Permeable Reactive Barriers: the 10p tour

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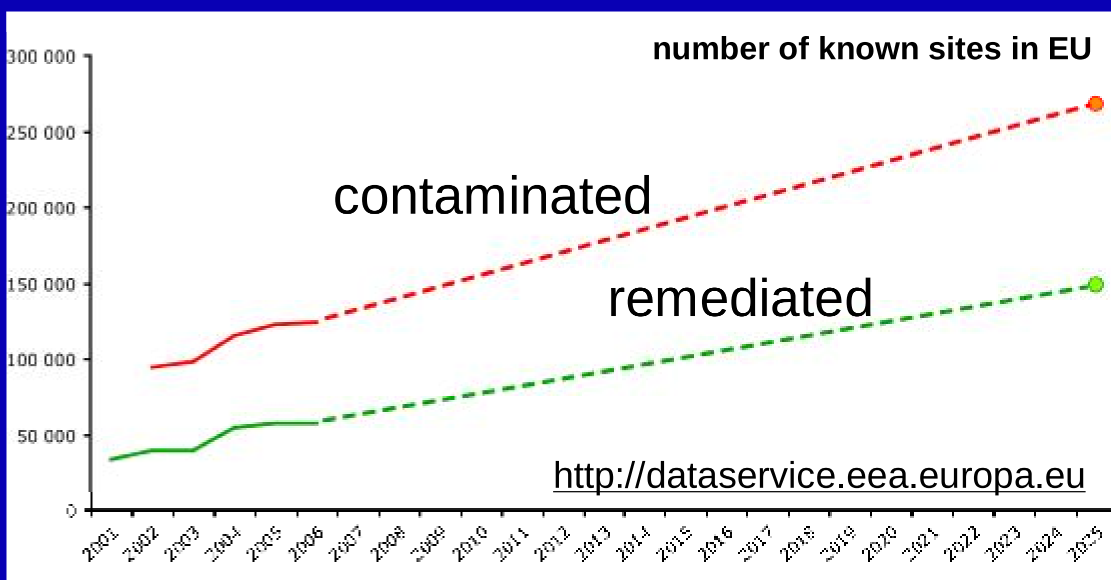
ConLand: what's it worth?

- remediation
  - if each site costs €300K to remediate, present market value is ~€39B
- value of the land…???
  - housing, business, industry, green space



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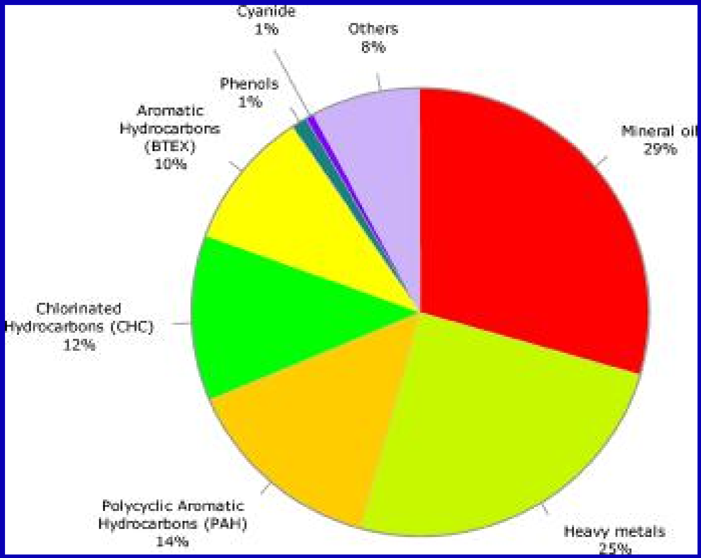
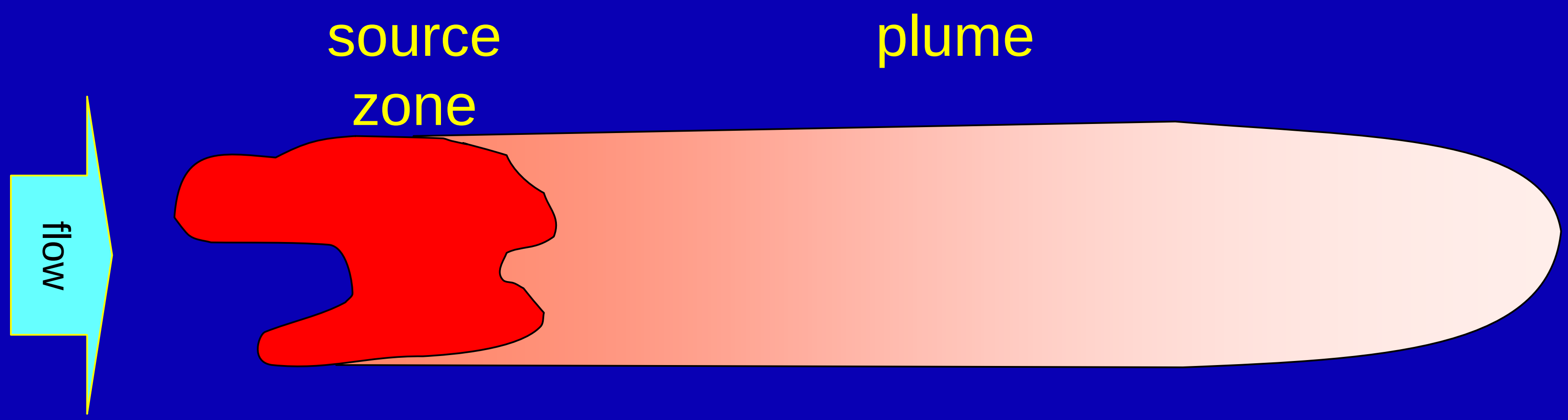
Types of contamination (point source)

- ~75% organics
  - petrol, coal tars, chlorinated solvents, oils
- 25% inorganics
  - mostly heavy metals



Groundwater Contamination: Conceptual Model



small area, large immobile mass

BLACK BOX

large area, small mobile mass dissolved and sorbed

GREY BOX

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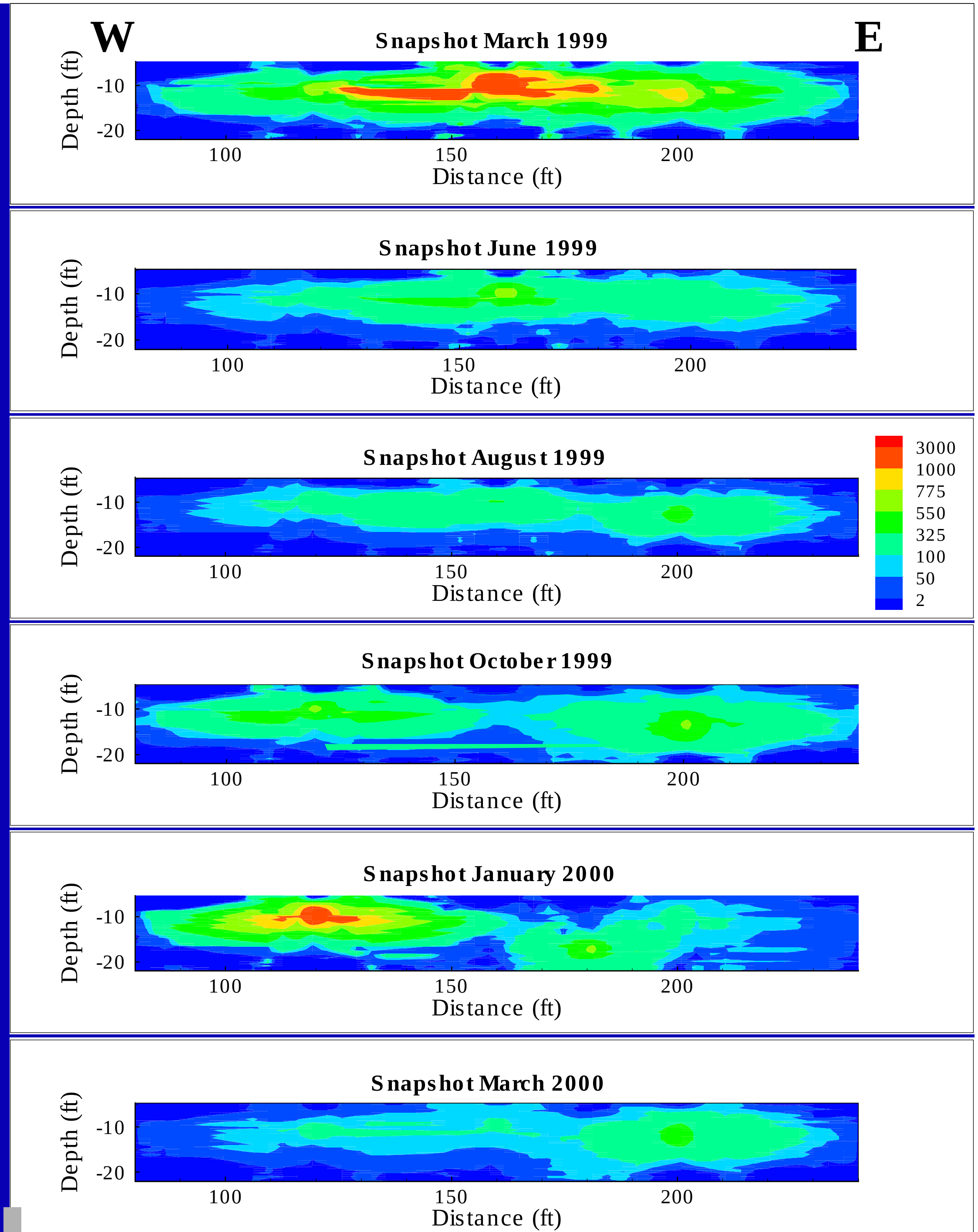
More common nature of plumes:

MTBE at VAFB, CA

snapshots across ML transect

no unique centreline

breakthrough would occur if design based on any one snapshot



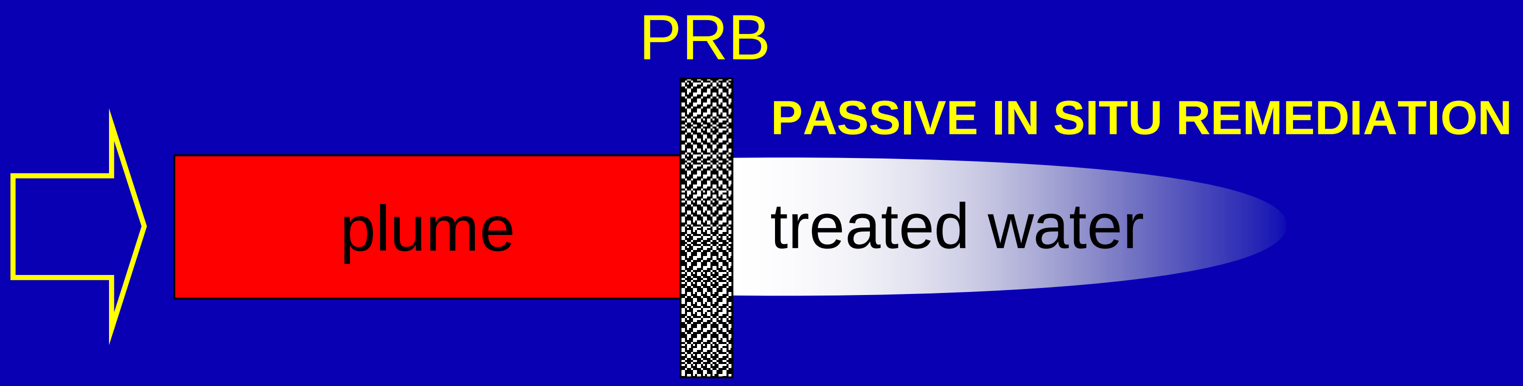
What is a PRB?

EA Guidance (NC/01/51) definition:

- an engineered zone placed in the path of a plume, consisting of a reactive material that results in remediation of contaminants as they flow through

Expanded definition:

- an engineered zone placed in the path of a plume within which is promoted chemical, biological and/or physical processes to immobilise or transform contaminants flowing through



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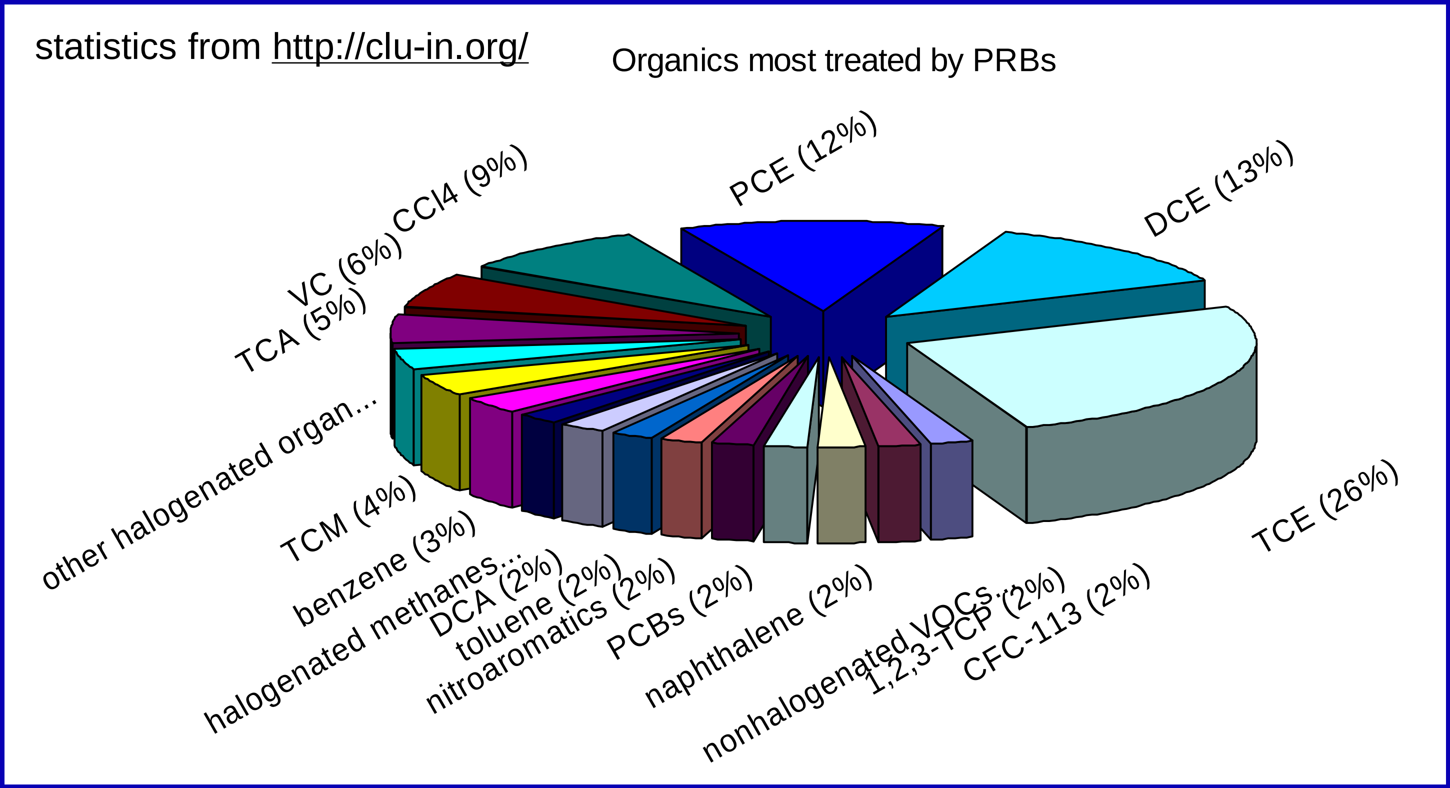
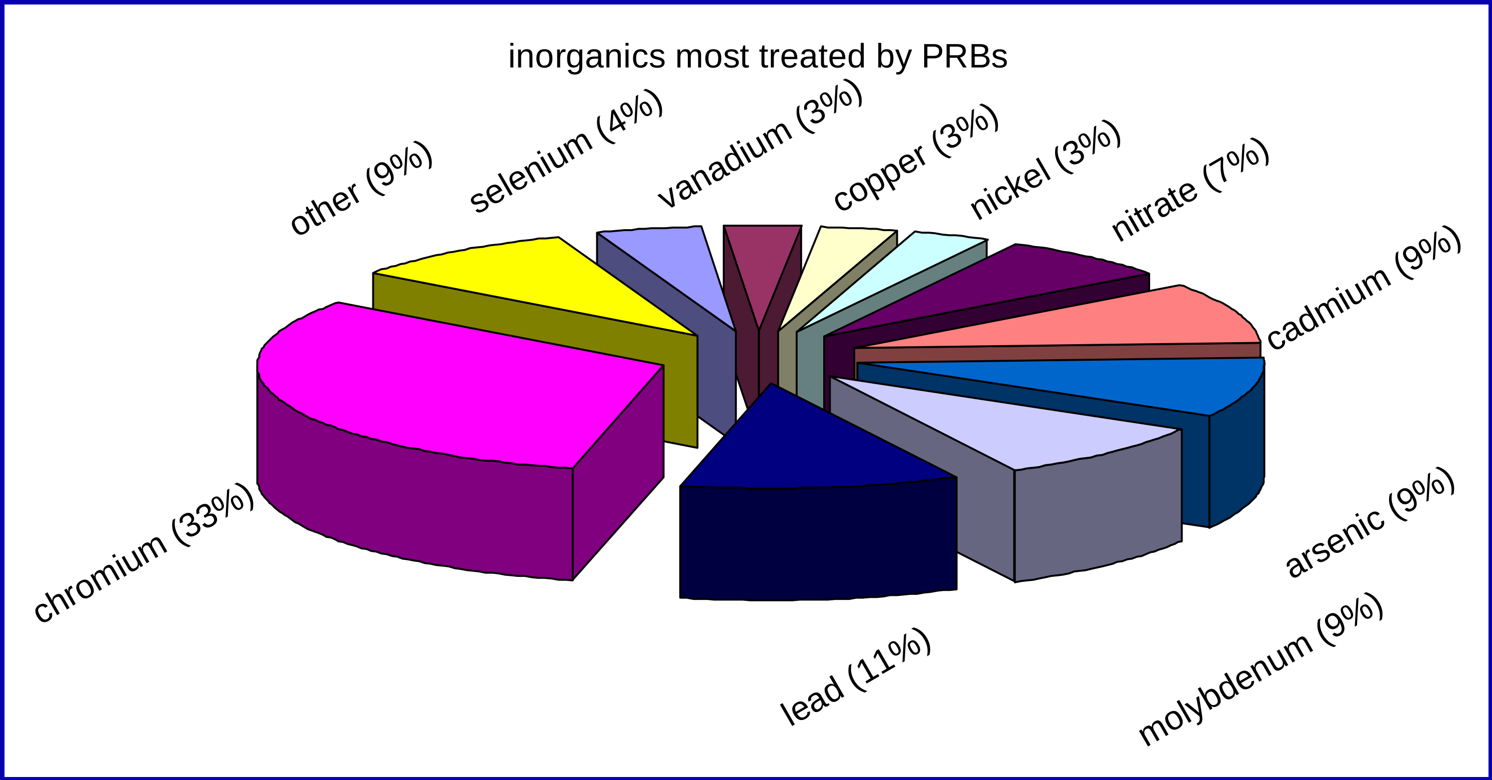
PRB applications - organics

- ~85% of PRBs used to treat halogenated hydrocarbons



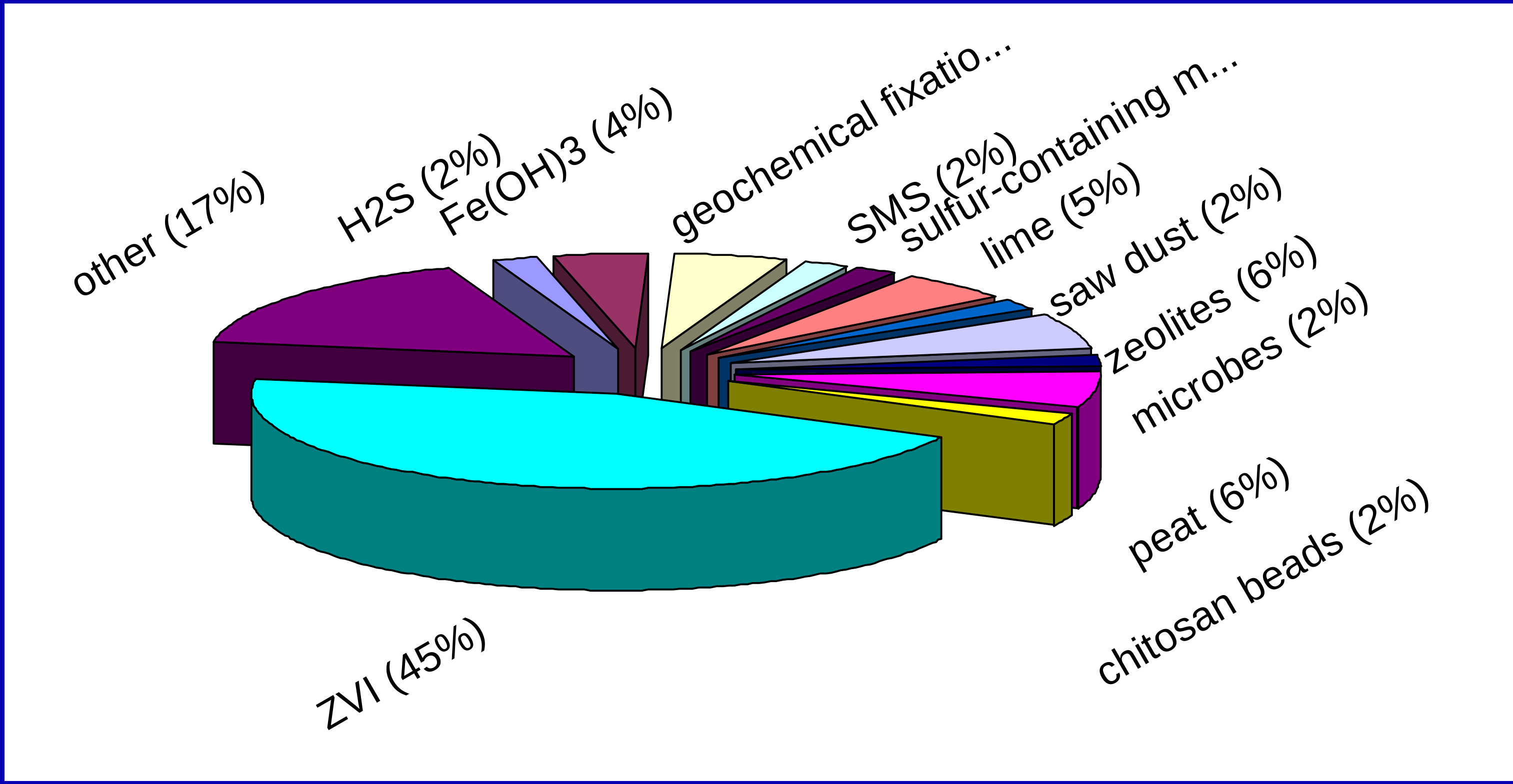
PRB applications - inorganics

- predominantly heavy metals



PRB types

- most frequently used materials



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Main types of barriers

- immobilisation
  - sorption, precipitation
- chemical transformation (irreversible)
  - zero valent iron and other metals, bimetals, oxide minerals
- biologically mediated transformation
  - supply of electron acceptor (oxidation) or donor (reduction) amendments
  - amendments may be solid, liquid or dissolved

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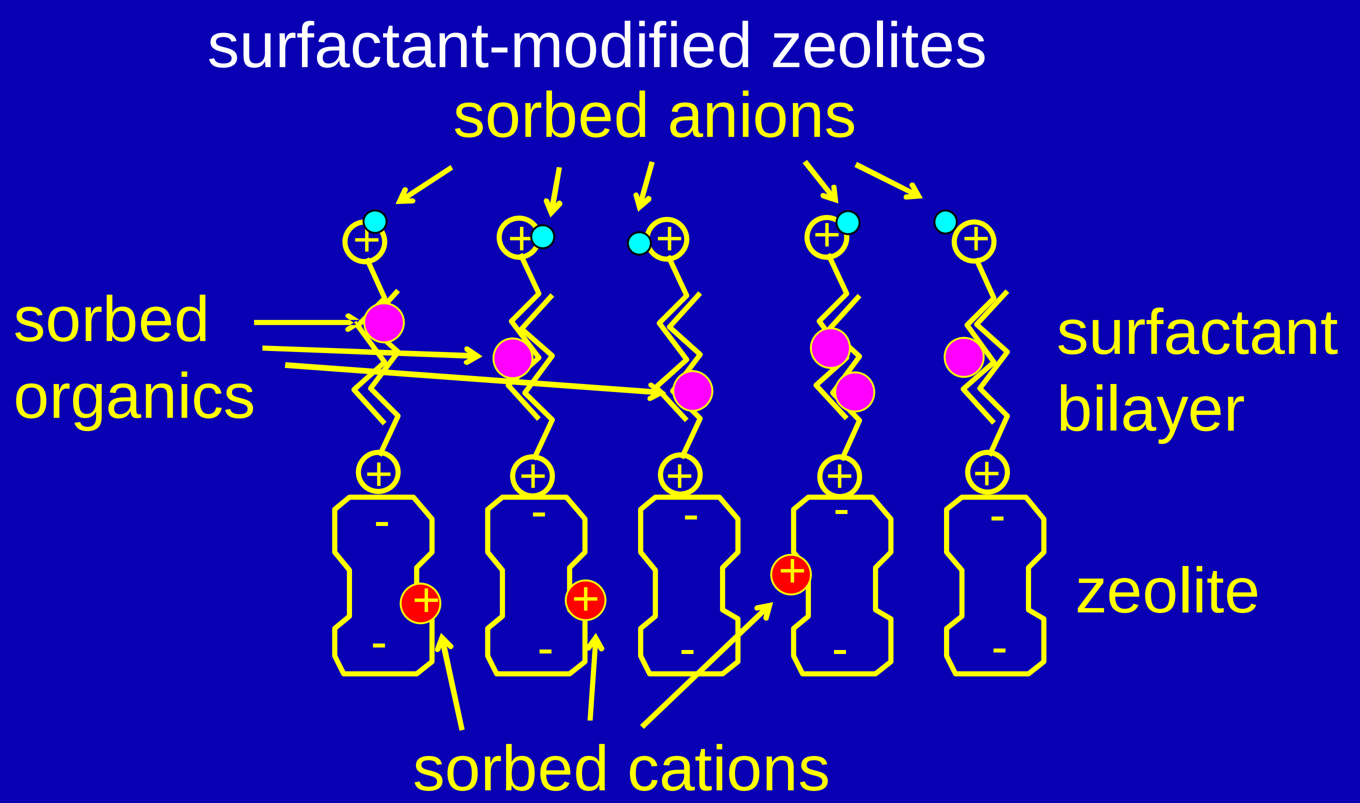
Sorption barriers

- use adsorption and/or absorption
- humic materials (peat, GAC), oxides, zeolites



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Precipitation barriers

- usually involve introduction of solution that changes pH to cause precipitation
  - $Ca(OH)_2$ and $CaCO_3$ increase pH
- or swamp the system with a complimentary ion species
  - e.g. add phosphate (hydroxyapatite)
    - precipitate hyxroxypyromorphite ($Pb_{10}(PO_4)_6(OH)_2$

Chemical transformation barriers

- destroy contaminants within barrier
  - not immobilised
- most common is zero valent iron
  - relatively new technology
    - first “discovered” in 1989, University of Waterloo
- key design issue is residence time

How does ZVI work?

- for halogenated hydrocarbons
  - reductive dehalogenation reaction (sequential)
    - PCE **à** TCE **à** cis 1,2 DCE **à** VC **à** ethene
  - reactions include 2 redox couples

1

$$Fe^{o} \rightarrow Fe^{2+} + 2e^{-}$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$

2

$$Fe^{o} \rightarrow Fe^{2+} + 2e^{-}$$

$$RCl + H^{+} + 2e^{-} \rightarrow RH + Cl^{-}$$

with a resulting pH rise to 9-10

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Reaction rates

- $t_{1/2}$ for a range of chlorinated solvents

compound	$t_{1/2}$ (hrs)
CT	0.25
TCM	33.0
TBM	0.24
DCM	no degradation
HCA	0.13
1,1,2,2 TeCA	19.2
1,1,1,2 TeCA	4.4
1,1,1 TCA	5.3
PCE	17.9
TCE	13.6
1,1 DCE	40.0
t 1,2 DCE	55.0
c 1,2 DCE	432.0
VC	347.0

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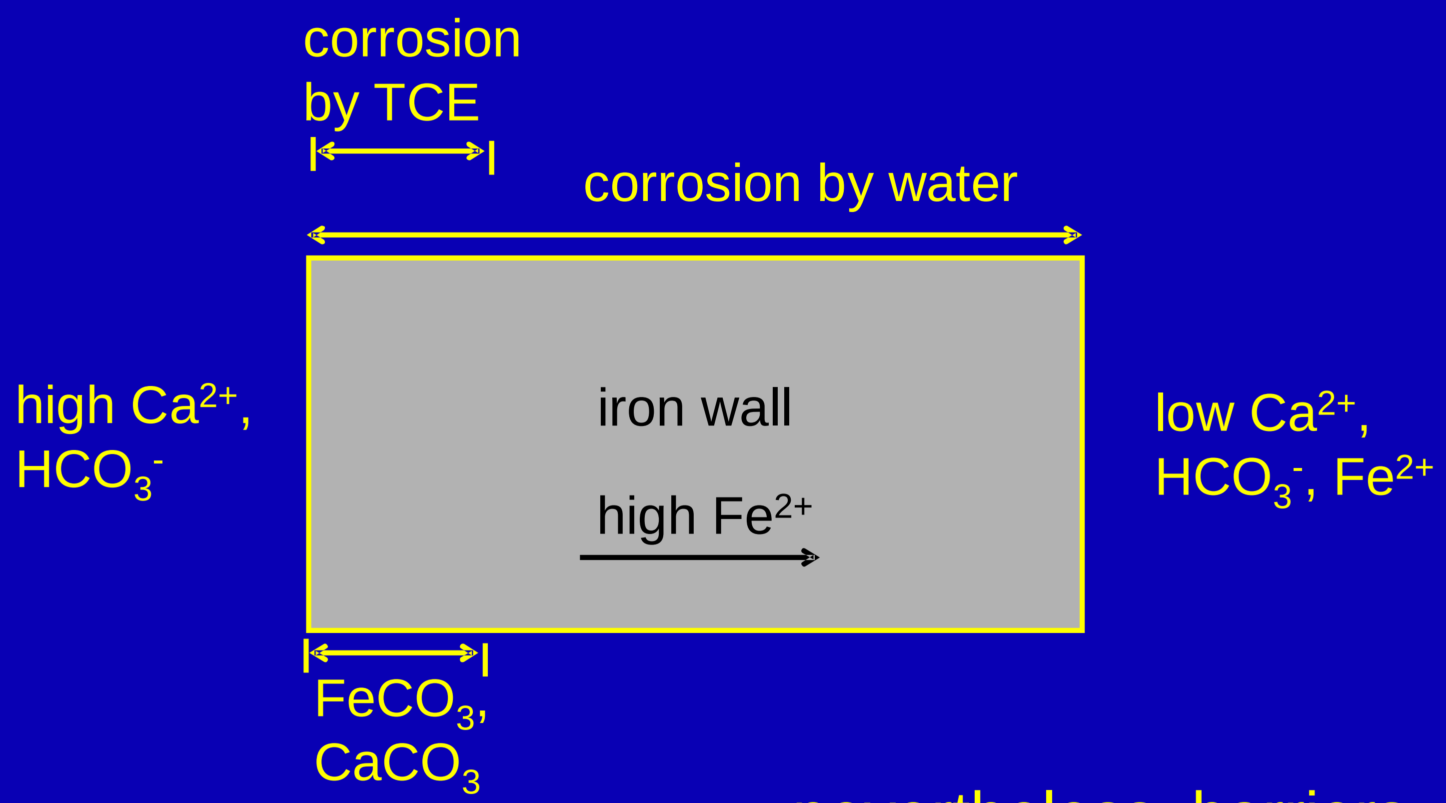
What goes on in a ZVI PRB?

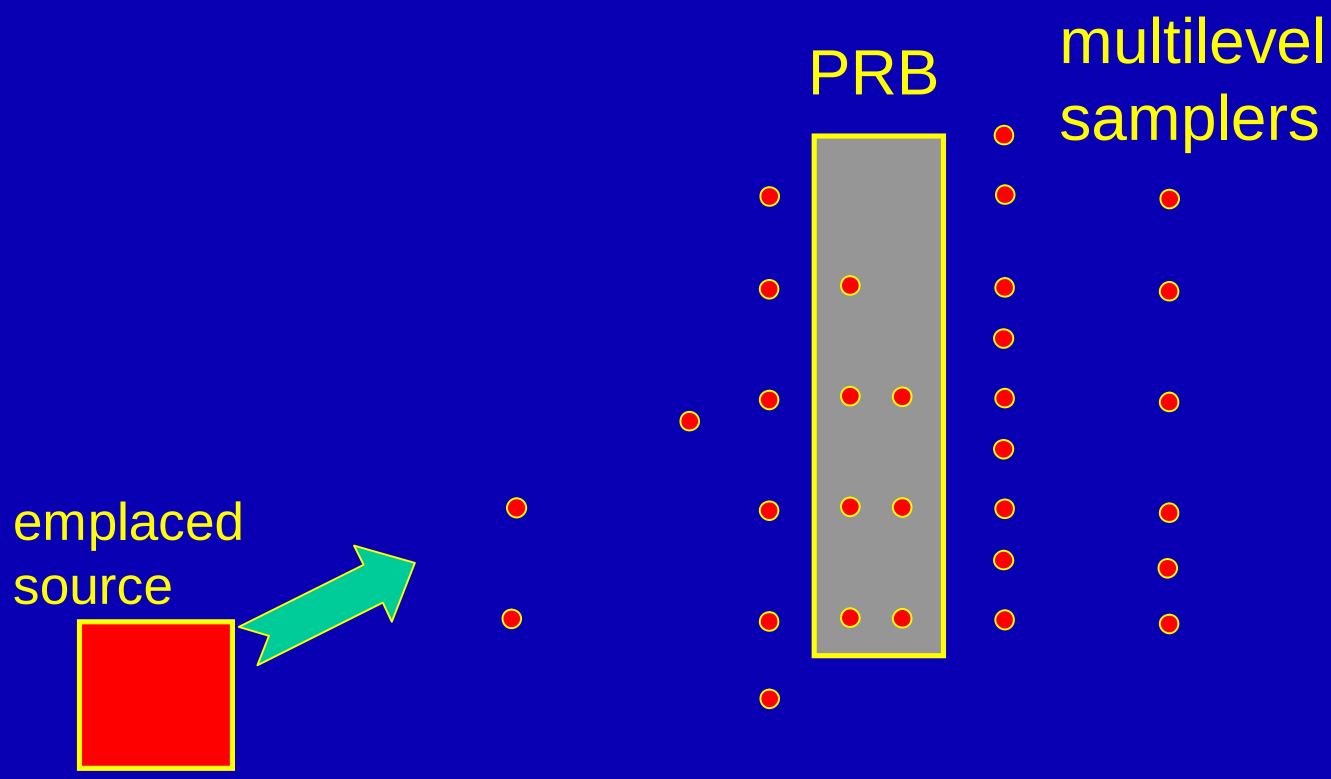
- Iron corrosion
  - produces 0.6 mmoles Fe^{2+}/kg Fe^{o}/day
  - passivates reactive surfaces
- chlorinated solvent reduction
  - produces 1 mole of Fe^{2+}/mole of Cl released to solution
- pH rise
  - precipitation of Fe oxides and carbonates

summary of ZVI barrier processes

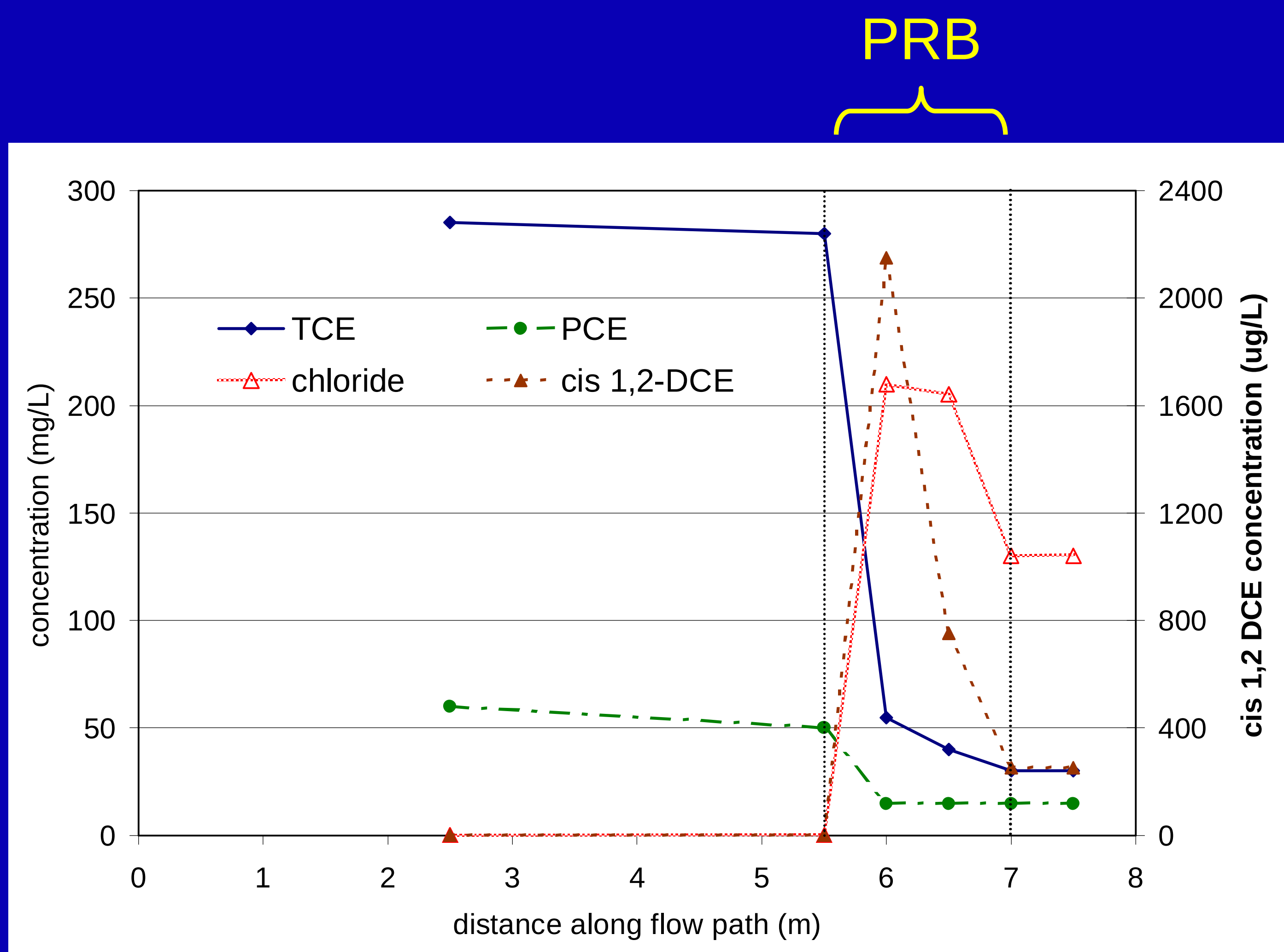


nevertheless, barriers
expected to last >20 years

First ZVI PRB field trial - CFB Borden, Canada



Results of field trial



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Learning from first field trial

- rapid removal of parents and daughters
- minor amount of precipitates
- barrier too thin to achieve full treatment
  - residence time miscalculated
- 15 years of consistent operation

Residence Time

- need to know:
  - groundwater velocity (magnitude and spatial variability)
  - reaction rate (half life)
  - contaminant concentration and cleanup target
    - gives number of half lives
- example:
  - velocity is 10 cm/day, $t_{1/2}$=5 hours and TCE is 1 mg/L (target is 0.005 mg/L so 8 half lives needed)
  - then reactive zone needs to be
    - 8 x 5 hrs x 10/24 cm/hr = 17 cm thick

Biological transformation barriers

- stimulate microbes to biodegrade contaminants
- barrier serves as amendment delivery zone
  - electron acceptors (oxygen, nitrate)
  - electron donors (labile carbon)
- reactions happen within and downgradient of barrier
  - not as sensitive to residence time

Amendment delivery methods

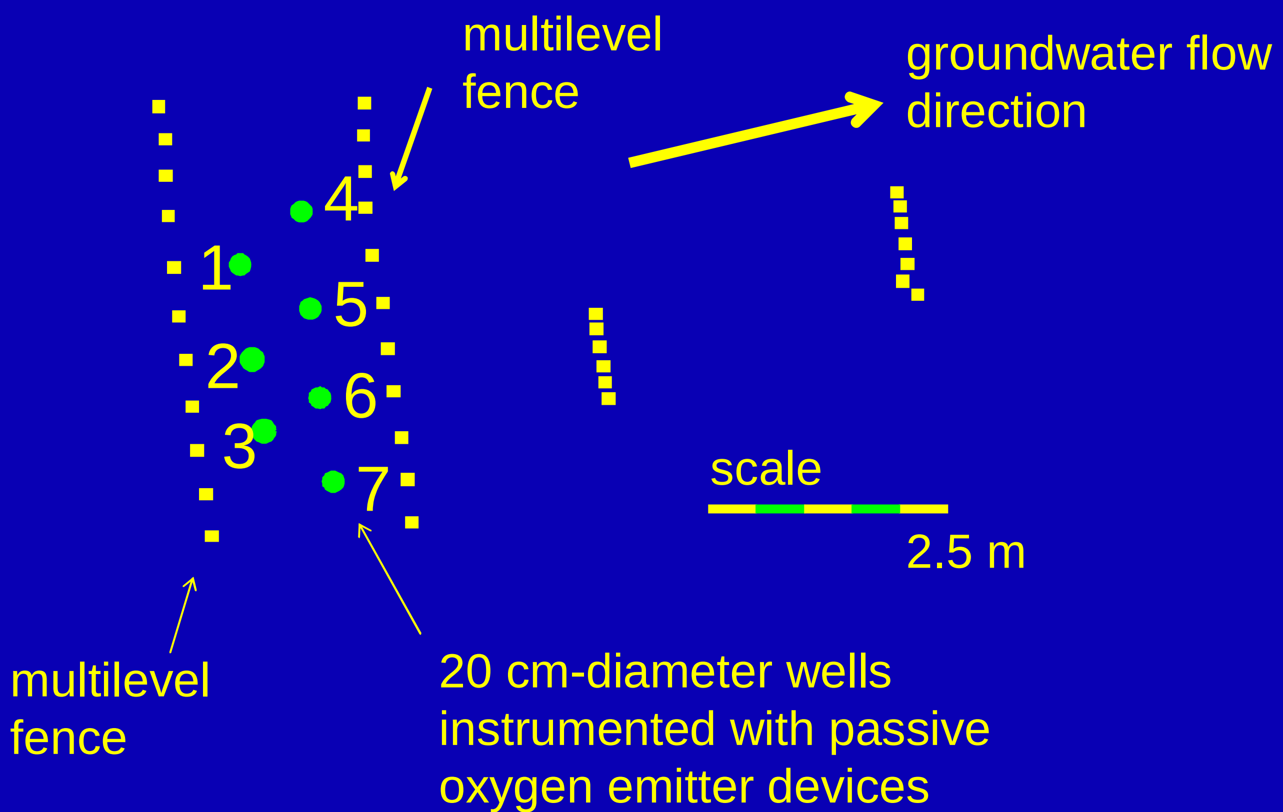
- from solids
  - ORC, salt-impregnated briquettes (nitrate)
- from liquids
  - HRC, edible oils, dissolved EAs or EDs
- gases
  - direct by sparging
  - diffusion (Waterloo Emitter, iSOC)

Requirements for biological systems

- 3 key questions:
  - are organisms capable of the reaction present?
  - can amendment supply meet demand?
  - can amendment, organisms and plume be effectively mixed?
- if any one of the above aren't true, success is unlikely

example at Strathroy, ON - diffusive Waterloo Emitters™

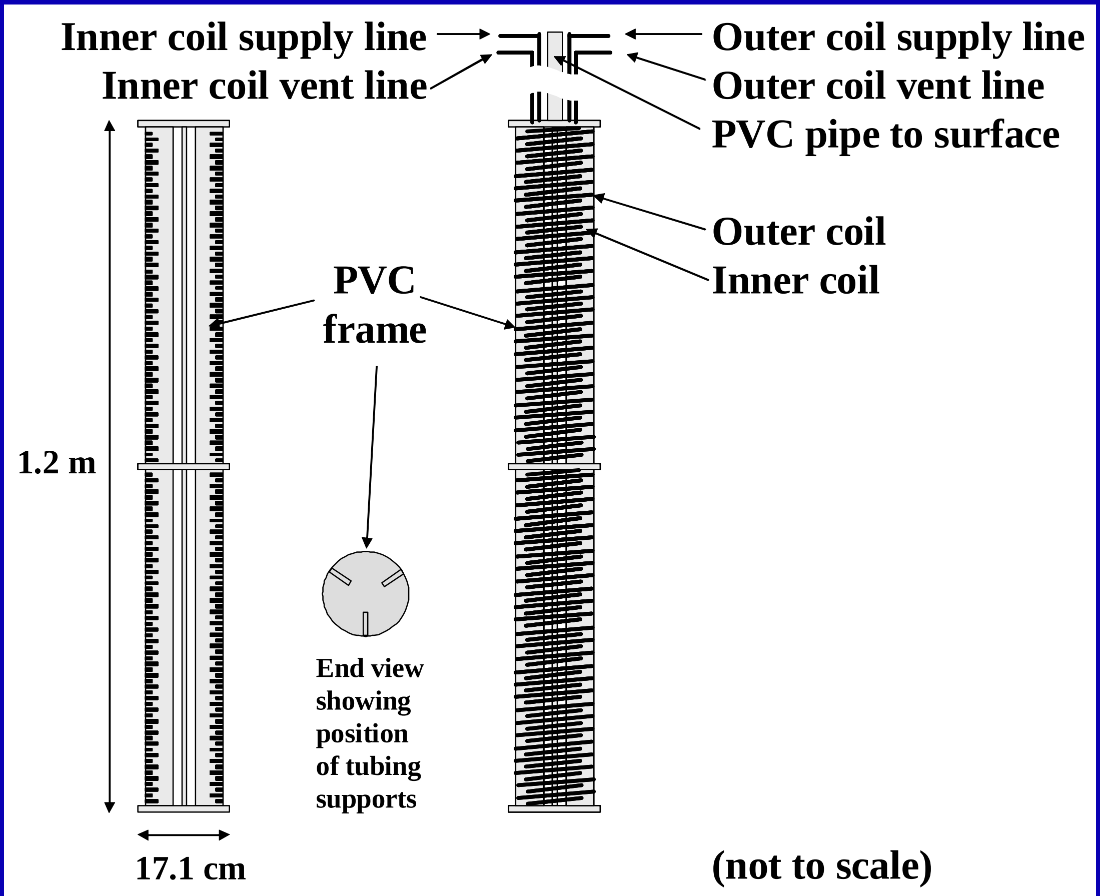
- plan of instrumentation



Diffusive emitters

- polymeric tubing on PVC frame
  - LDPE or silicone
- tubing pressurised with O_2/SF_6 mixture
- concentration gradient across tubing wall drives gases through by diffusion
- gases dissolve immediately into water flowing through well - no bubbles
- see Wilson and Mackay, GWMR , 2002

diffusive emitters



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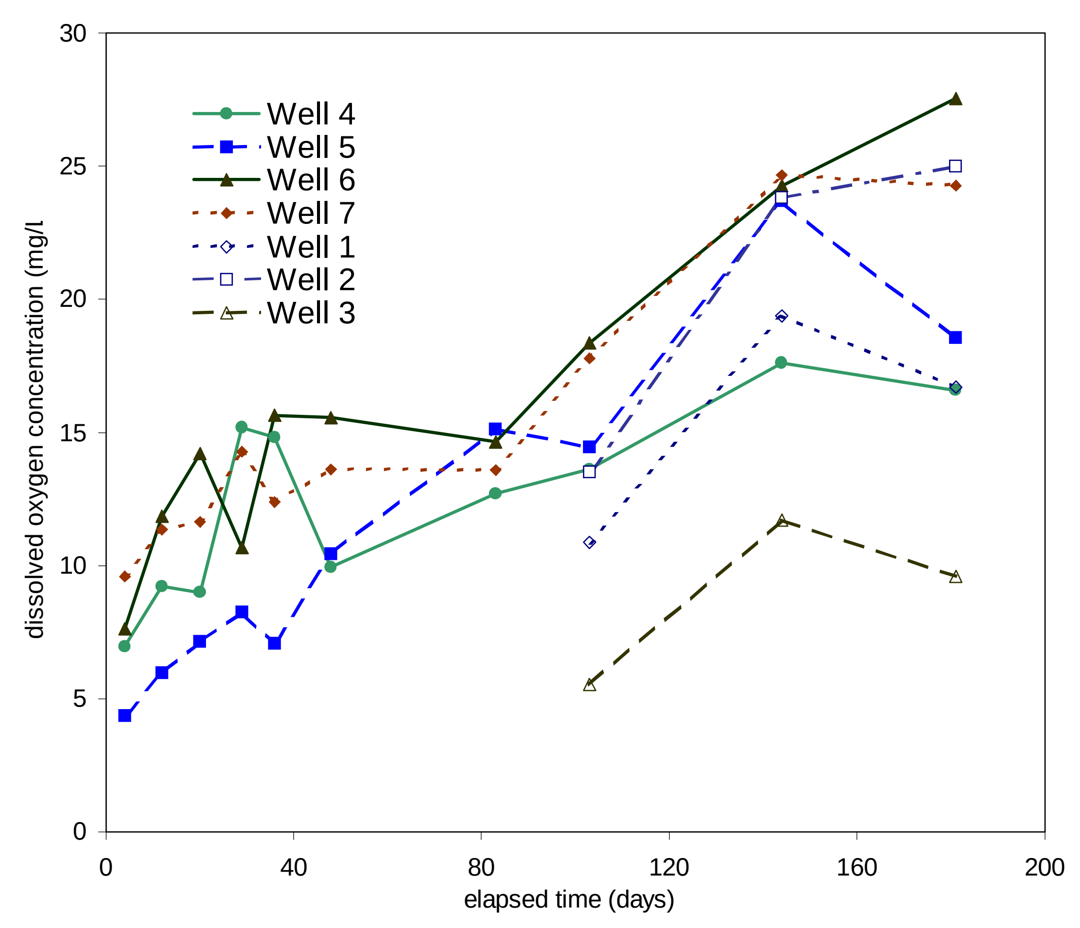
DO concentration in emitter wells

- pressure in tubing increased on day 90
- steady state DO matched predicted values
  - 15 mg/L from 0-90 days
  - 25 mg/L from 90-185 days
- 15 mg/L DO can degrade only ~5 mg/L BTEX
- Strathroy plume is more like 80 mg/L



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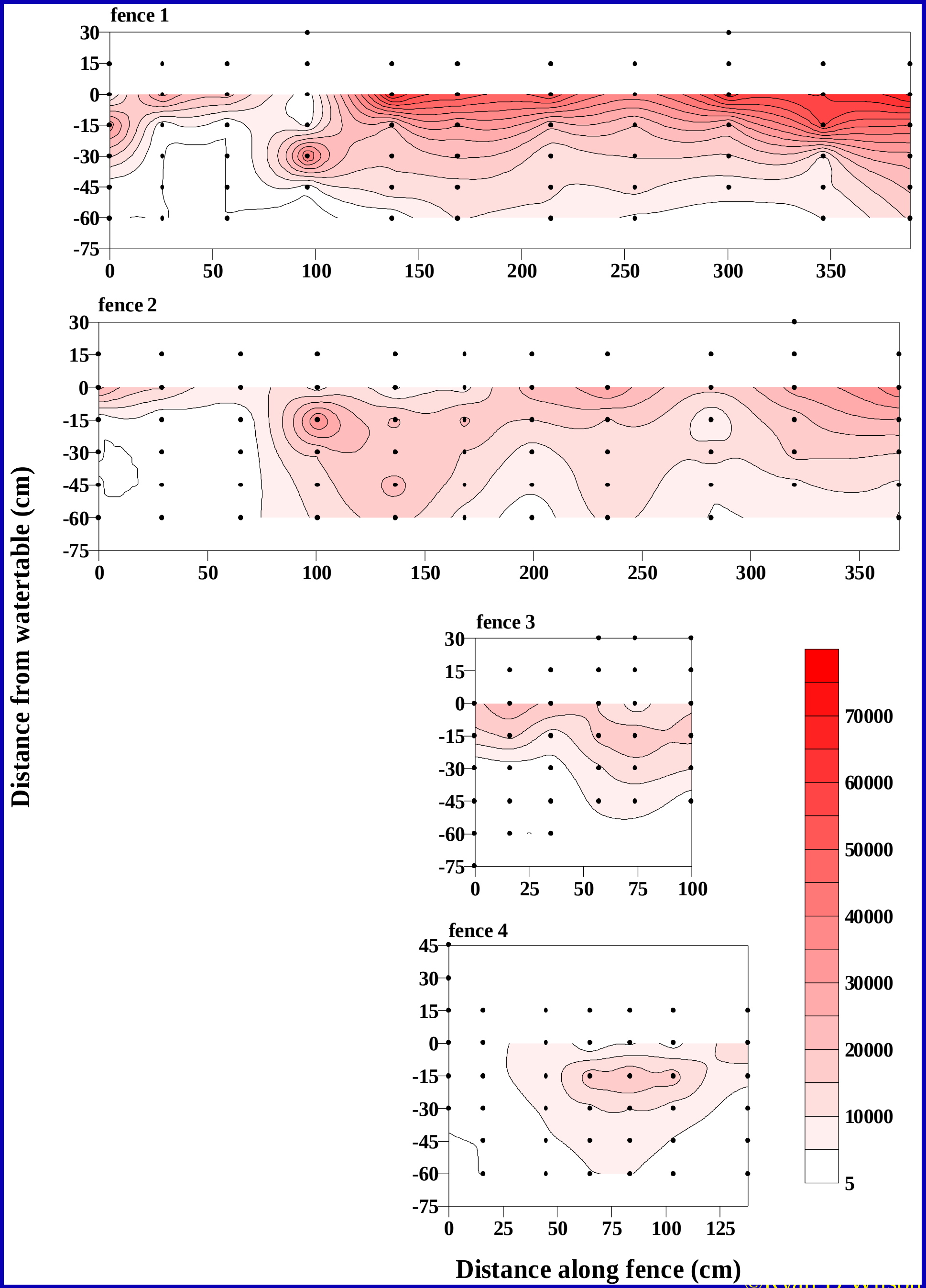
- snapshot of BTEX treatment as a result of oxygen release
- aerobic degradation may have stimulated nitrate reducers
  - facultative anaerobes



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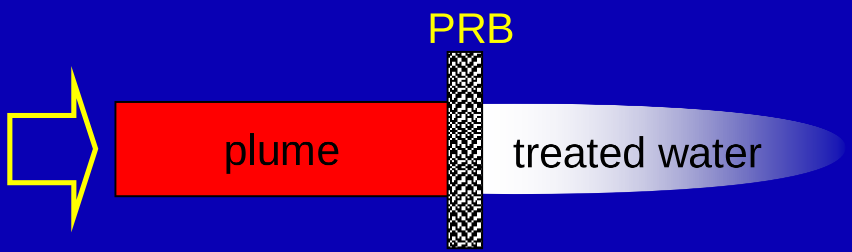
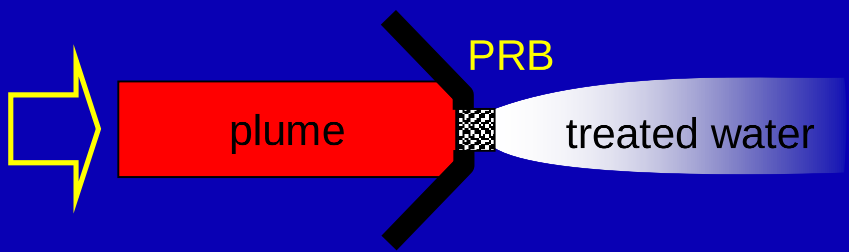
PRB deployment options

continuous in unconsolidated media



funnel and gate in UC media



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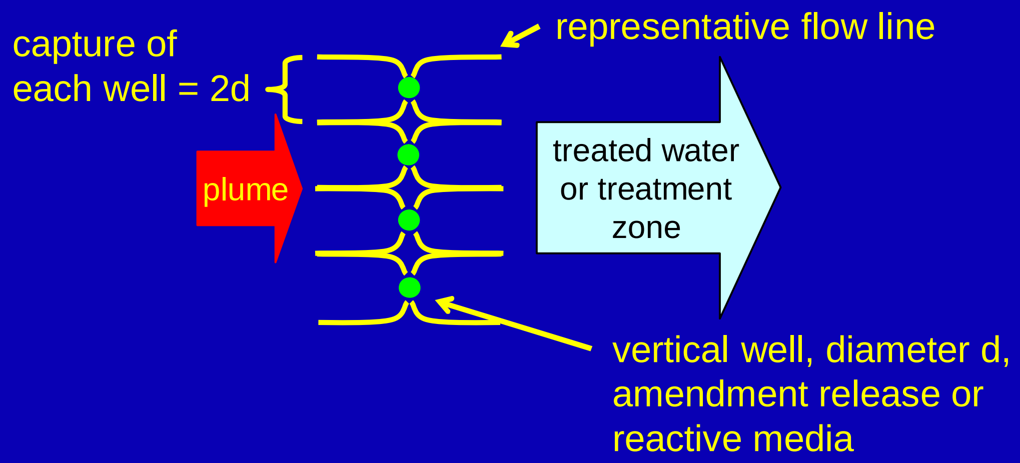
discontinuous array in UC media



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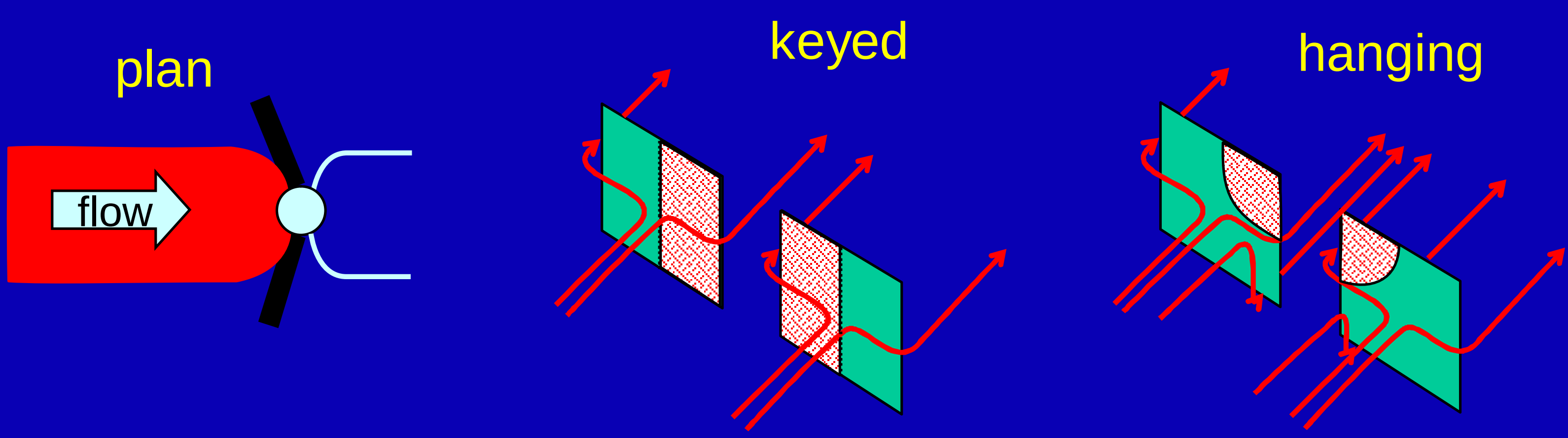
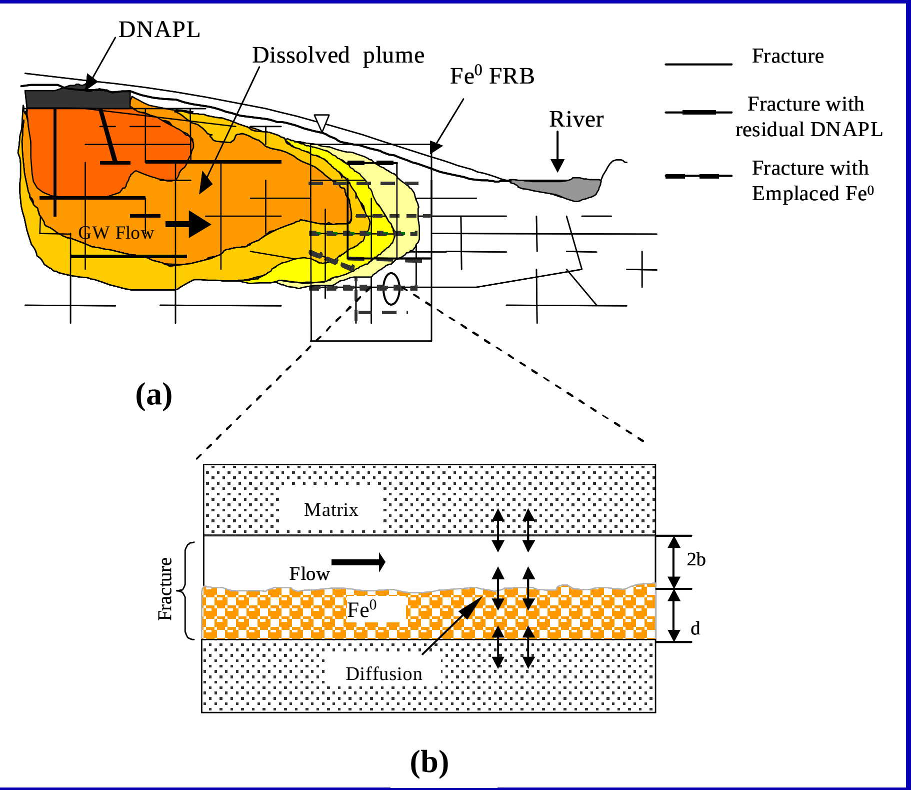
funnel and gates hydraulics



- keyed systems (anchored in fine grained sediments) focus more plume through treatment gate than do hanging systems

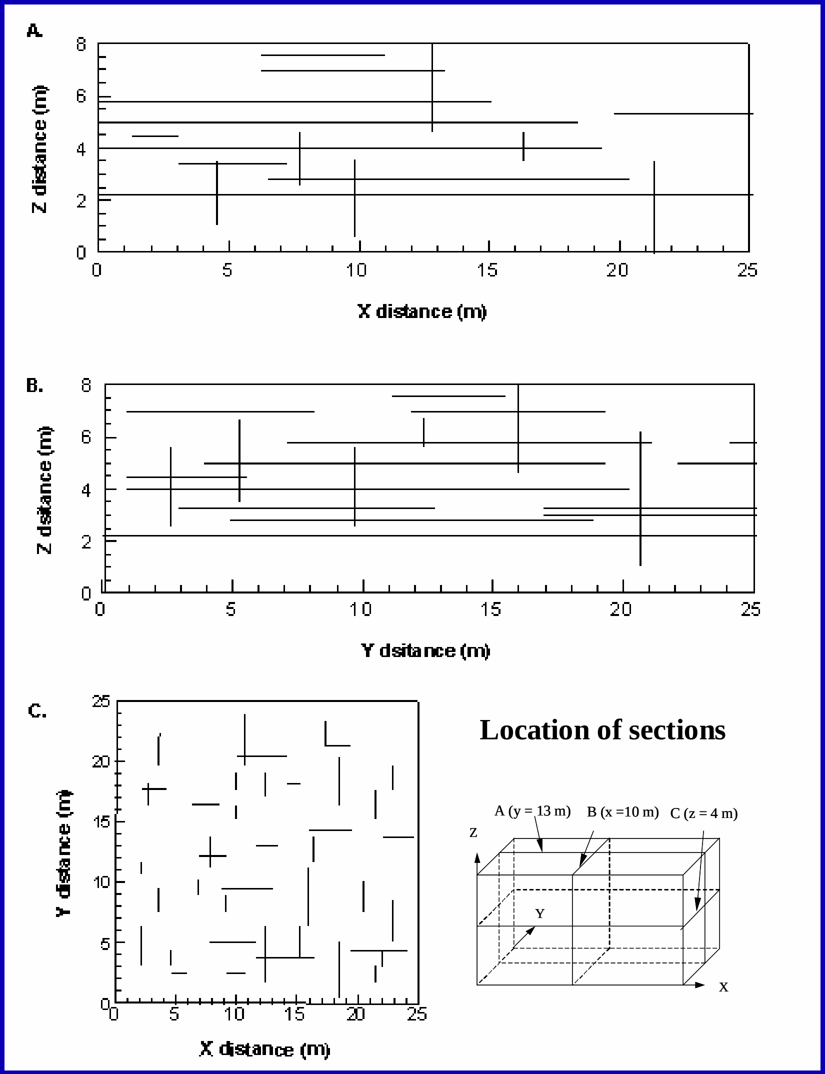
What about fractured rock?

- ZVI – Fracture Reactive Barrier
- Inject iron into fractures
  - supported using biopolymers
- micro or nano iron
- creates a layered system: iron and open fracture

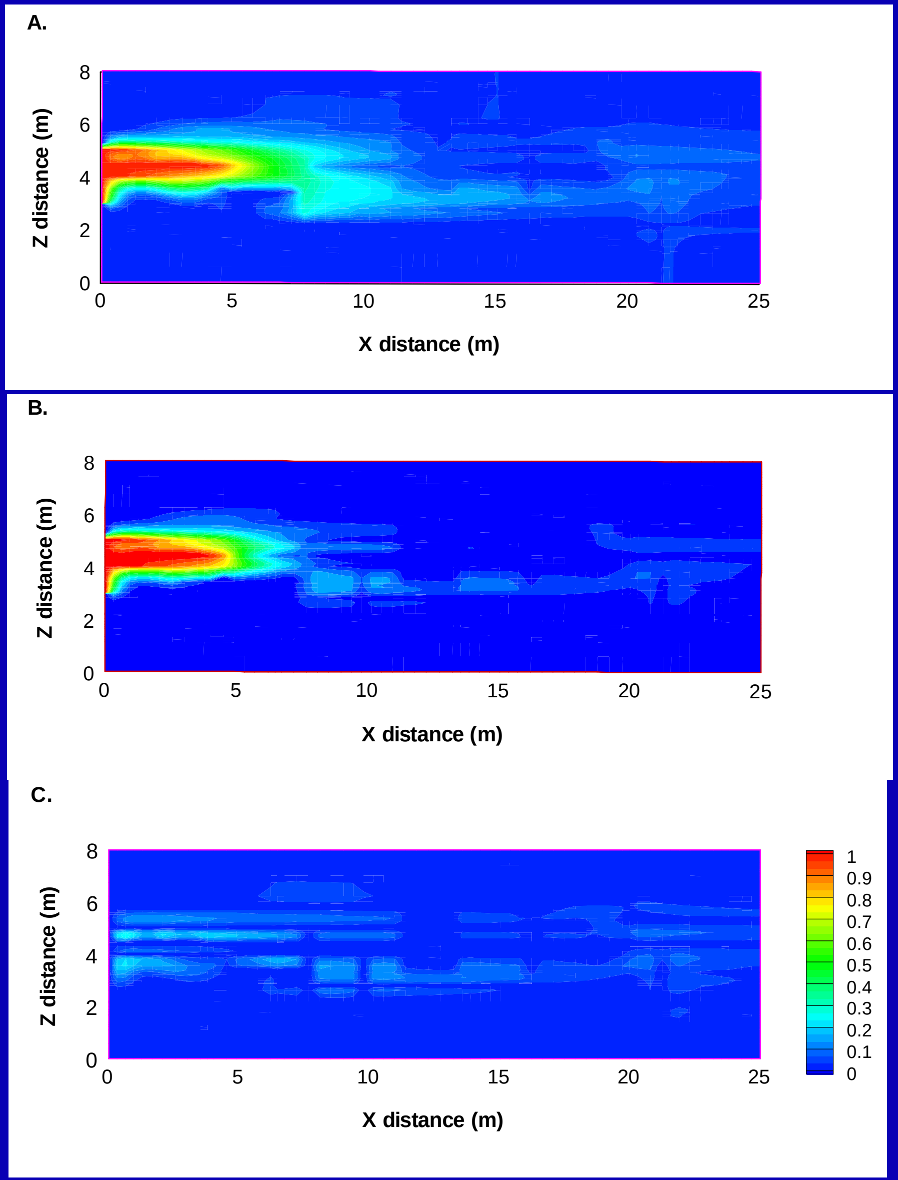


Explore concept via modelling

- Simulations using HydroGeoSphere
  - Waterloo discrete fracture network code
  - fractures as linear node elements in a finite element domain
  - iron in fractures modelled using lumped approach accounting for reaction in iron and mass transport in open fracture, iron and matrix



- TCE treatment for optimised FRB
  - Normal iron (top)
  - Nano-scale iron (middle)
  - Normal iron with finite source (bottom)



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PRBs.....

not just zero valent iron!!!

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