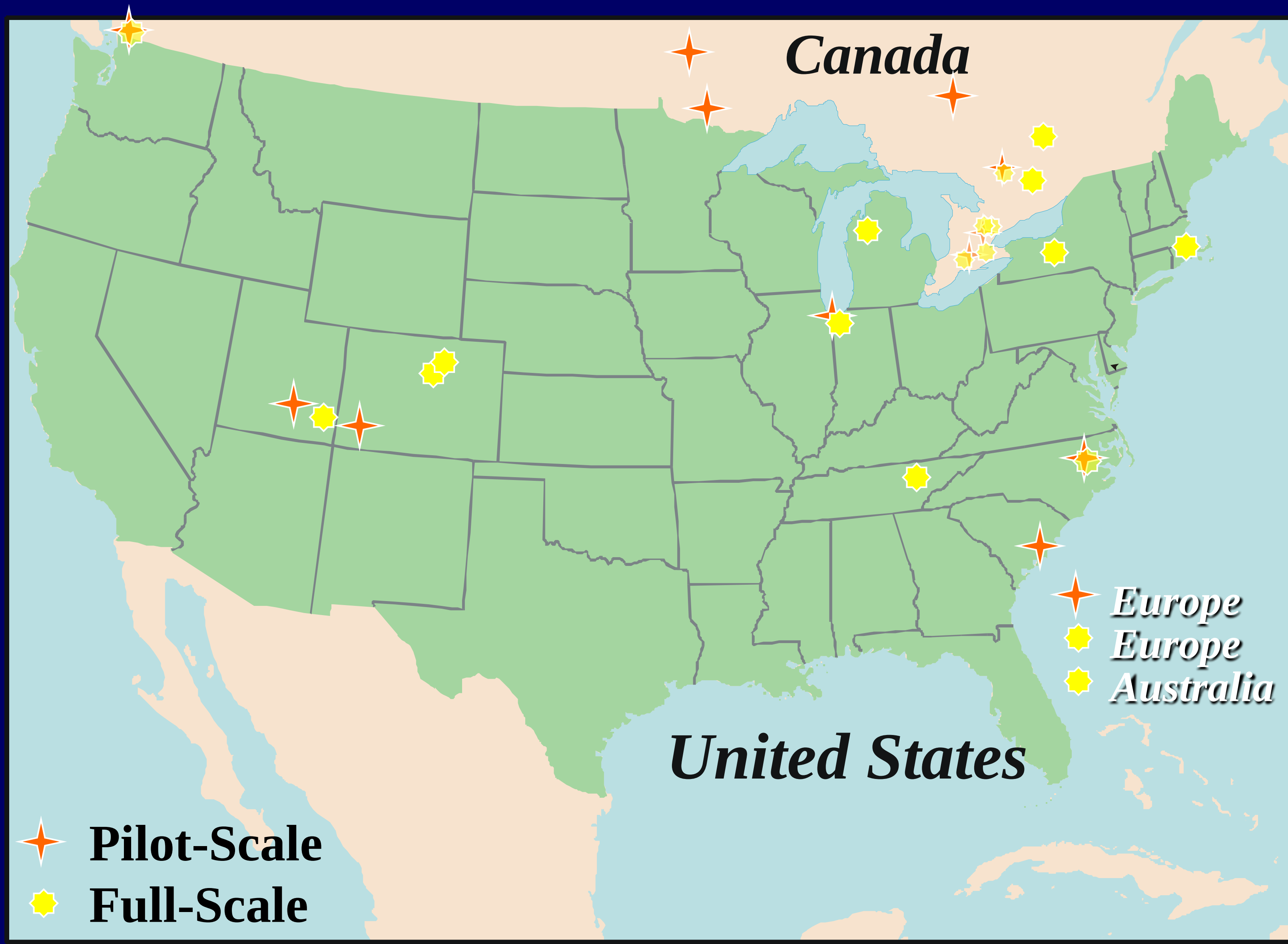
n=14

Full-Scale PRB Installations



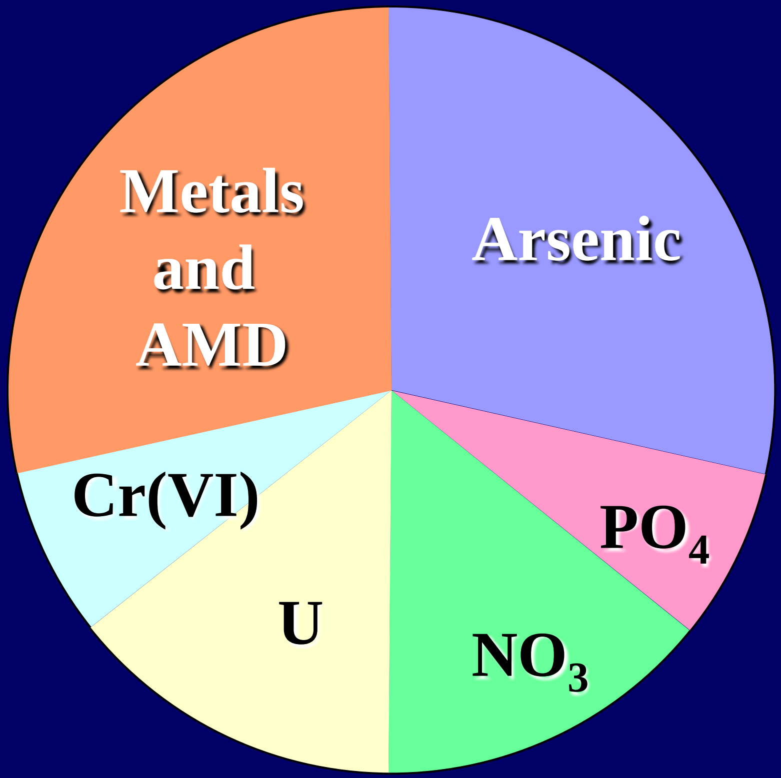
n=21

Inorganic PRB Sites

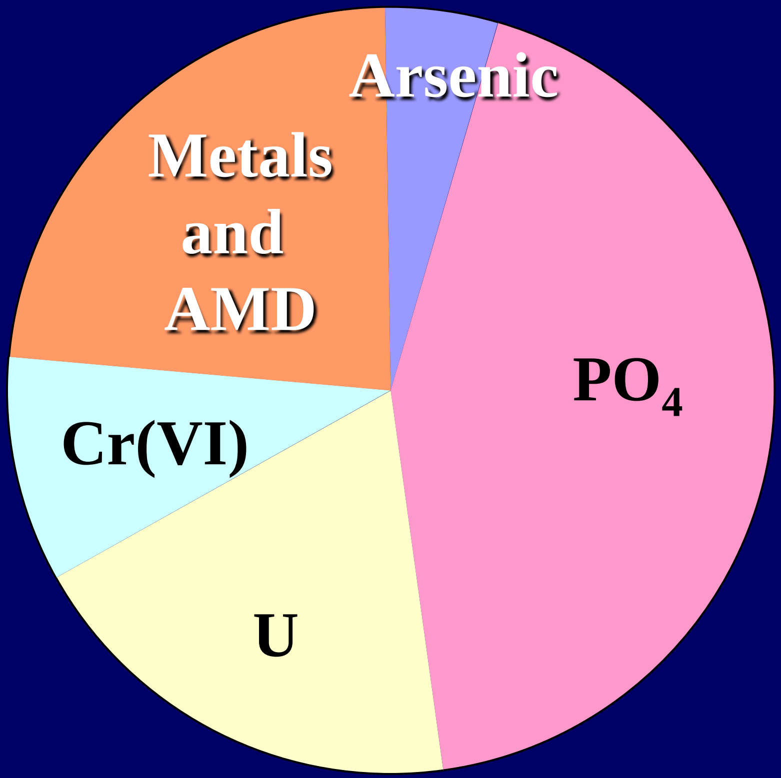


Contaminants Treated

Pilot Scale Installations



Full-Scale PRB Installations



Zero-Valent Iron for Electroactive Metals

- Field Installation: Chromium (VI), Elizabeth City, NC
- Radionuclides (DOE Facilities)
- Arsenic, selenium, mercury
- Reductive precipitation on grain surfaces; precipitation or co-precipitation

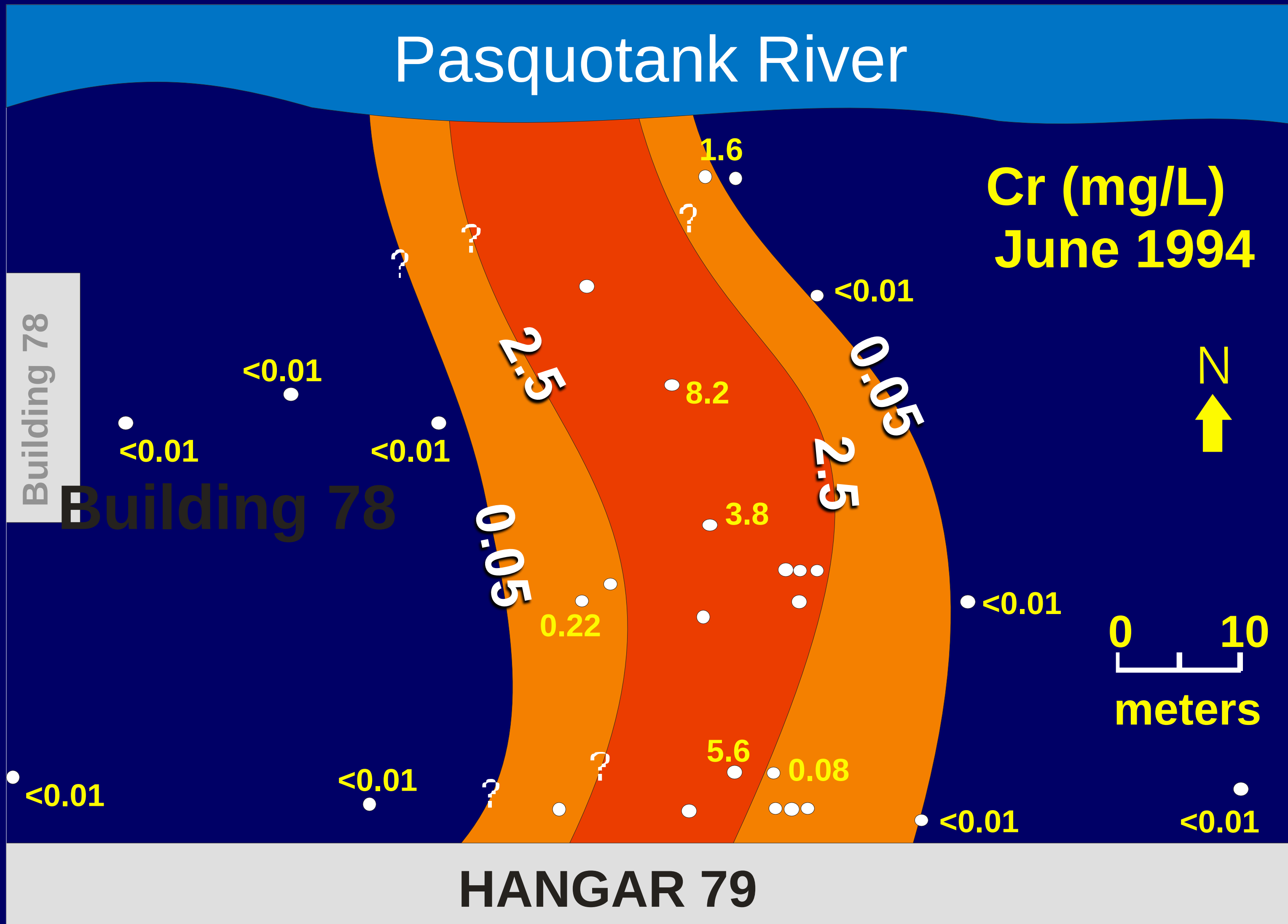
© University of Waterloo 2002

Elizabeth City Site

U.S. EPA Project

- **Reference**
  - **Blowes, D.W., et al., 1999. An *In-Situ* Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water: Volume 1 Design and Installation. Volume 2 Performance Monitoring. Volume 3 Multicomponent Reactive Transport Modeling United States Environmental Protection Agency, Cincinnati, OH, Report EPA/600/R-99/095abc.**
  - **http://www.epa.gov/ada/pubs/reports.html**

© University of Waterloo 2002



T.A. Bennett, M.Sc. Thesis,
University of Waterloo, 1997

© University of Waterloo 2002

Reactive Material

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

© University of Waterloo 2002

One-Pass Continuous Trencher

© University of Waterloo 2002

One-Pass Continuous Trencher

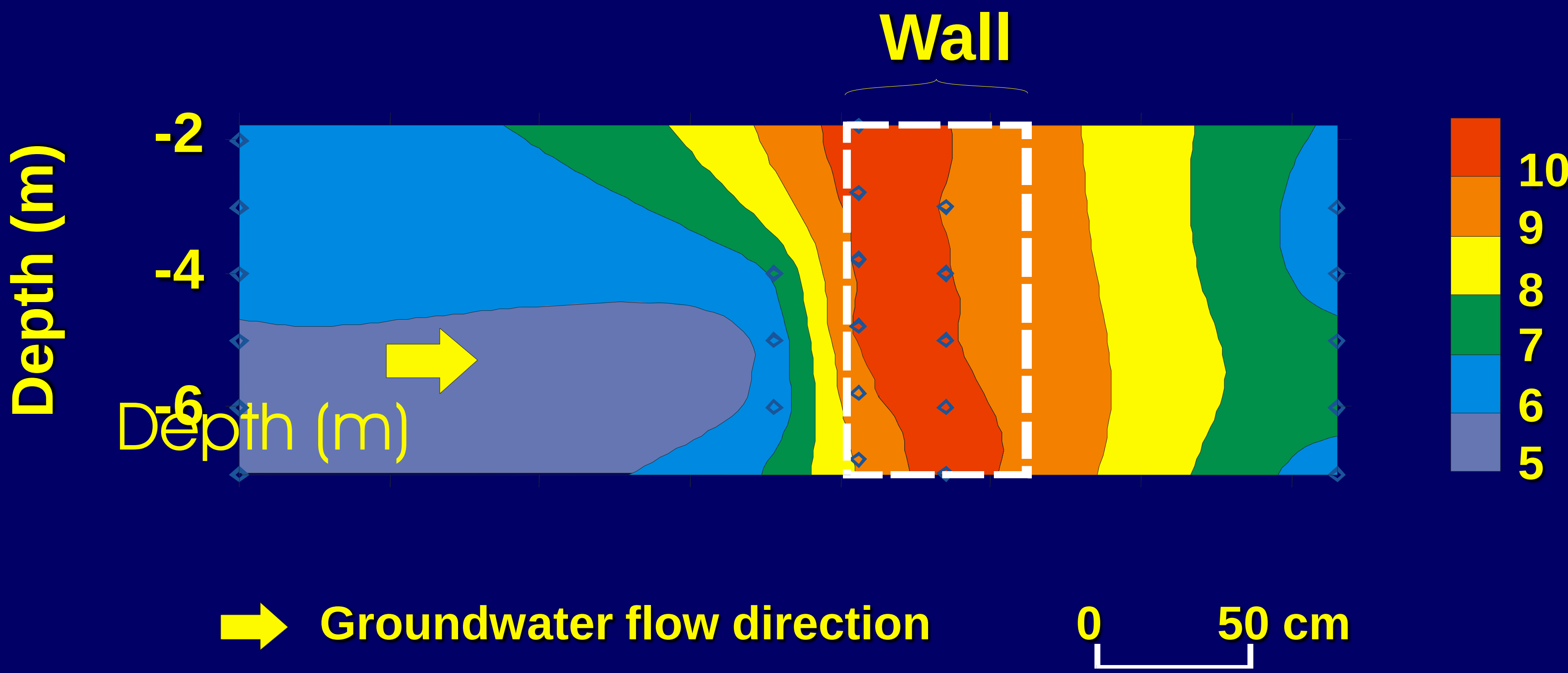
- Depths of < 30 ft
- Width 1-2 ft
- Very rapid installation
- Big equipment
- Mobilization

© University of Waterloo 2002

USCG Wall Installation

© University of Waterloo

pH

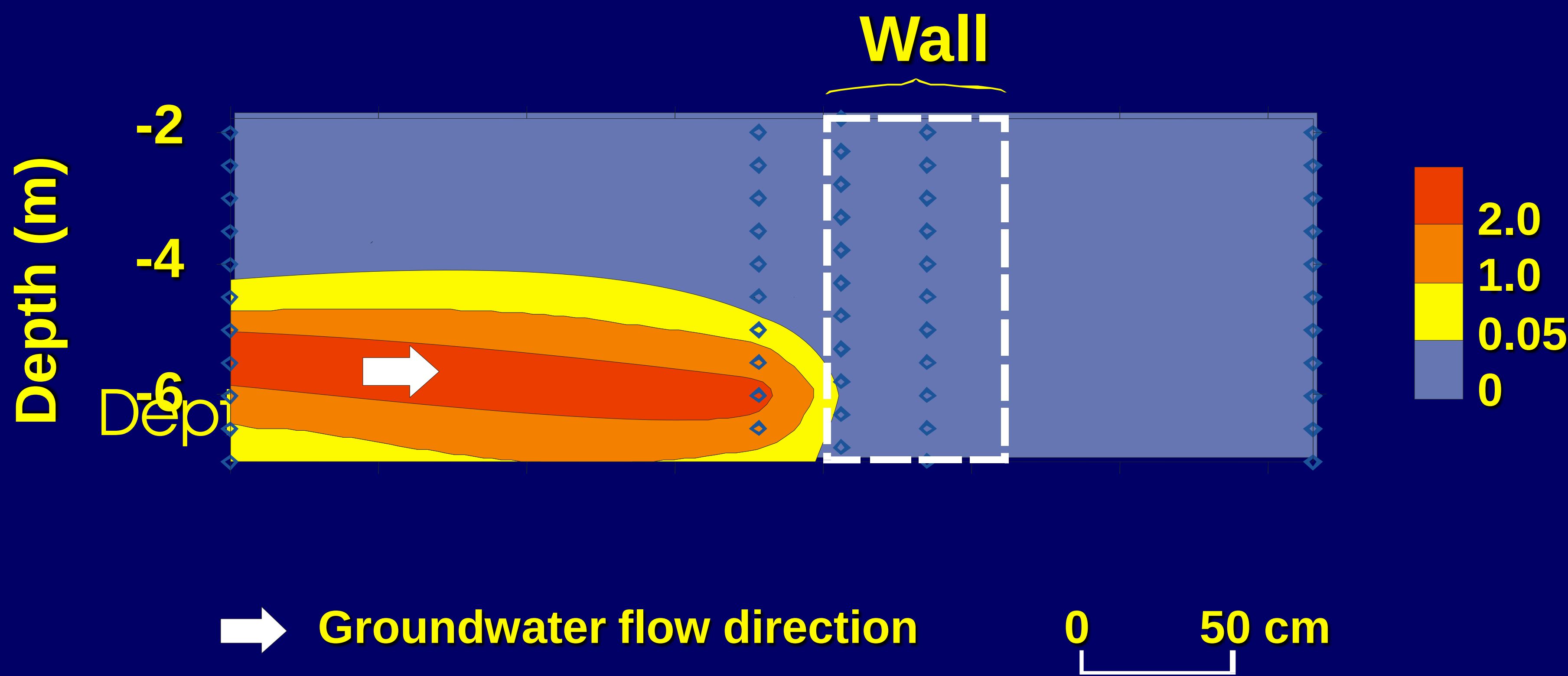


Transect 1 (November 1996)

T.A. Bennett, M.Sc. Thesis,
University of Waterloo, 1997

© University of Waterloo 2002

Cr(VI) (mg/L)



Transect 1 (November 1996)

T.A. Bennett, M.Sc. Thesis,
University of Waterloo, 1997

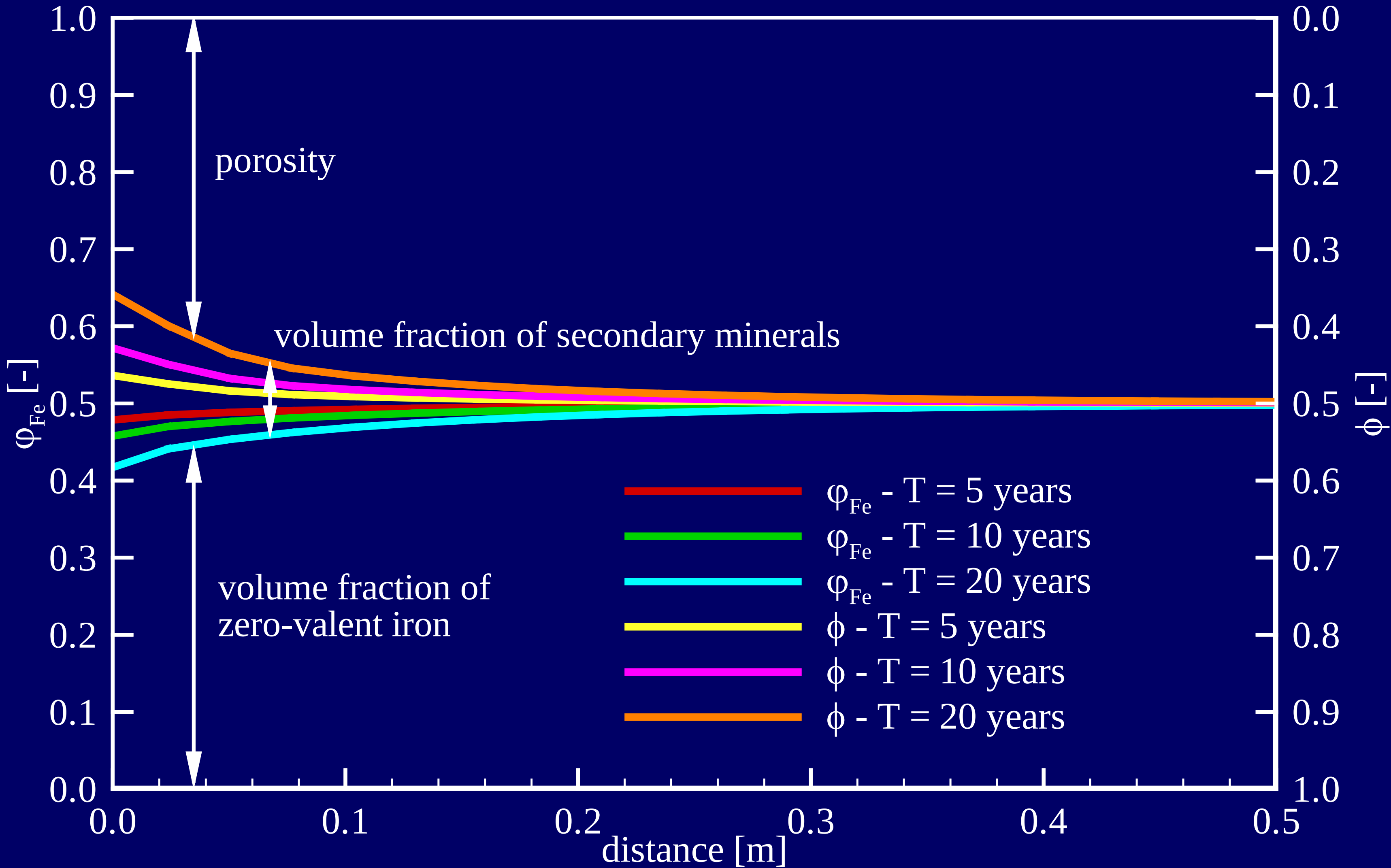
© University of Waterloo 2002

Mineralogical Characterization

- Increased solid-phase carbon
  - Carbonate mineralogy
- Iron oxyhydroxides
  - goethite
  - ferrihydrite
  - green rust
- Iron Sulfides

© University of Waterloo 2002

Long-Term Efficiency (Mayer)



© University of Waterloo 2002

ARSENIC

Mechanisms for Removal

1) Reduction and Co-precipitation with Goethite

i) $4Fe^{0}_{(s)} + 3O_{2(g)} + 6H_{2}0_{(l)} \nwarrow 4Fe^{3+}_{(aq)} + 120H^{-}_{(aq)}$

ii) $Fe^{3+}_{(aq)} + H_{3}AsO_{3(aq)} + 2H_{2}0_{(l)} \nwarrow FeO(OH,H_{2}AsO_{4})_{(s)} + 5H^{+}_{(aq)}$

2) Sulphate Reduction

i) $4Fe^{0}_{(s)} + SO_{4}^{2-}{}_{(aq)} + 10H^{+}_{(aq)} \nwarrow H_{2}S_{(aq)} + 4Fe^{2+}_{(aq)} + 4H_{2}O_{(l)}$

ii) $2As^{3+}_{(aq)} + 3H_{2}S_{(aq)} \nwarrow As_{2}S_{3(s)} + 6H^{+}_{(aq)}$

3) Adsorption

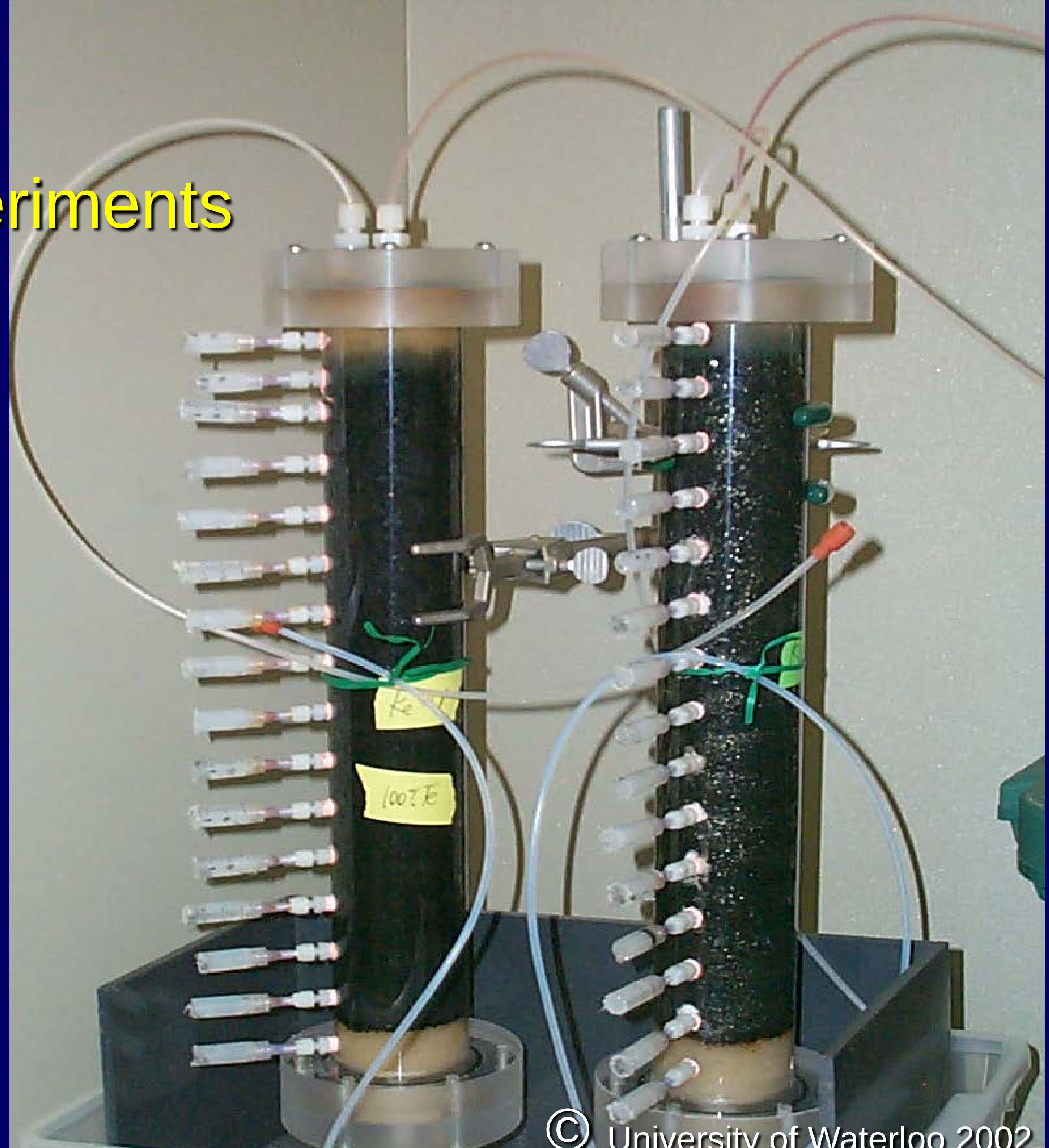
© University of Waterloo 2002

McRae (1999): Arsenic Removal Mechanisms

- Energy Dispersive X-Ray Analysis
  - As present in grain coatings and possibly on zero-valent iron grain surface
- X-Ray Photoelectron Spectroscopy
  - As(III) predominant in solid phase
  - Reductive precipitation and co-precipitation with goethite in coatings

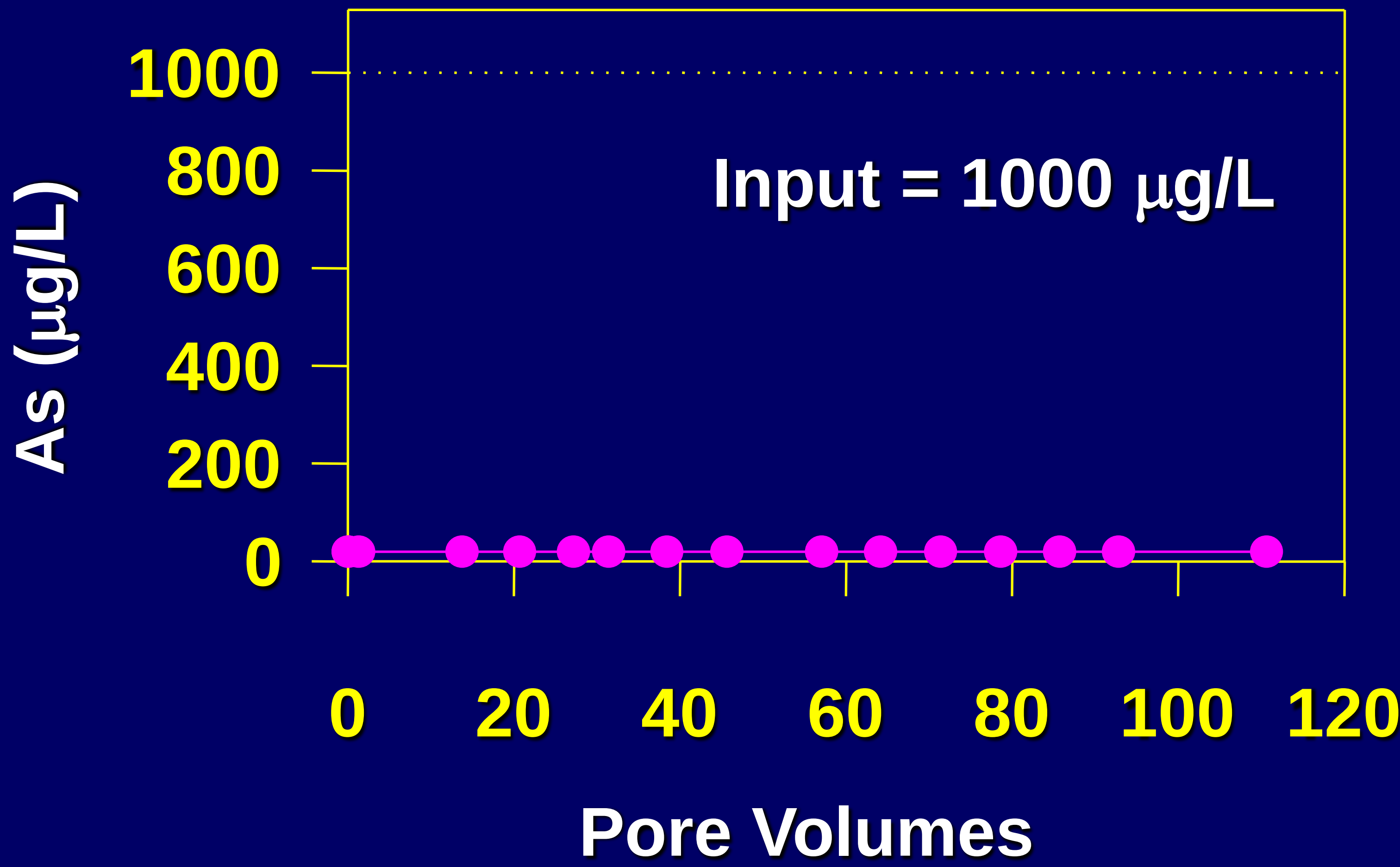
© University of Waterloo 2002

Column Experiments



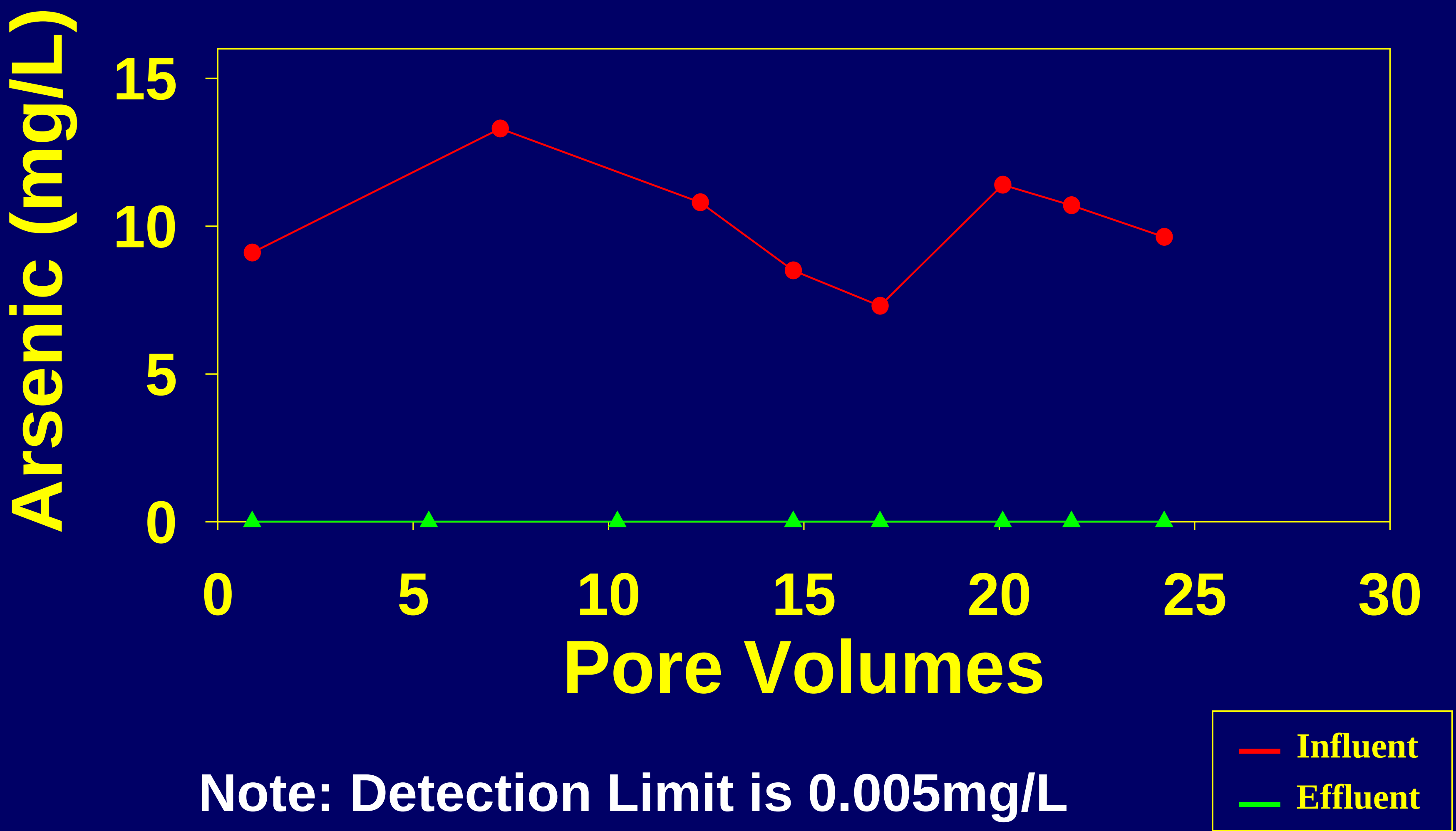
© University of Waterloo 2002

Zero Valent Iron Column



© University of Waterloo 2002

Arsenic Concentration in 100% Iron Column

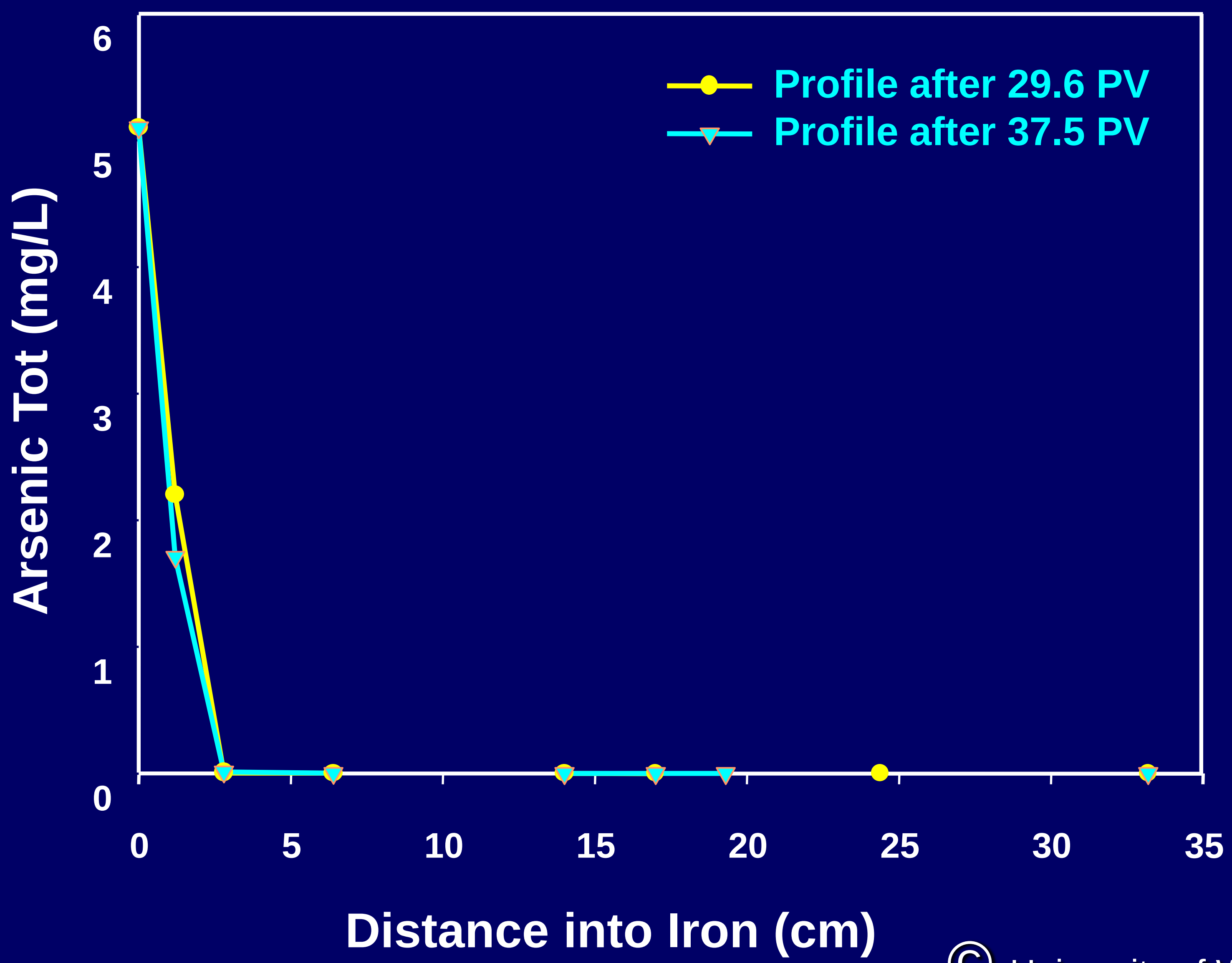


Note: Detection Limit is 0.005mg/L

© University of Waterloo 2002

Total Arsenic Concentration Profiles in ZVI Column

Mine Groundwater at Velocity of 6.75 cm/day



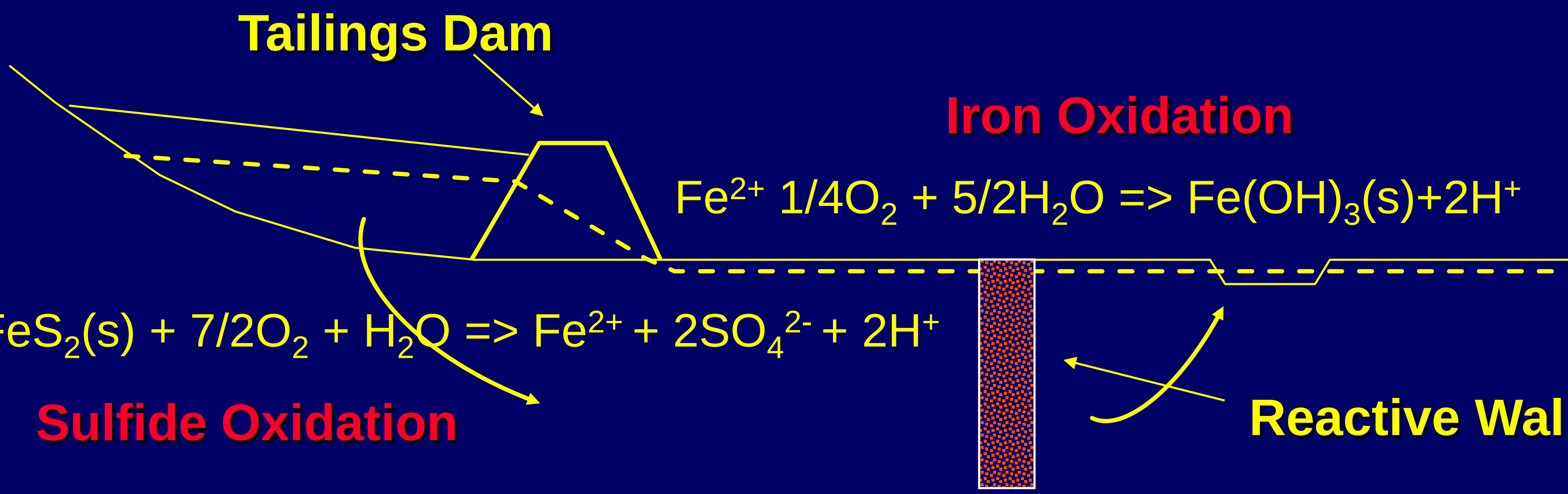
© University of Waterloo 2002

Sulfate-Reduction PRBs

- Metals in sulfate rich water- AMD
- Sulfate reduction is microbially mediated process
- Purpose of PRB is to intercept groundwater flow and enhance sulfate reduction
- Generation of H_2S and precipitation of metal sulfide minerals
- Decrease acid-generating potential; remove dissolved metals

© University of Waterloo 2002

Acid Mine Drainage and Sulfate Reduction



Sulfate Reduction

SO_4^{2-} + 2CH_2O => H_2S +2HCO_3^-

Fe^{2+} + H_2S => FeS + 2H^+

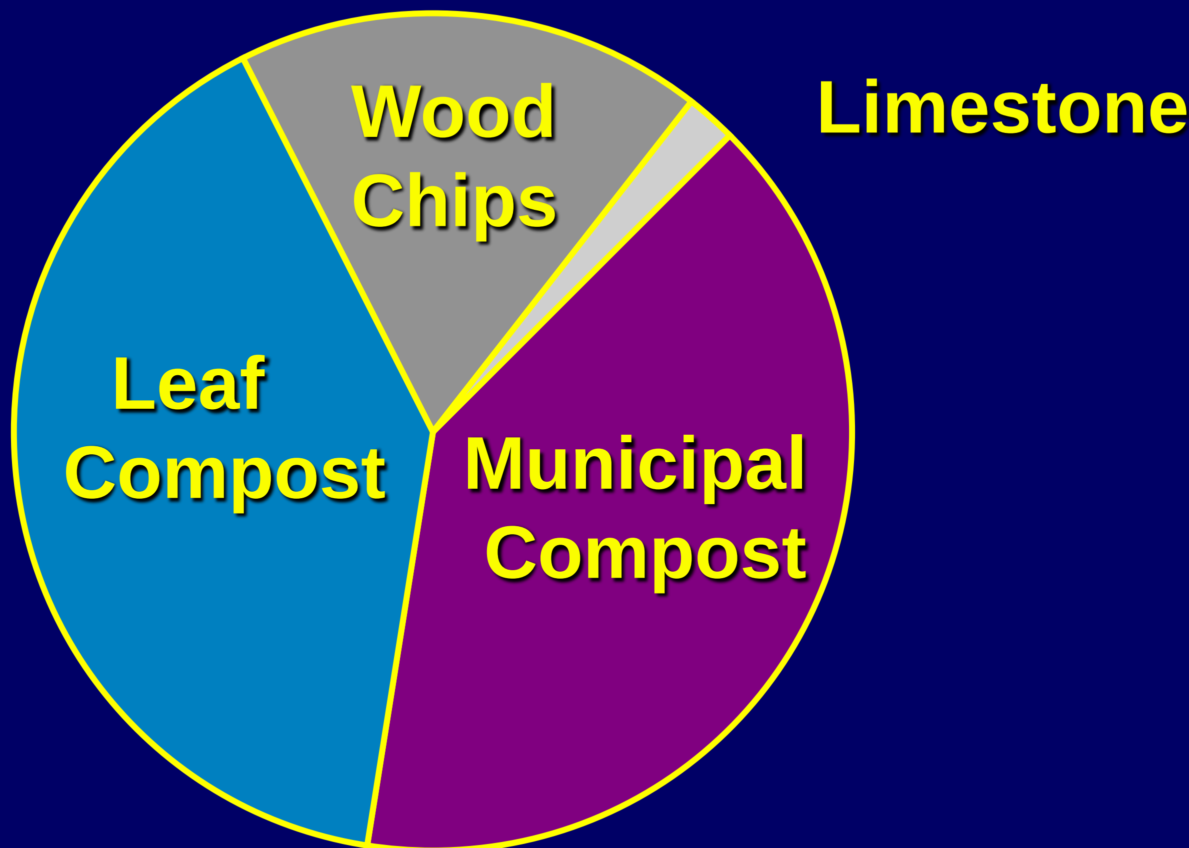
© University of Waterloo 2002

Nickel Rim Mine, Sudbury, ON

- Laboratory batch and column study
- Predictive groundwater flow modelling
- Field installation (1995)
- Benner et al., 1997; 1999
- Waybrant et al., 1998

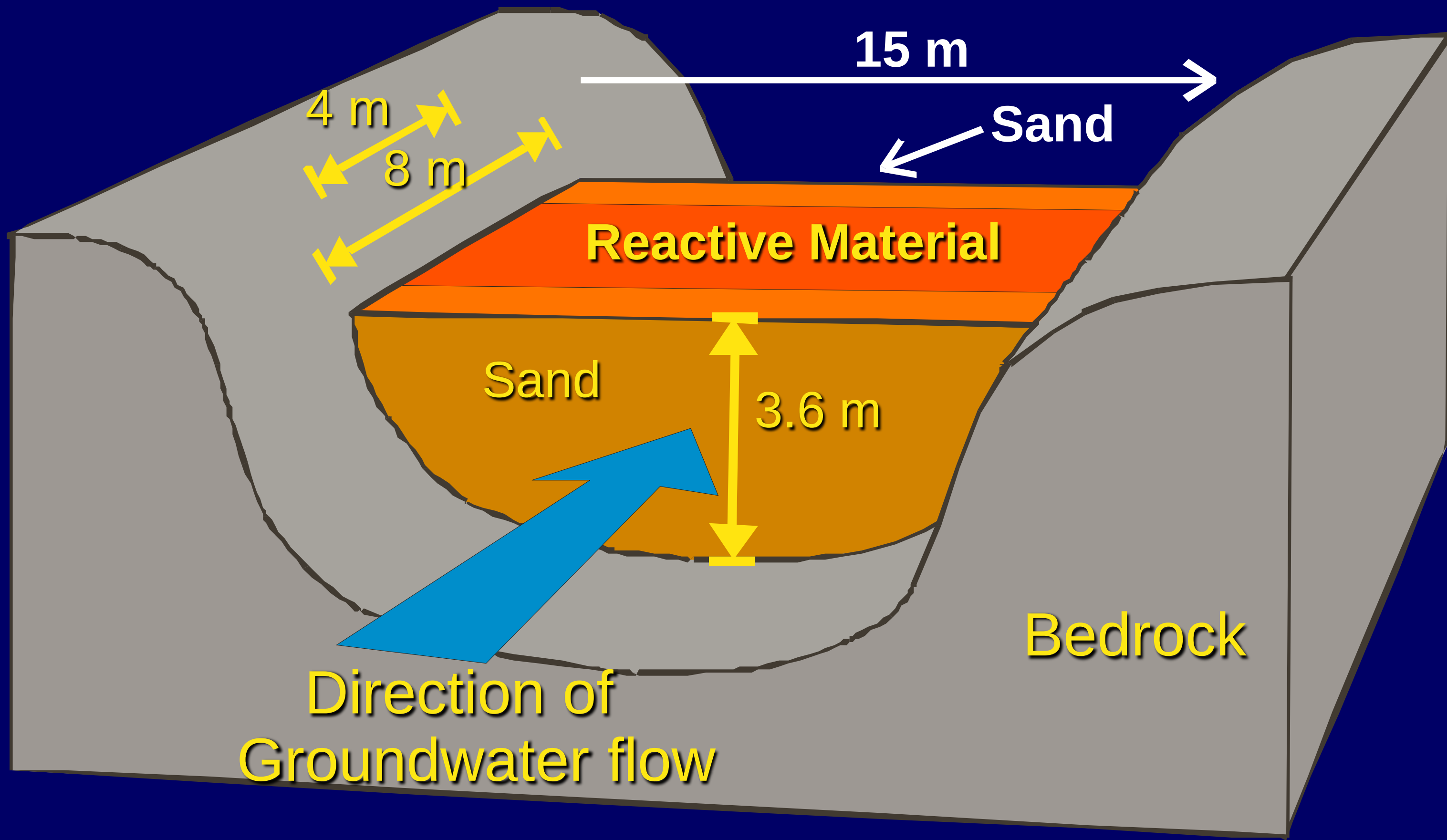
© University of Waterloo 2002

Reactive Mixture Composition for PRB



© University of Waterloo 2002

Porous Reactive Wall Installation



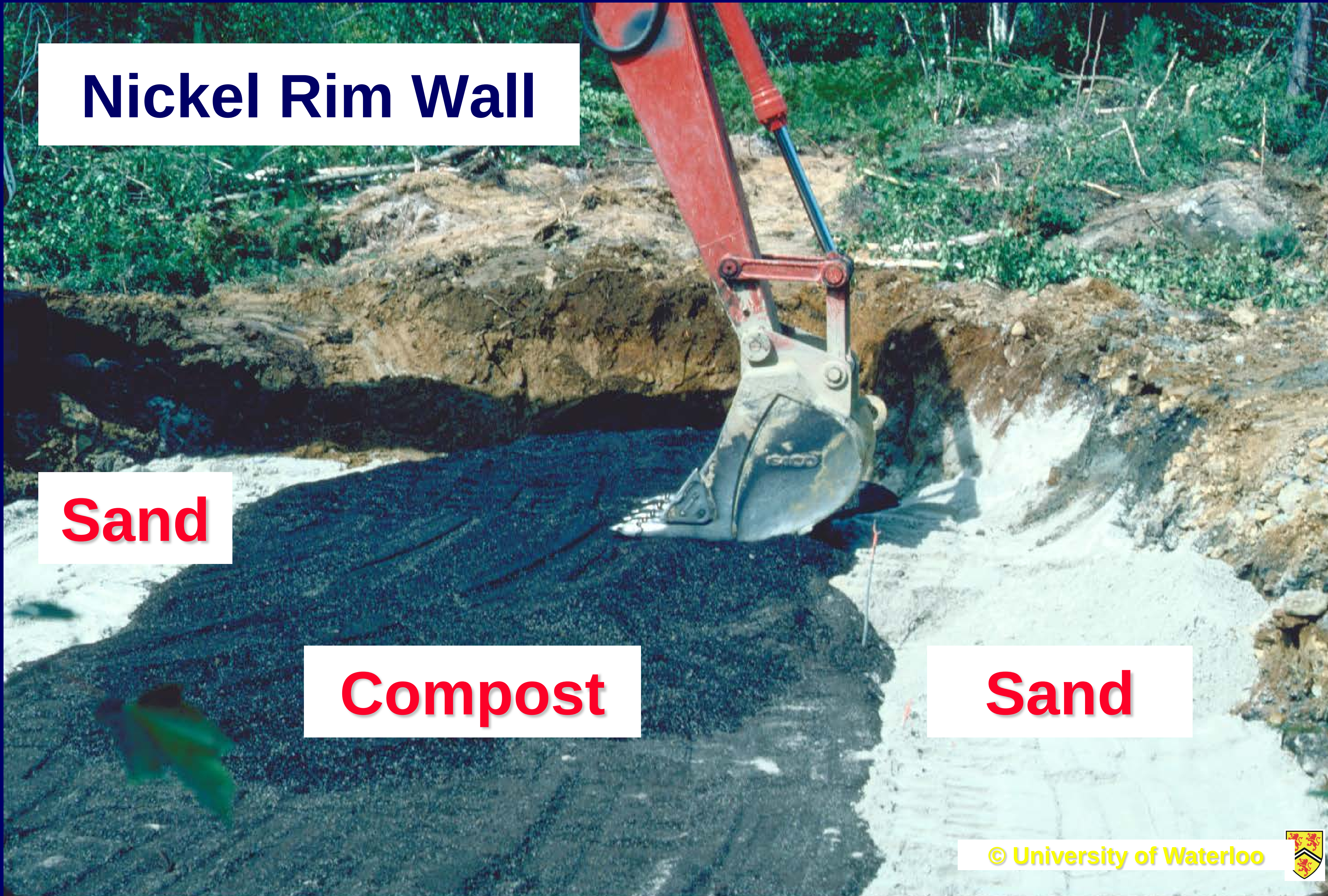
© University of Waterloo 2002

Nickel Rim Wall Materials

© University of Waterloo

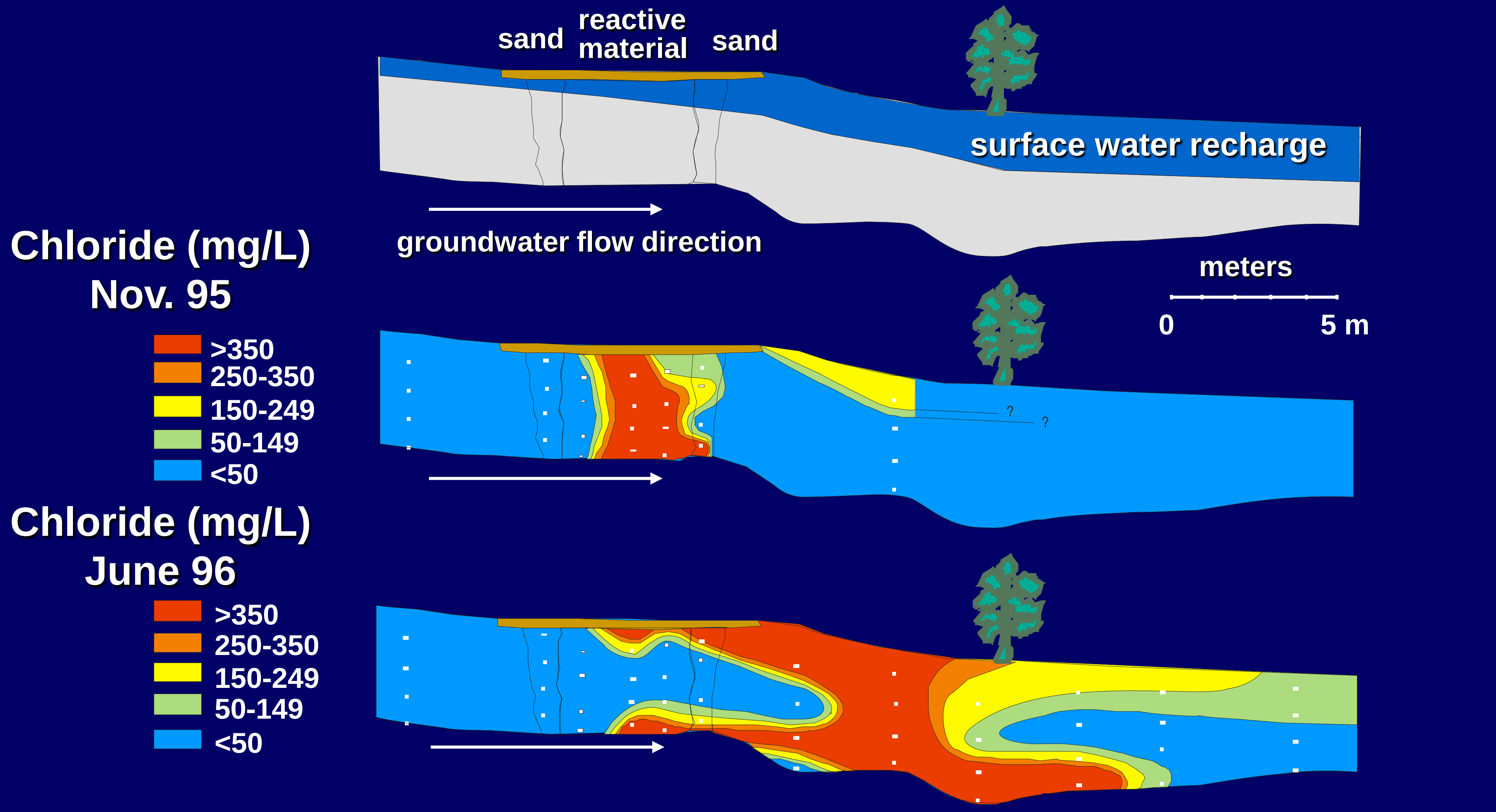
NR Wall Installation

© University of Waterloo


Nickel Rim Wall
Sand
Compost
Sand
© University of Waterloo


Nickel Rim Wall
Clay Cap
© University of Waterloo

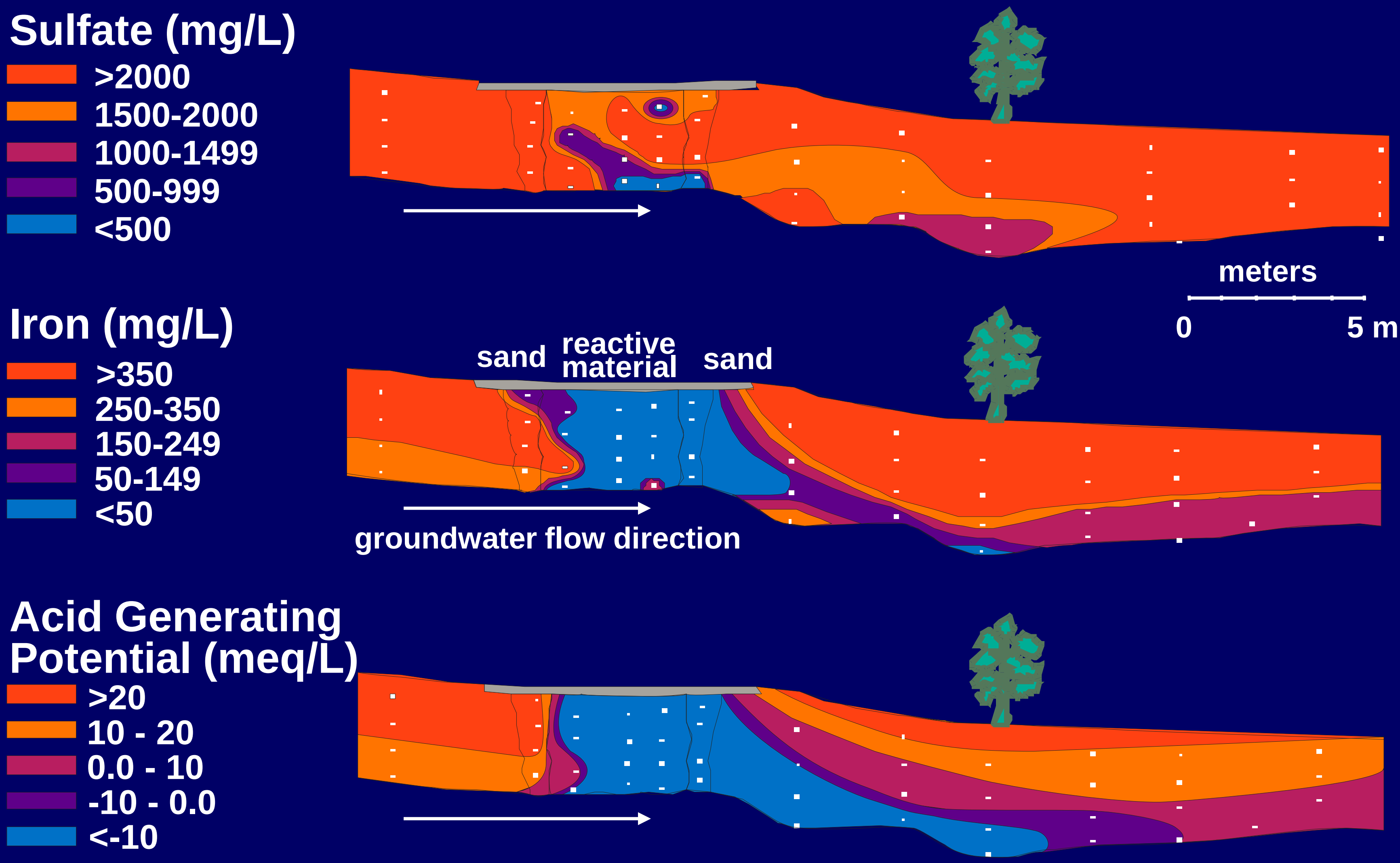
Groundwater Flow



Benner et al., 1997

© University of Waterloo 2002

Treatment Results



Benner et al., 1997

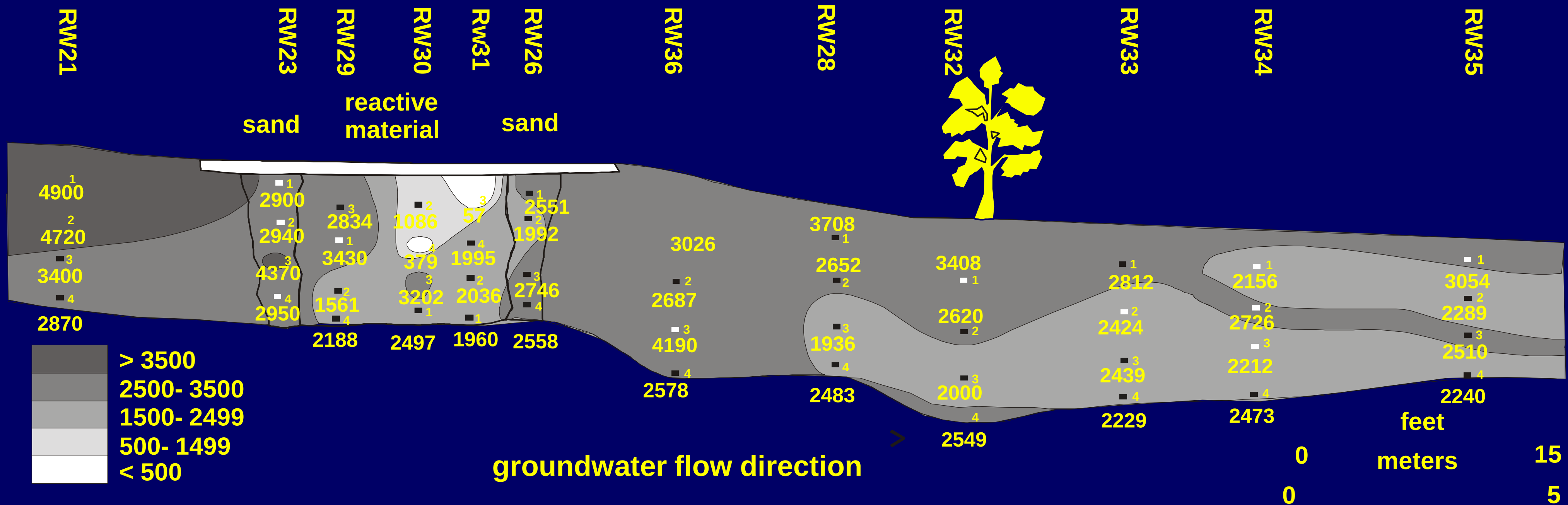
© University of Waterloo 2002

Sulfate Reduction in PRB

- Decreasing sulfate concentrations
- Sulfate-reducing bacteria
- Dissolved sulfide present
- Isotopic enrichment of ^{34}S in remnant sulfate
- Iron monosulfides identified in cores

© University of Waterloo 2002

Sulfate (mg/L)
August 2001



0

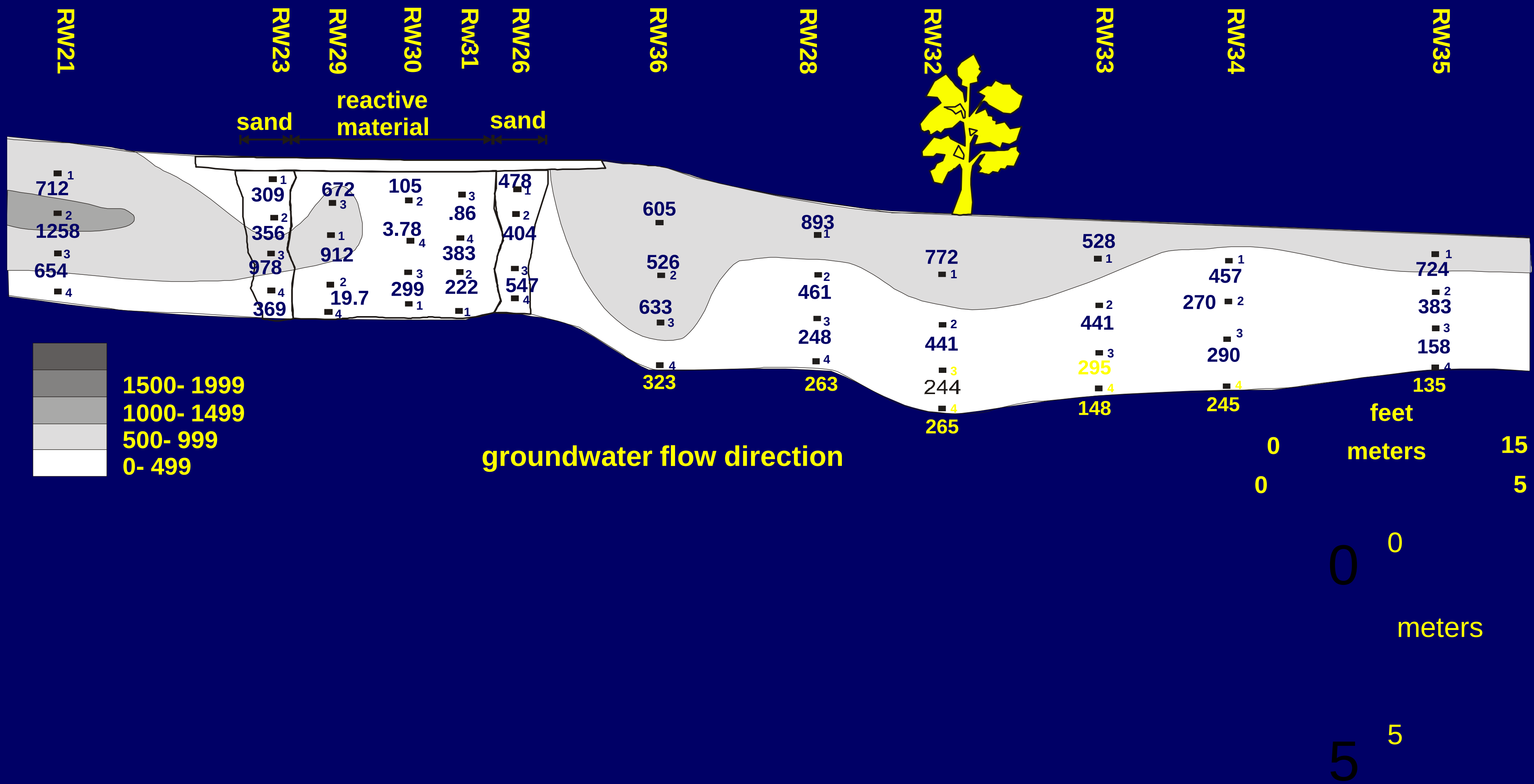
0

meters

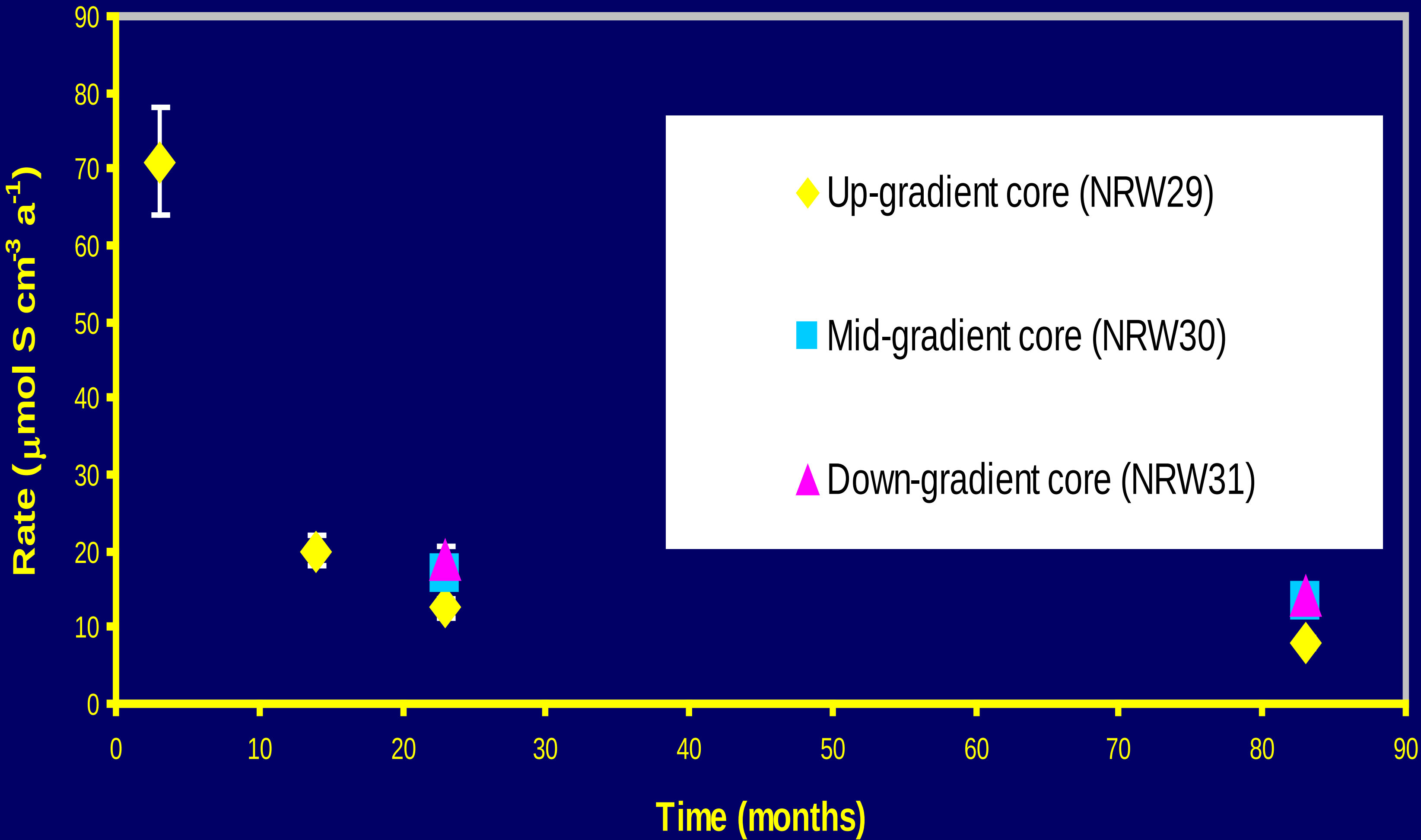
5

5

Iron (mg/L)
August 2001



Sulfide Accumulation in Nickel Rim PRB (Daignault 2002, UW B.Sc.Thesis)



Summary of Nickel Rim PRB

- The reactive wall is removing significant portion of the dissolved iron from the plume; full treatment would have required thicker PRB with longer residence time
- Reduced flux of contaminants in groundwater; reduced acid-generating potential of groundwater in receiving surface water
- Cost for materials and installation approximately $25 K (US) in 1995

© University of Waterloo 2002

Issues

- Heterogeneities in PRB/ residence time of contaminated groundwater in PRB is critical to level of treatment achieved
- Some loss of reactivity with time; sustained availability of organic carbon
- Influence of temperature in shallow PRB systems

© University of Waterloo 2002

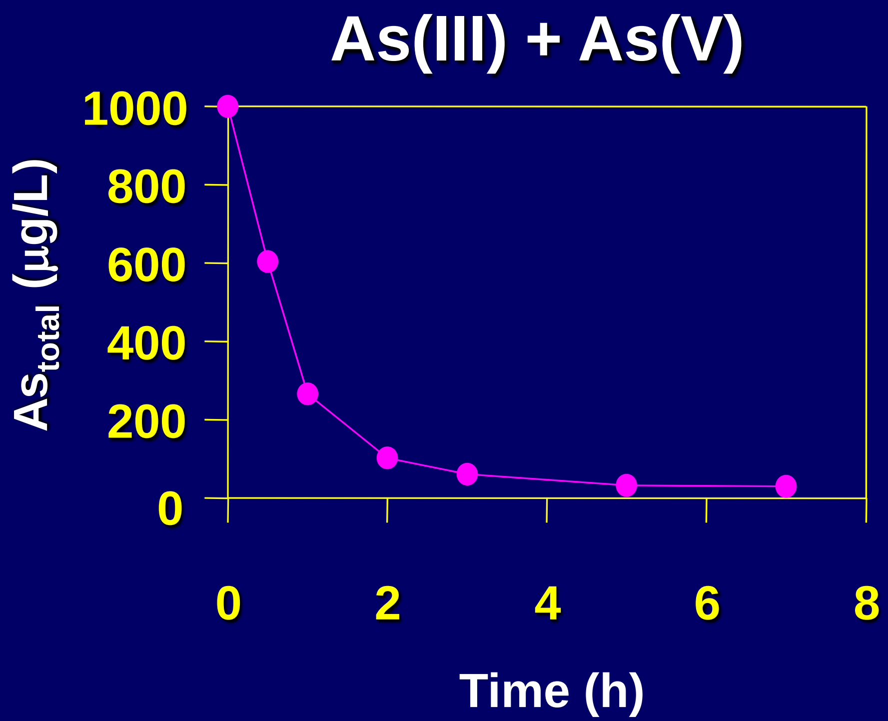
STEEL PRODUCTION WASTES
Basic Oxygen Furnace (BOF) Slag

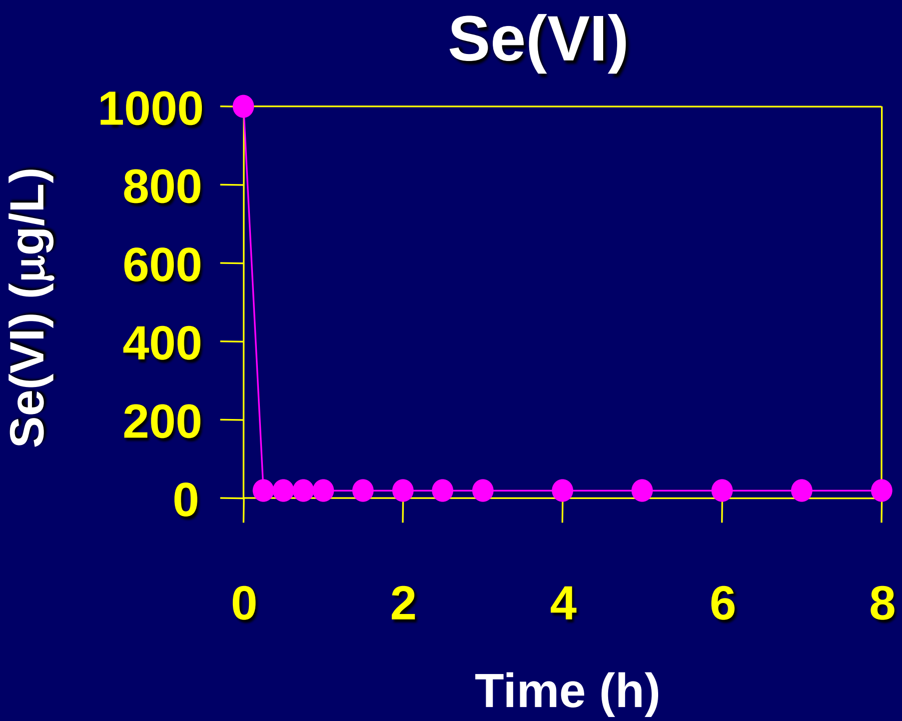
- Steel production waste product
- Used as aggregate for construction
- High Ca and Fe oxides and hydroxides
- Interaction with water: high pH
- Removal of phosphate (Baker et al., 1997; 1998) and arsenic(McRae et al., 1999)

© University of Waterloo 2002


Solid Reactive Mixtures
Aquifer Materials
Silica Sand
Limestone
Reactive Materials
BOF-Oxide
Zero Valent Iron
Activated Alumina

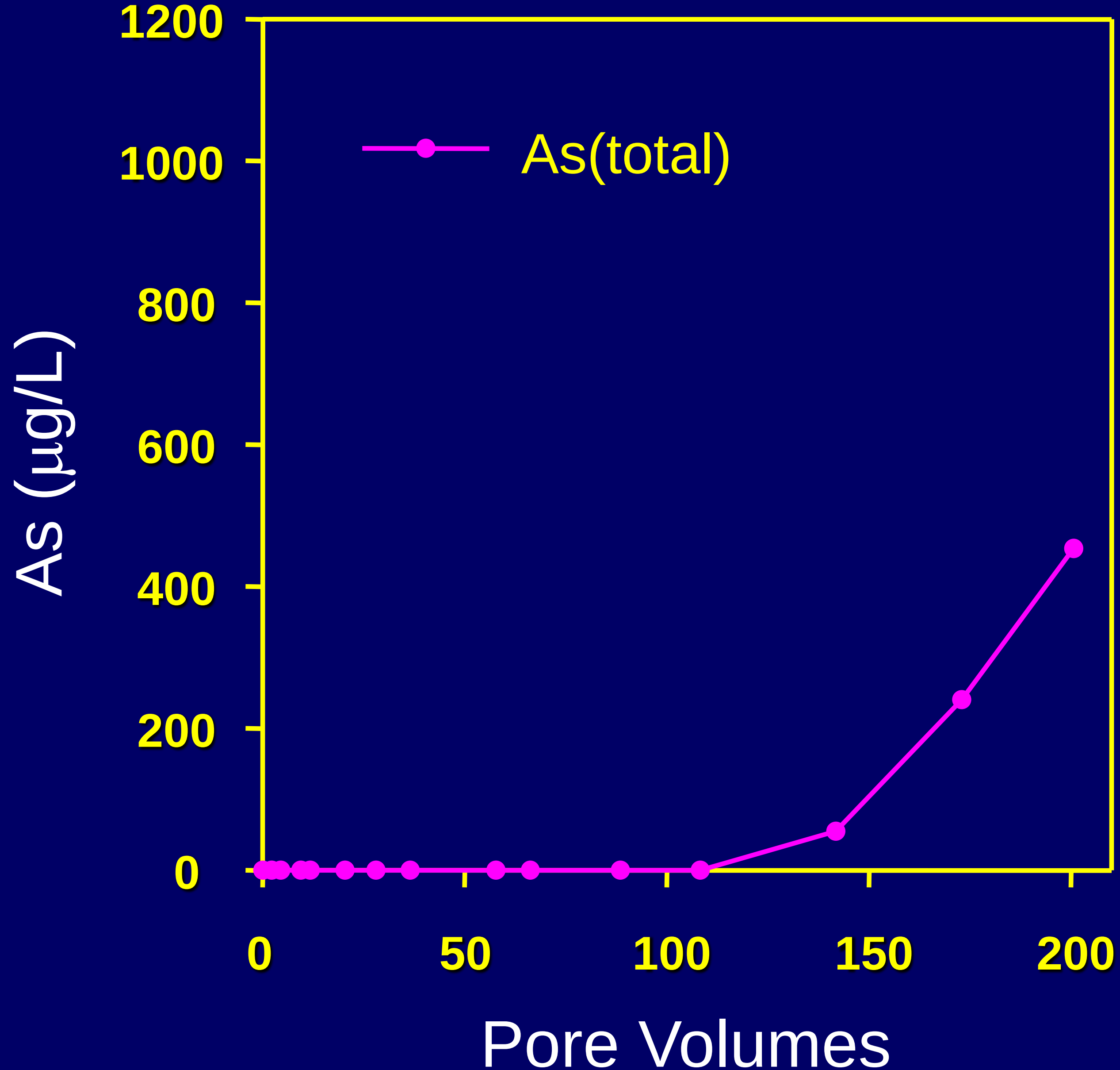
Batch Removal Rates





Iron Slag

BOF Slag Column



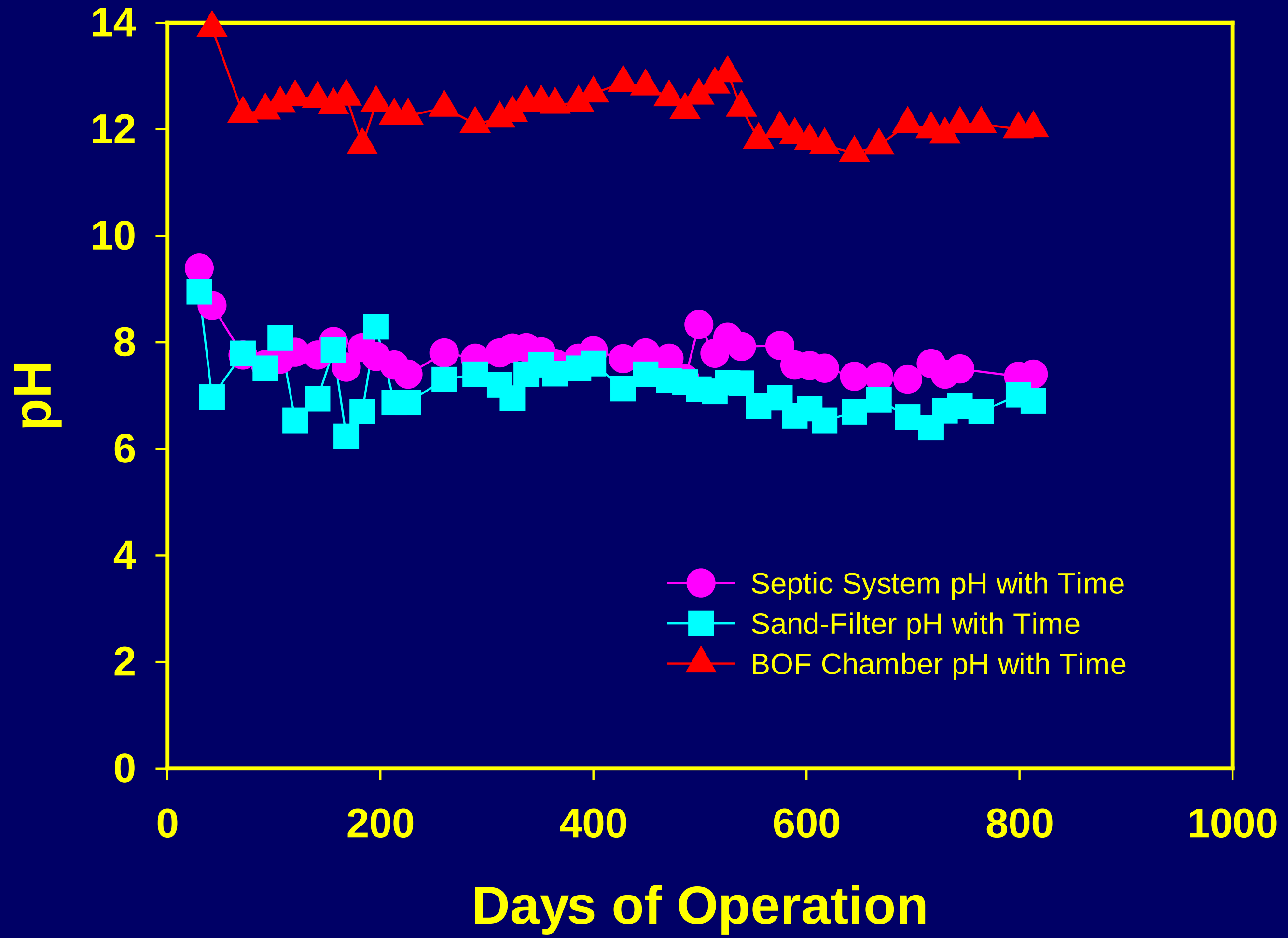
Second Column Test

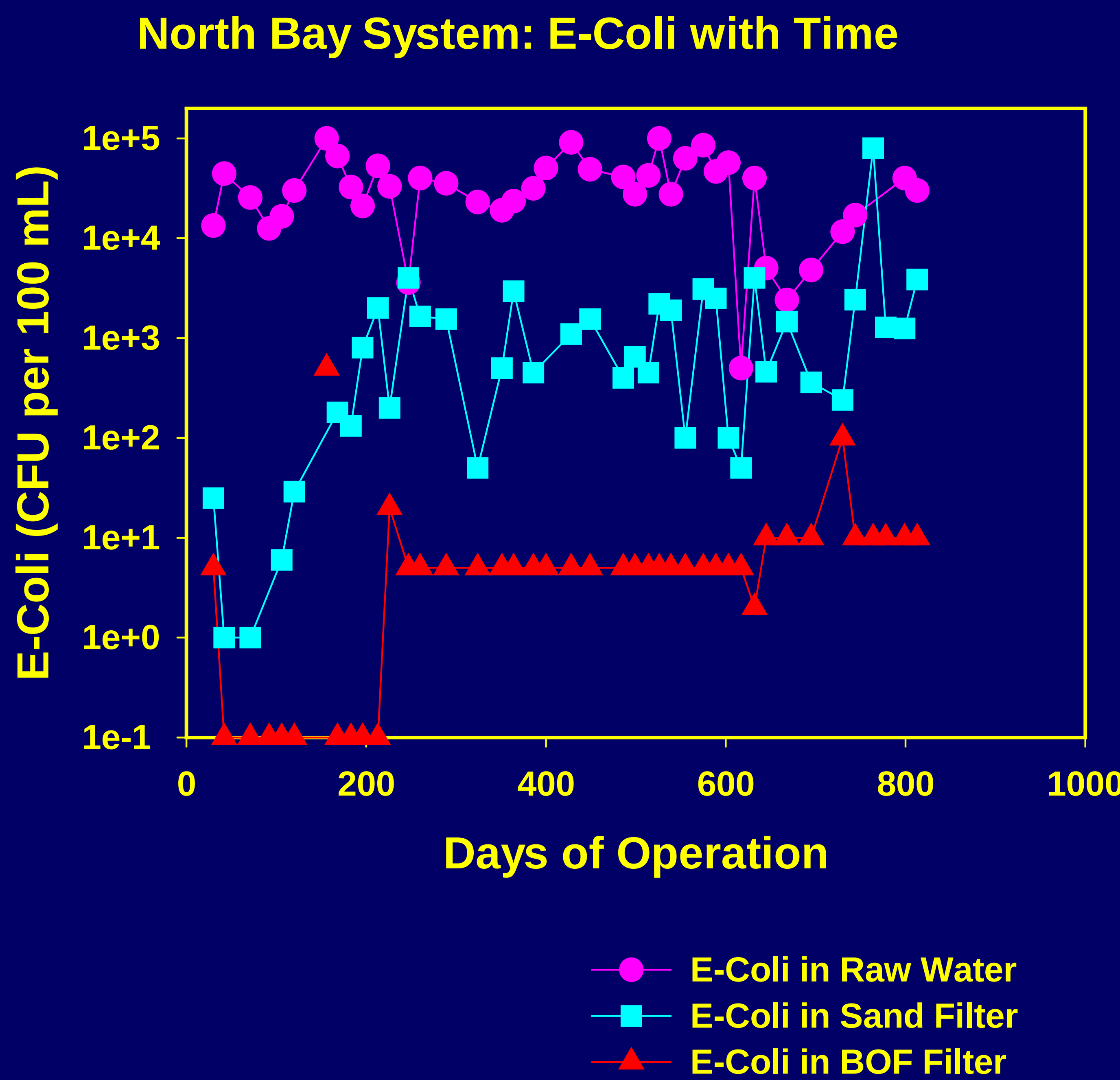
- 50 % BOF slag/ 50 % gravel
- Low pH site groundwater with 4 mg/L arsenic
- More than 75 pore volumes of flow (velocity of 0.3 m/day)
- Total arsenic concentration in effluent less than 0.01 mg/L

Arsenic Removal by BOF Slag

- Removal of arsenic oxyanions by sorption iron and manganese oxyhydroxides in BOF
- Removal to low levels (<0.005 mg/L total arsenic)
- Sustained performance for 100 pore volumes of 10 % BOF mixture

North Bay System: pH with Time




North Bay System: E-Coli with Time
E-Coli (CFU per 100 mL)
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1e-1
0
200
400
600
800
1000
Days of Operation
E-Coli in Raw Water
E-Coli in Sand Filter
E-Coli in BOF Filter

BOF-Chamber Performance

- Effective removal of phosphorus
- Effective removal of E-Coli
  - Elevated pH provides environment that eliminates bacteria
- Elevated pH of 12 or higher
  - Elevated pH is buffered by soils and sediments upon release to subsurface
  - pH of groundwater approximately 1 m down-gradient of discharge gallery was 6.2 to 7 (August 2000)

© University of Waterloo 2002

Zero-Valent Iron and Other Reactive Materials

- Excellent removal of electroactive metals
- Sulfate reduction and AMD treatment
- Excellent treatment of nutrients
- Performance of field-scale applications
- Removal mechanisms
- Reactive capacity
- Formation of secondary precipitates

© University of Waterloo 2002