CALIFORNIA STATE UNIVERSITY
LONG BEACH

Remediation of Contaminated Groundwater in Fractured Bedrock

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Outline

- Remediation Goals
- Remediation Methods

Objectives for Today

- Talk about reasonable goals for remediation
- Review some technologies available for cleaning groundwater
- Consider the challenges to remediation presented by bedrock systems

Remediation

- Remediation means returning groundwater to an acceptably clean condition
- But what is acceptably clean?
- Can we accomplish this goal?

Alternative Remediation Goals

- Complete Restoration: return to prior condition
- Non-degradation: clean to detectable limits
- Health Based Standards: e.g. MCLs
- Risk Based Standards: reduce risk to receptors
- Technology Limits: clean as much as possible
- Partial Use: limit access
- Containment: prevent offsite migration

National Research Council, 1994, Alternatives for Ground Water Cleanup

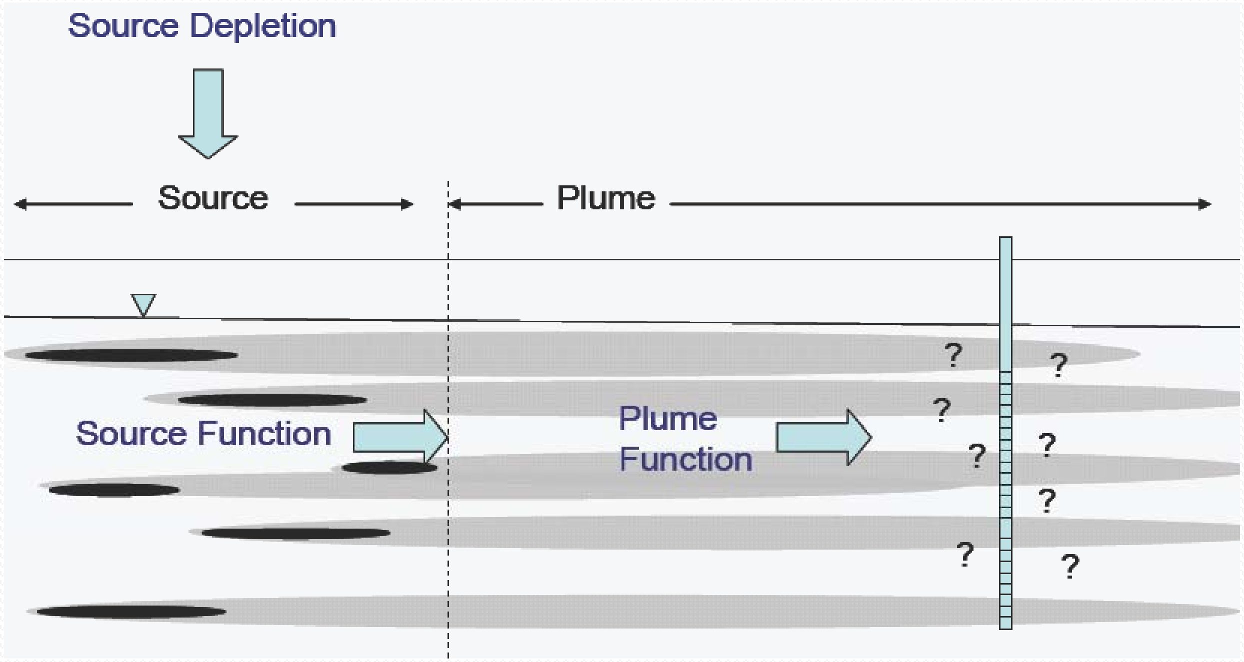
Risk Based Limits

- Who is at risk?
  - What is the most sensitive receptor?
- When will they be at risk?
  - Is the risk immediate and critical?
- Can the risk be reduced at the receptor?
  - For example, switch from wells to city water?
- Are there multiple pathways for exposure
  - For example, air deposition + drinking water

pe0064021 [RF] © www.visualphotos.com

Source Reduction

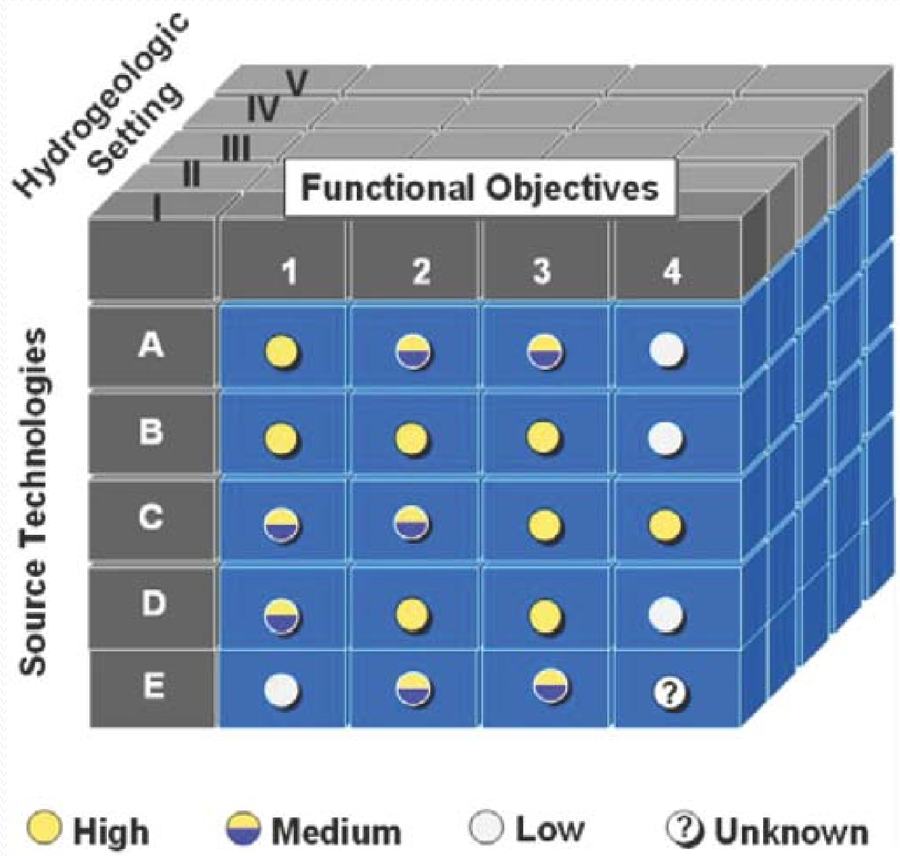
- A common goal is to reduce the source mass or the flux from the source
- Idea is plume will dissipate if source is contained.



Environmental Security Technology Certification Program, 2005, FAQ about Chlorinated Solvents in Soil and Groundwater

Potential for Success

- National Research Council Panel cube indicates potential for treating solvent source zones
- Remediation methods must be tailored for
  - Hydrogeology
  - Cleanup Goal



National Research Council, 2005, Contaminants in the Subsurface, Source Zone Assessment and Remediation

Focus here on TCE in Bedrock (a nationwide problem…)

A.I.W. Frank/Mid-County Mustang	Exton, PA
Active Chemical Manufacturing Facility	Not provided, TN
Active Dry Cleaning Facility	central area, IN
Active Manufacturing Site (Article #32)	Northeastern
Aircraft manufacturing site	Newbury Park, CA
Altus Air Force Base OU-1	Altus, OK
Altus Air Force Base SS-17	Altus, OK
Andersen Air Force Base MARBO Annex	Yigo, GU
Battery Tech (Duracell-Lexington)	Lexington, NC
Boston Industrial Facility	Boston, MA
Caldwell Trucking	Fairfield Township, NJ
Chlorinated-ethene contaminated site	Unknown, CT
Clariant Corporation	Fair Lawn, NJ
Closed Municipal Landfill	Unknown, VA
Crossley Farm	Hereford Township, PA
DNAPL Site	Boston, MA
Donaldson's Drycleaners	Neenah, WI
Dry Cleaner Site	Coastal Area, MA
Dublin TCE Site	Dublin Borough, PA
Edwards AFB - Site 61	Edwards AFB, CA
Edwards Air Force Base, Operable Unit 1, Site 18	Edwards Air Force Base, CA
Electronic Component Manufacturer	Northeastern Area, MA
Electronics Manufacturing Facility	North-central Area, NJ
Fischer & Porter Company	Warminster, PA
Fmr Naval Surface Warfare Center, White Oak - OU19	Silver Spring, MD
Former chlorinated hydrocarbon chemical transfer f	Buffalo, NY
Former CWML Site (Smithville PCB Site)	Smithville, ON, Canada
Former Department of Defense (DoD) Facility	Unknown
Former Groce Laboratory	Greenville County, SC
Former Landfill	Unknown, VA
Former Manufacturing Facility	Kansas City, MO
Former Manufacturing Facility	Lancaster, PA
Former MEC Building	Hudson, NH
Former Metal Fabrication Facility	Unknown
Former Naval Air Warfare Center	West Trenton, NJ
Former PR-58 Nike Missile Battery Site	Davisville, RI
Former PVC Manufacturing Facility	Not Provided, NJ
Former Tenneco Polymers, Inc.	Flemington, NJ
Heleva Landfill	North Whitehall Township, PA
Hunters Point Shipyard: Remedial Unit C4	San Francisco, CA
Industrial Facility located close to the St. Lawre	Not provided, ON, Canada

ITT Night Vision	Roanoke, VA
Lehigh Valley Railroad	Le Roy, NY
Letterkenny Army Depot: Building 37	Chambersburg, PA
Linemaster Switch Corporation	Woodstock, CT
Mallory Capacitor Company	Waynesboro, TN
Malvern TCE	East Whiteland Township, PA
Manufacturing Facility	Oconee County, SC
Nease Chemical Site	Salem, OH
New Jersey Former Manufacturing Facility	Unknown, NJ
Newark Basin	Unknown, PA
Newton County Wells	Joplin, MO
Norden Systems Inc.	Norwalk, CT
Ortho-Clinical Diagnostics	Raritan, NJ
Portsmouth DOE Facility	Portsmouth, OH
R&D Facility	Chatham, NJ
Recticon/Allied Steel Corp.	East Coventry Township, PA
Re-Solve, Inc.	North Dartmouth, MA
Rocky Mountain Arsenal: North of Basin F	Unknown, CO
Rodale Manufacturing Company	Emmaus, PA
Schofield Barracks	Schofield, HI
Site 49 Operable Unit 1 Edwards Air Force Base	Los Angeles County , CA
Solvent Recycling Facility	Henry County, KY
Stamina Mills	North Smithfield, RI
Stanley Kessler	King of Prussia, PA
Stringfellow	Mira Loma, CA
Tarheel Army Missile Plant (TAMP)	Burlington, NC
Tenneco Automative	Hartwell, GA
Test Area North - INEEL	Idaho Falls, ID
Tinker AFB	Oklahoma City, OK
Tinkham Garage	Londonberry, NH
Trichloroethene-contaminated site in New Jersey	Not provided, NJ
Trichloroethylene-contaminated site in Tennessee	Unknown, TN
Union Chemical Company Superfund Site (Pilot-scale	Hope, ME
Unknown manufacturing facility	Western, NC
Unknown TCE-contaminated site	Unknown
Unknown TCE-contaminated site	Southern United States
Valmont TCE	West Hazleton, PA
Watervliet Arsenal: Building 40	Watervliet, NY
West Kingston Town Dump/Uri Disposal Area	South Kingstown, RI

Examples from EPA database CLU-IN.org (not complete)

Evolving thinking about solvents

Old School Paradigm (Period of prevalence)	New School Paradigm (Time of broad acceptance)
Given the volatility of chlorinated solvents, land disposal is an appropriate practice. *(1940s through 1970s)*	Releases of chlorinated solvents to subsurface environments can create big problems. Few things are more important than limiting future releases. *(Beginning in the 1980s)*
Aquifers may be restored by pumping out the contaminated water (pump and treat). *(1970s through 1980s)*	Solvents sorbed to solids, present as DNAPL, and stored in low permeability zones can sustain groundwater concentrations in transmissive zones for long periods. *(1990s through 2000s)*
Chlorinated solvents are recalcitrant. *(1970s through 1990s)*	Chlorinated solvents will degrade under a range of natural and engineered conditions. *(Beginning late 1990s)*
Emerging technologies will frequently achieve MCLs in source zones. *(early to mid 1990s)*	Our experience to date indicates attaining MCLs throughout source zones has been very rare. Nevertheless, significant mass depletion has been achieved and technologies continue to improve. *(Beginning mid 1990s)*
Primary risks and site care costs can be addressed by removal and/or depletion of source zones. *(1970s through early 2000s)*	Contaminants often remain after source zone treatment in source zones and plumes. What remains can sustain exceedances of MCLs and necessitate site care for long periods of time. *(Mid 2000s)*
Source zone remediation is a necessary component of corrective action. *(1970s through early 2000s)*	Source zone remediation should be considered but is not always a necessary component of corrective action. Long-term management, containment, and monitored natural attenuation (MNA) may be adequate and more cost-effective strategies at some sites. *(2000s)*
Groundwater represents the primary pathway and media of concern. *(1970s through late 1990s)*	Vapor intrusion is recognized as a pathway of concern of the same order as groundwater. *(2000s)*

Environmental Security Technology Certification Program, 2005, FAQ about Chlorinated Solvents in Soil and Groundwater

First Step: Remedial Investigation

- Before you can remediate, you need to know
  - Compounds of concern
  - Source zone mass and extent
  - Transport and fate of contaminants
  - Chemistry of the groundwater
  - Hydraulics of the subsurface

DNAPL detected during coring in fractured rock

Former Naval Air Warfare Center, West Trenton, NJ

Sudan IV shake kit – red indicates NAPL

Cloth with hydrophobic dye – staining occurs where dye dissolves in NAPL

From Allen Shapiro, USGS

Now What?

- Given this understanding of the problem…
  - Can we clean it up?
  - Is it possible to make it worse?
  - What will happen if we leave it there?
  - How much time do we have?
- Remediation alternatives must be selected with these questions and the ultimate remediation goal in mind

Remediation Alternatives

Not Likely to be Effective for Bedrock

- Excavation
- Permeable Reactive Barriers

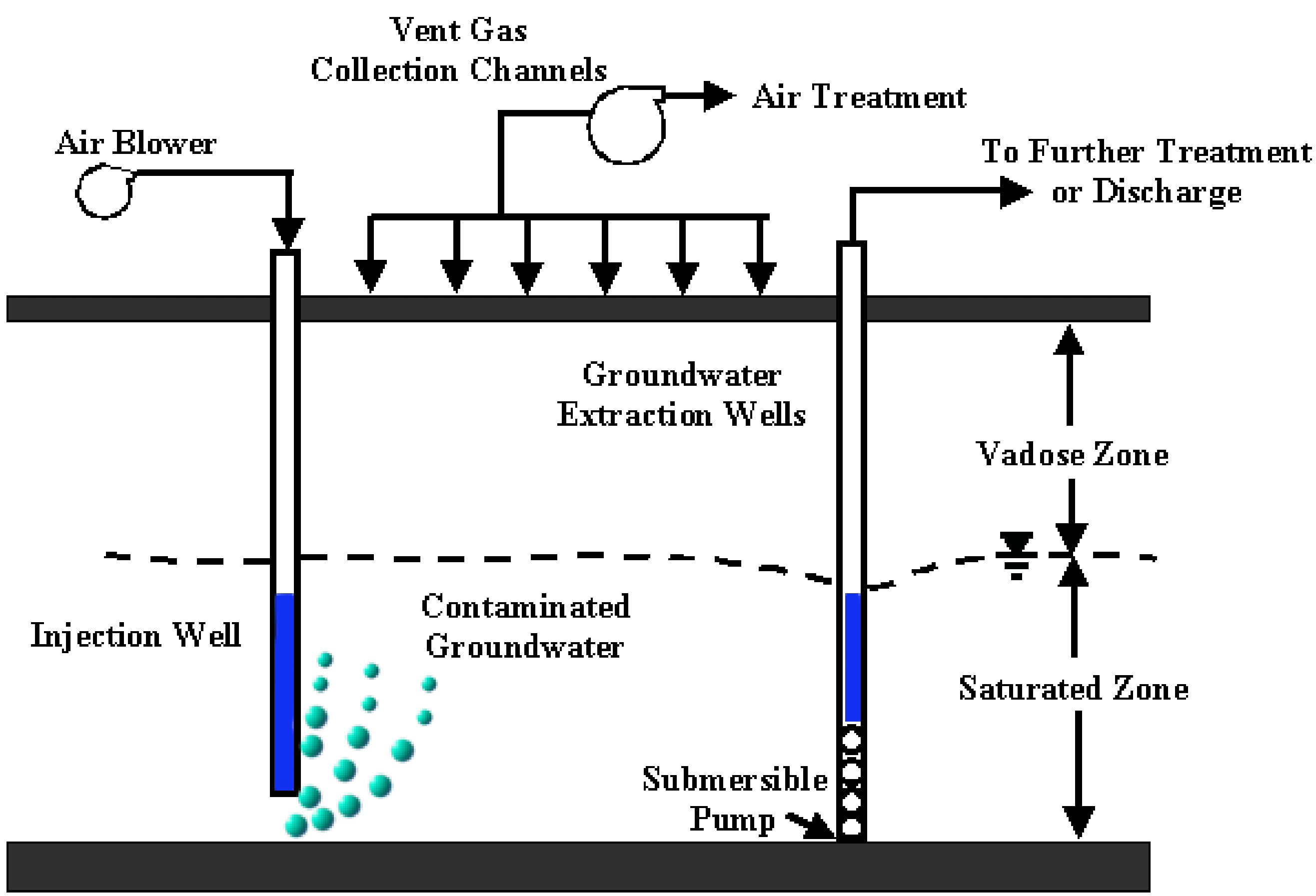
Potentially Effective for Bedrock

- ✓ Vapor Extraction/Sparging
- ✓ Pump-and-Treat
- ✓ Physical Barriers / Collectors
- ✓ Chemical Oxidation
- ✓ Thermal Treatments
- ✓ Bioaugmentation /Stimulation
- ✓ Monitored Natural Attenuation
- ✓ Perpetual Containment

Remediation Approaches

- ✓ Ex-Situ Treatment (remove and treat)
  - Vapor Extraction/Sparging
  - Pump-and-Treat
  - Physical Barriers / Collectors
- ✓ In-Situ Treatment (treat in place)
  - Chemical Oxidation
  - Thermal Destruction/Stimulation
  - Bioaugmentation /Stimulation
  - Monitored Natural Attenuation
- ✓ No Treatment:
  - Perpetual Containment

Vapor Extraction / Air Sparging



Vapor Extraction / Air Sparging

Vapor Extraction

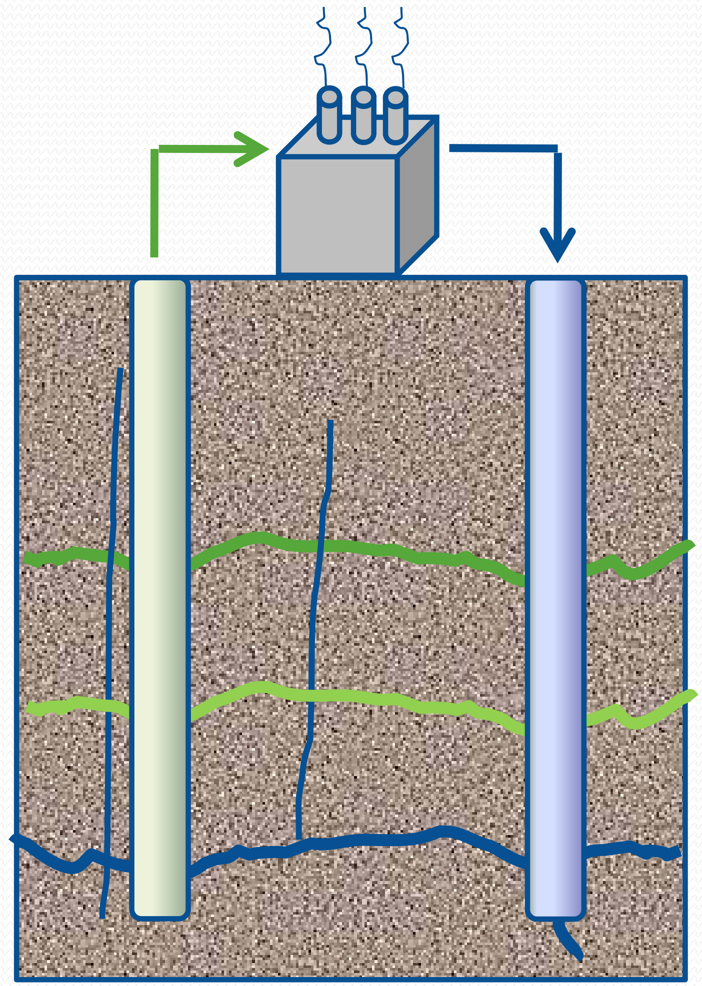
- Vacuum volatile organic carbon (VOC) from vadose zone (above water table)
- Vapor is usually treated using activated carbon stripping towers
- Often combined with pneumatic fracturing

Air Sparging

- Air stripping performed in place
- Bubble air through water to mobilize VOC
- VOC/Air must be removed through vapor extraction
- Often combined with hydraulic fracturing

Pump and Treat

- Oldest groundwater remediation technology
- Simply pump water from wells and treat it then reinject or dispose off site
- By mid-1990's it was clear it didn't work well in bedrock
- An early reduction was soon followed by a "rebound" in contaminant concentration



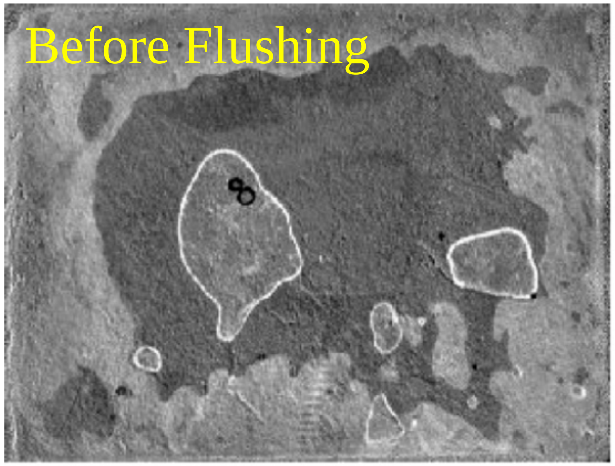
Pump and Treat Performance

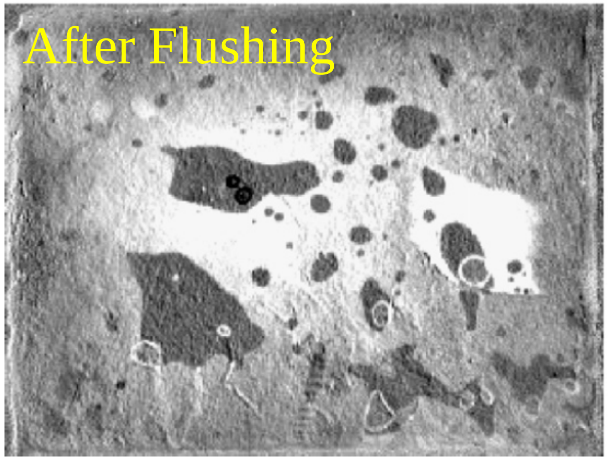
Difficulty of Cleanup	Number of Sites	Number Contained	Number Cleaned	Number Not Cleaned
1	2	1	1	1
2	13	8	4	9
3	19	12	4	15
4	36	18	0	36

National Research Council, 1994, Alternatives for Ground Water Cleanup

Pump & Treat of Immiscible Phase

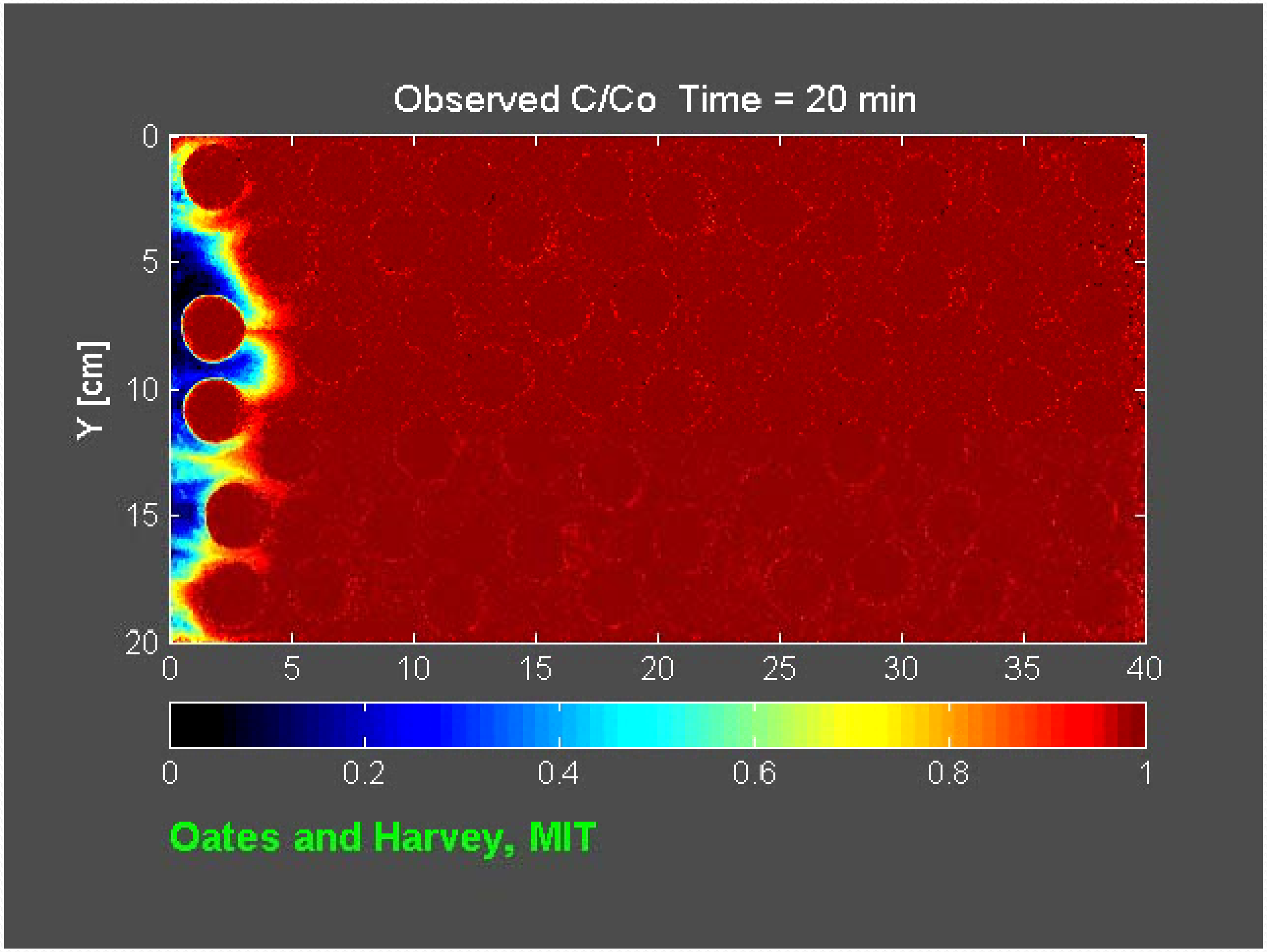
- Trying to flush NAPL from fracture leaves residual “ganglia”
- Ganglia cannot be forced from fracture but must be dissolved
- Dissolution is slow because surface area is slow





Bergslien, E., Fountain, J., 2006. The effect of changes in surface wettability on two-phase saturated flow in horizontal replicas of single natural fractures. Journal of Contaminant Hydrology, 88(3-4): 153-180.

Pump & Treat of Dissolve Phase

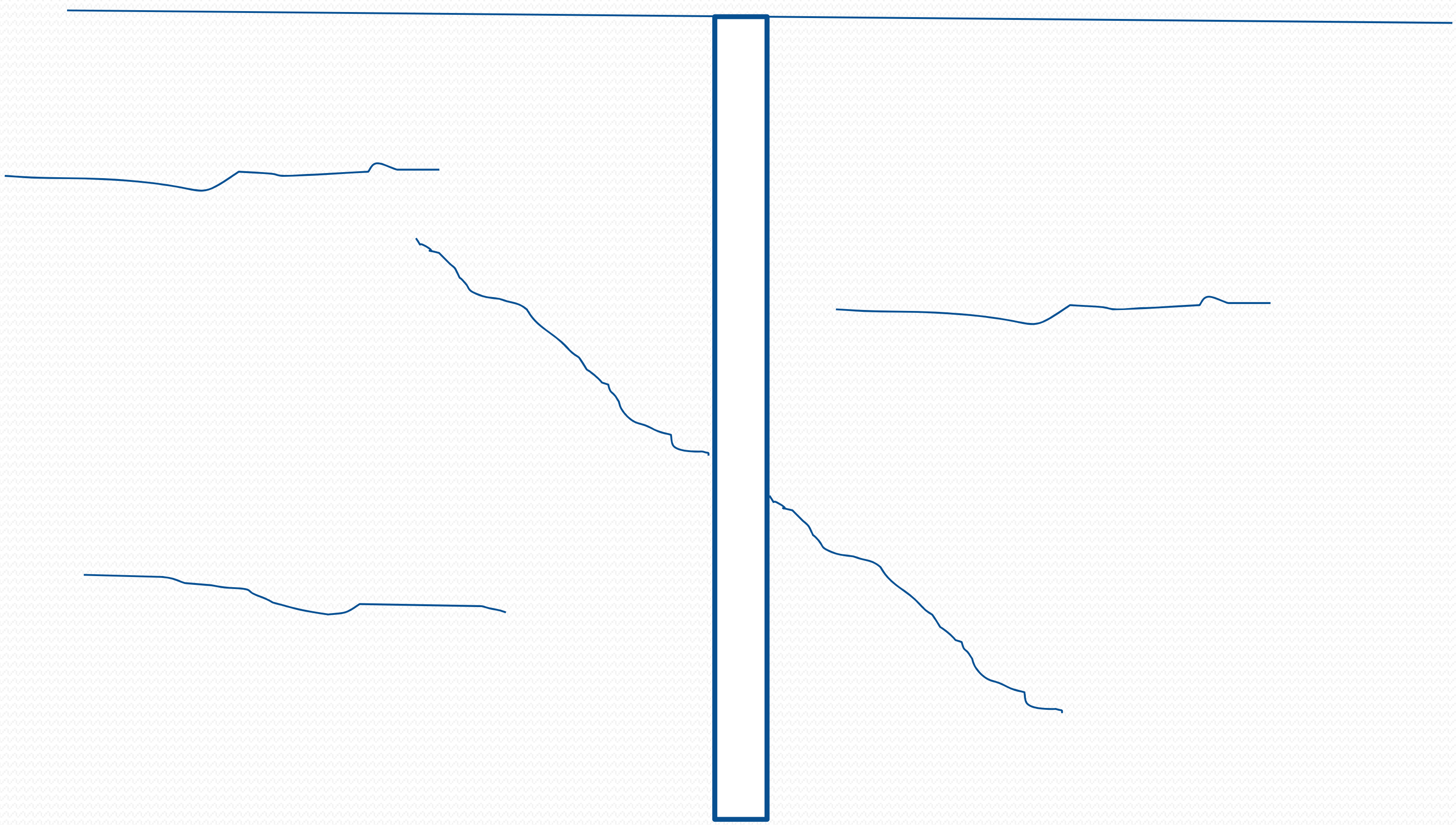


See http://web.mit.edu/harvey-lab/Reactive_Transport.html

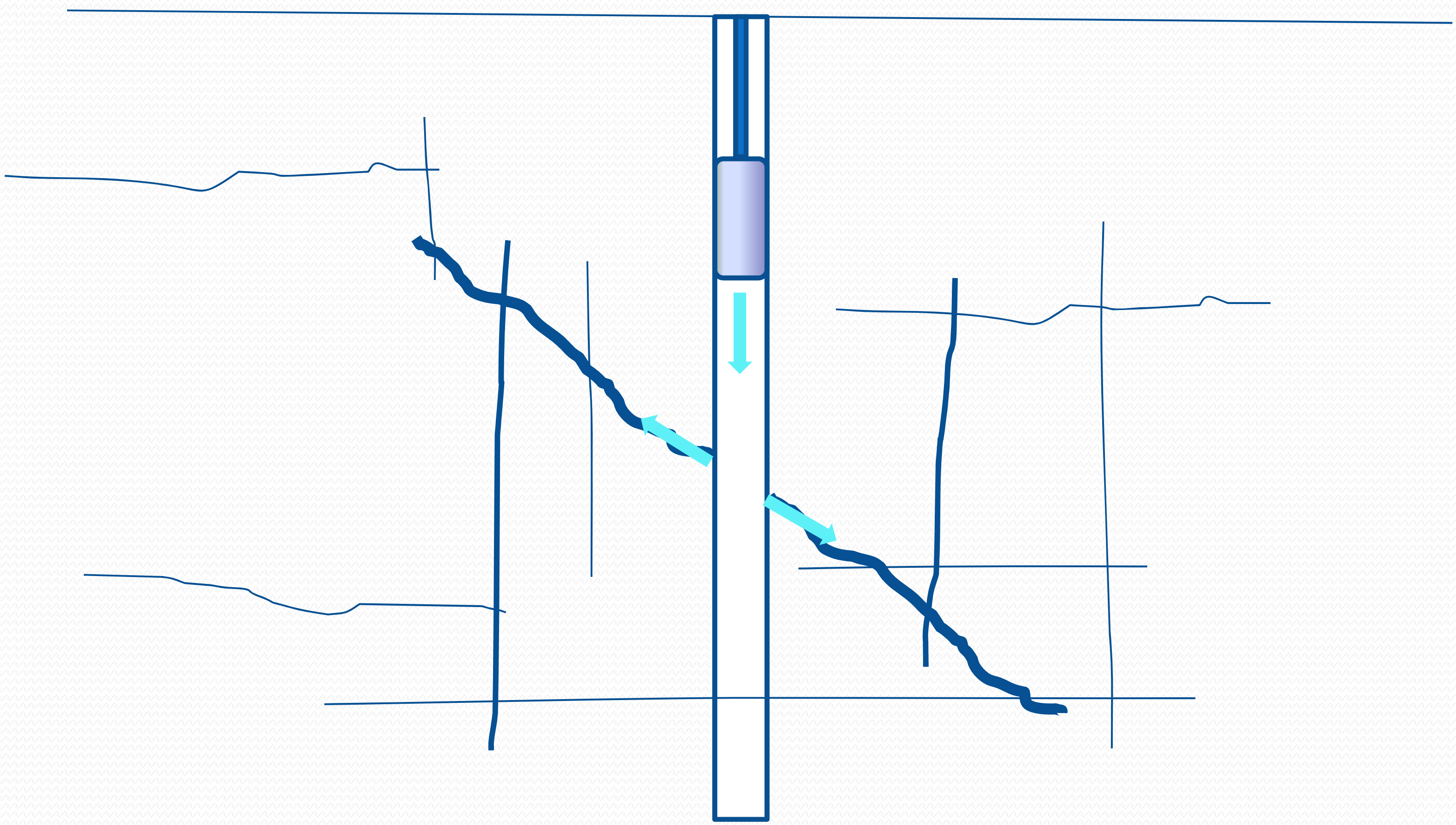
Physical Barriers / Collectors

- Typically used to increase efficiency of another treatment technology
- Barriers:
  - Fractures can be grouted to reduce permeability (typically done for tunnel seepage)
- Collectors:
  - Fractures can be hydrofractured or blasted to increase flow

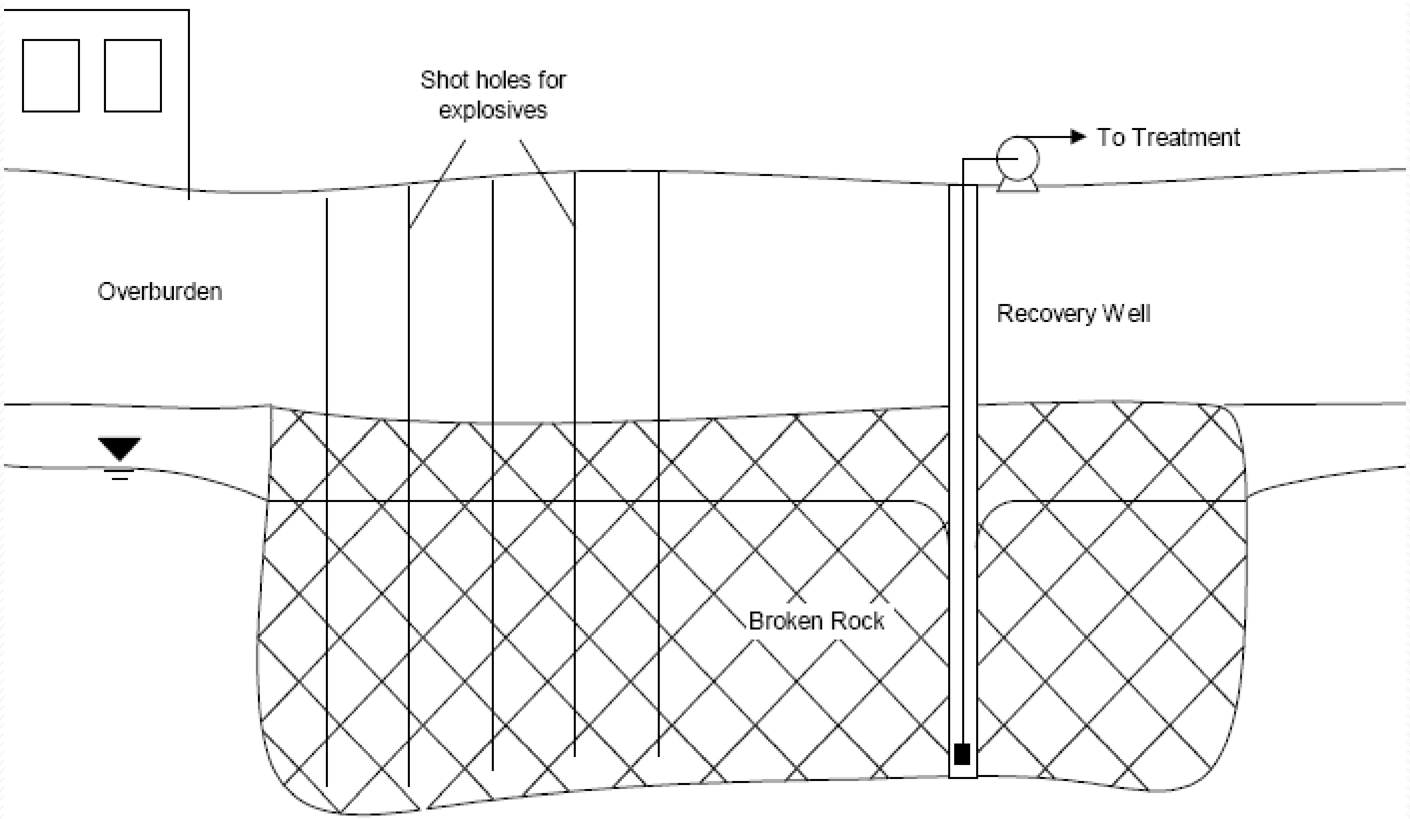
Hydraulic Fracturing: Before



Hydraulic Fracturing: After

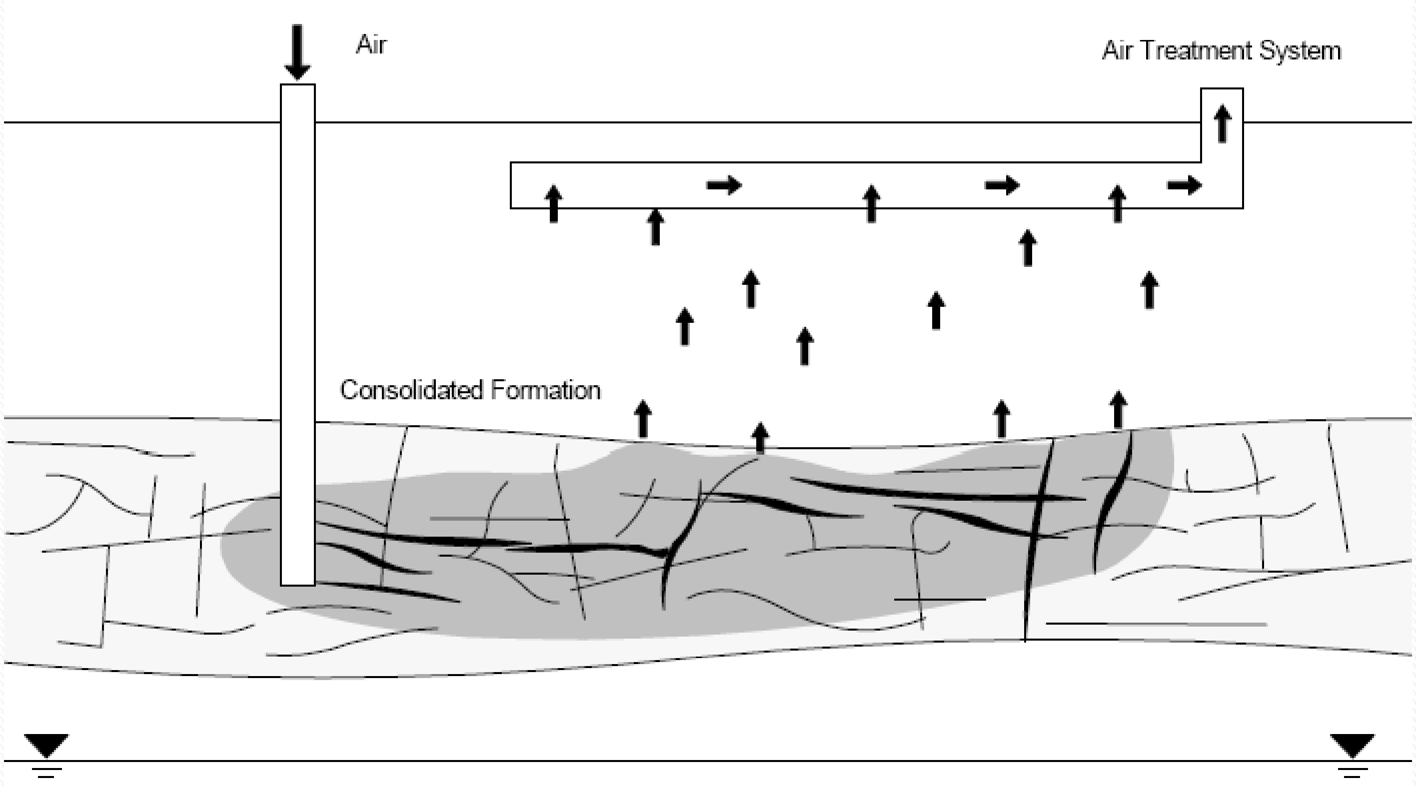


Blast Trenching to Enhance Pump and Treat



Ground-Water Remediation Technologies Analysis Center, Technology Status Report Number TS-00-01

Pneumatic Fracturing to Enhance Vapor Extraction



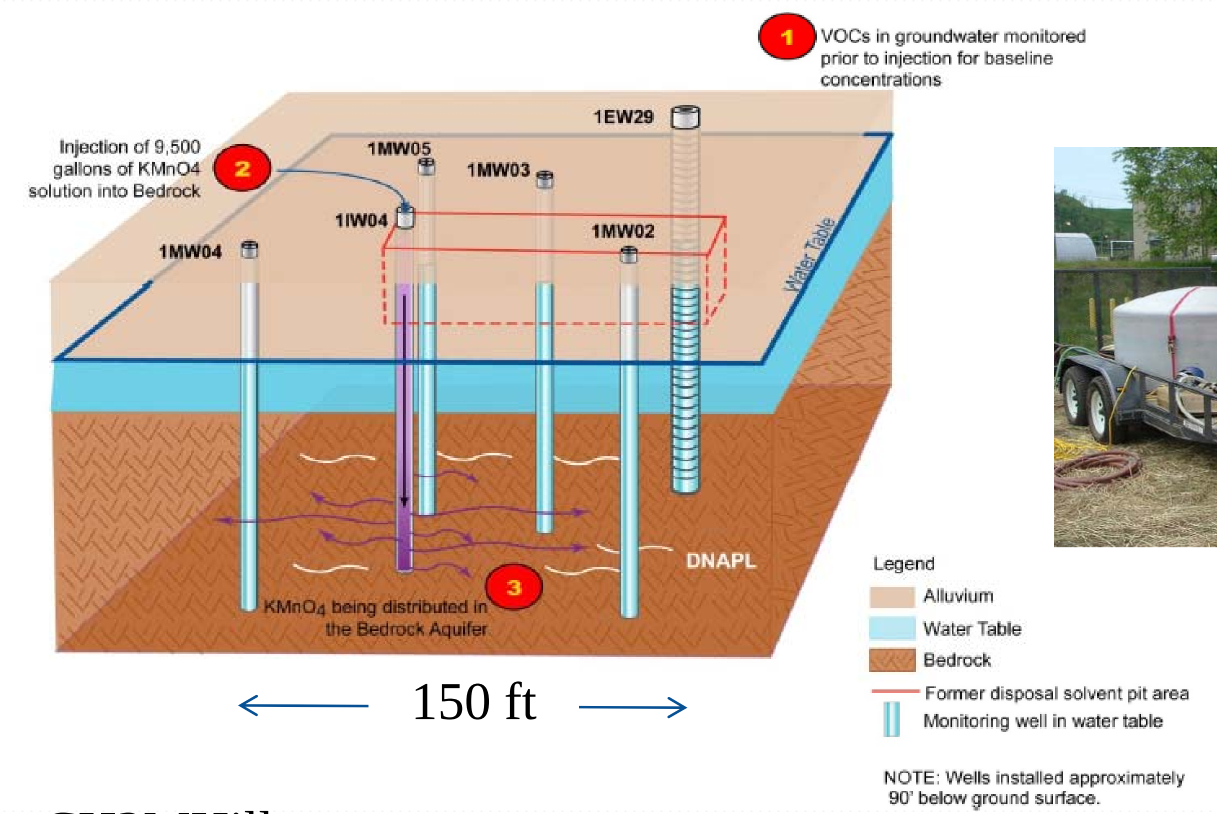
Ground-Water Remediation Technologies Analysis Center, Technology Status Report Number TS-00-01

Chemical Oxidation

- *Ozone*: gas can oxidize contaminants directly or through the formation of hydroxyl radicals (OH^-)
- *Peroxide*: Liquid hydrogen peroxide (H_2O_2) yields free hydroxyl radicals (OH^-)
- *Fenton's Reagent*: H_2O_2 with ferrous iron (Fe^{+2})
- *Permangate:* liquid or solid $KMnO_4$, manganese (Mn) can participate in numerous reactions

Example: Allegany Ballistics Lab

- TCE contamination in shale bedrock



CH2MHill

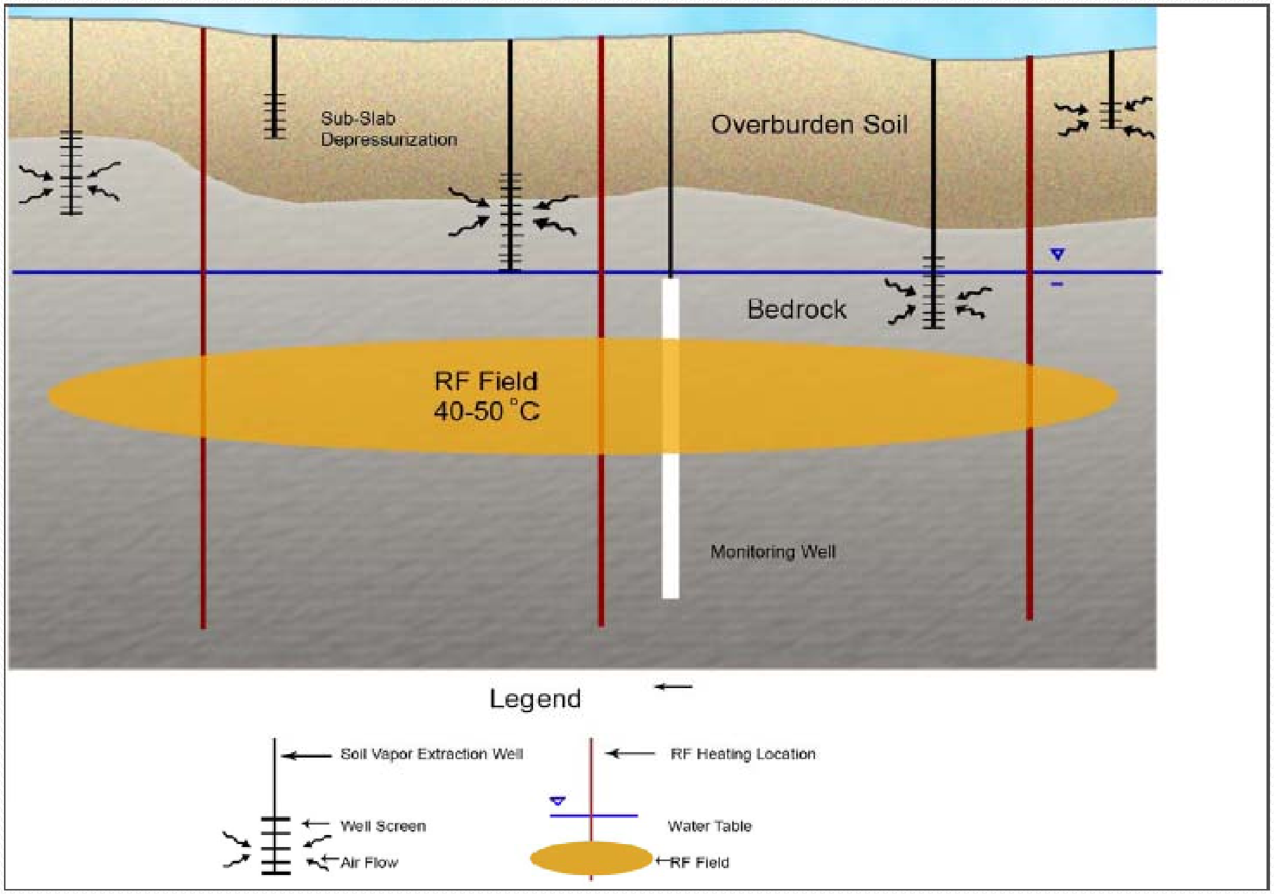
Thermal Treatment

- Heating rock/water causes volatilization of organic contaminants and increase in reaction rates
- Heating can be performed using steam, electricity, radio frequency radiation
- Generally requires closely spaced wells and treats limited area

Example: Loring Air Force Base

- Sedimentary rock in Maine
- Steam injection used to remediate TCE plume.
- Couldn't deliver enough heat to destroy TCE
- Did warm up the rock to 50˚C which increased volatilization and biodegradation.

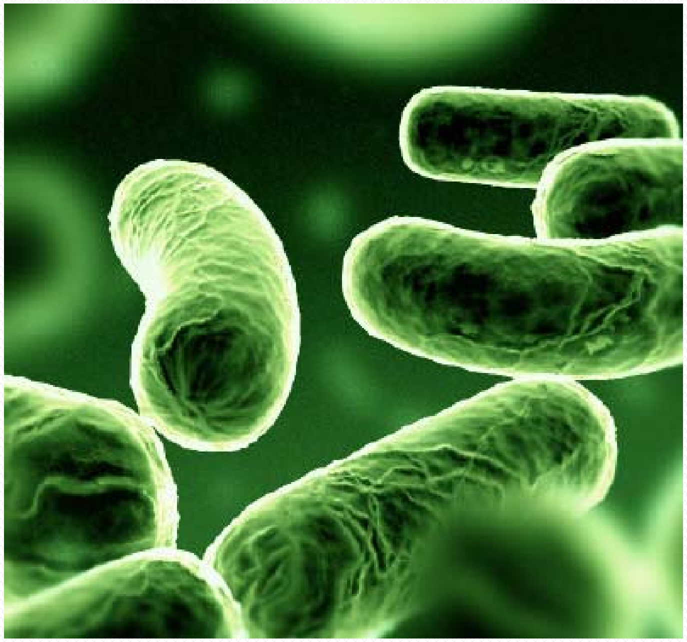
RF Treatment



Environmental Resources Management, Inc.

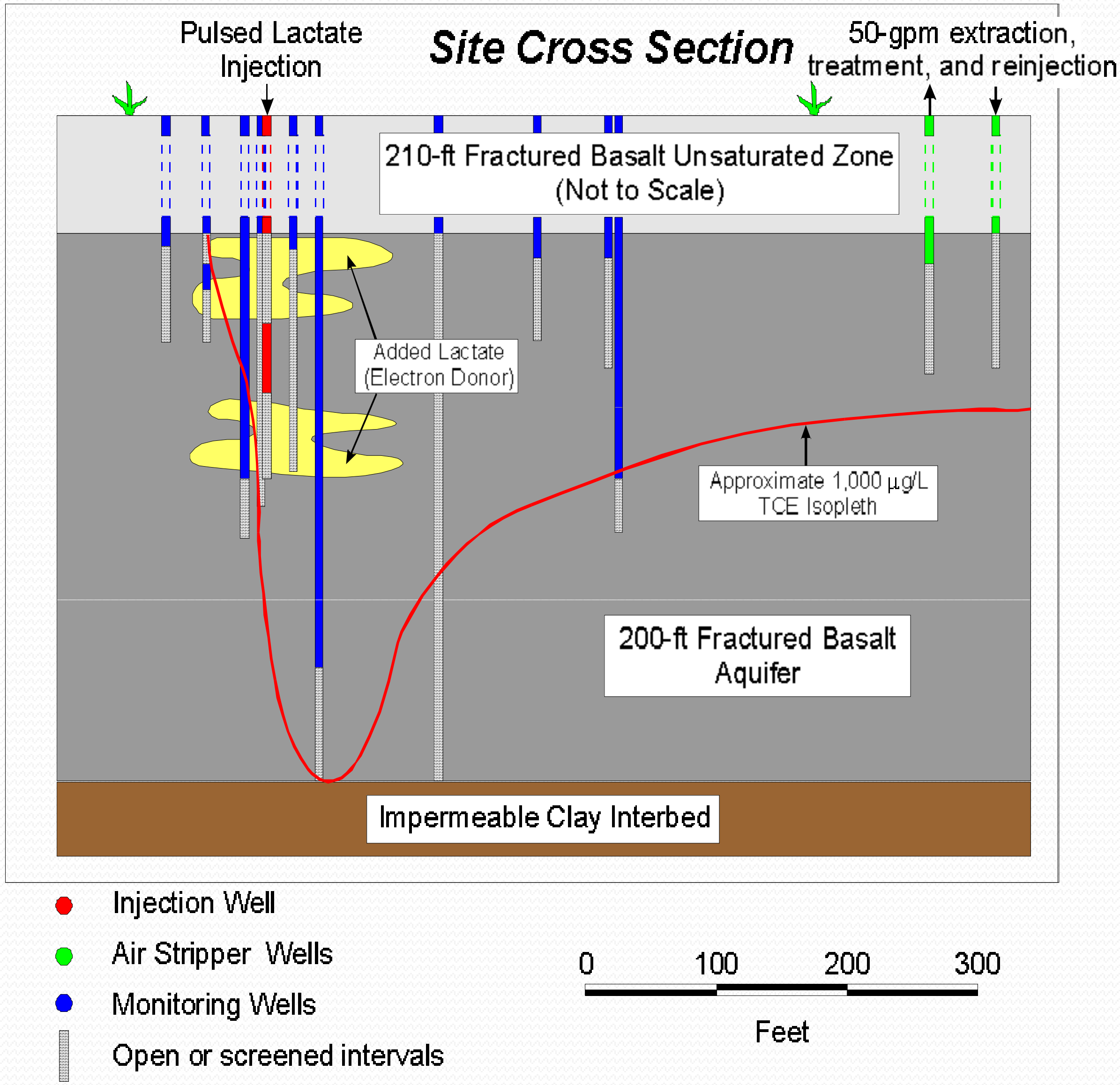
Bioaugmentation/Biostimulation

- Introduce additional microbes or stimulate the growth of native microbes
- Adding microbes difficult because they may be outcompeted by natives
- Stimulation involves adding nutrients or electron acceptors (e.g. carbon)
- Limited by ability to get solution to the contaminated zone



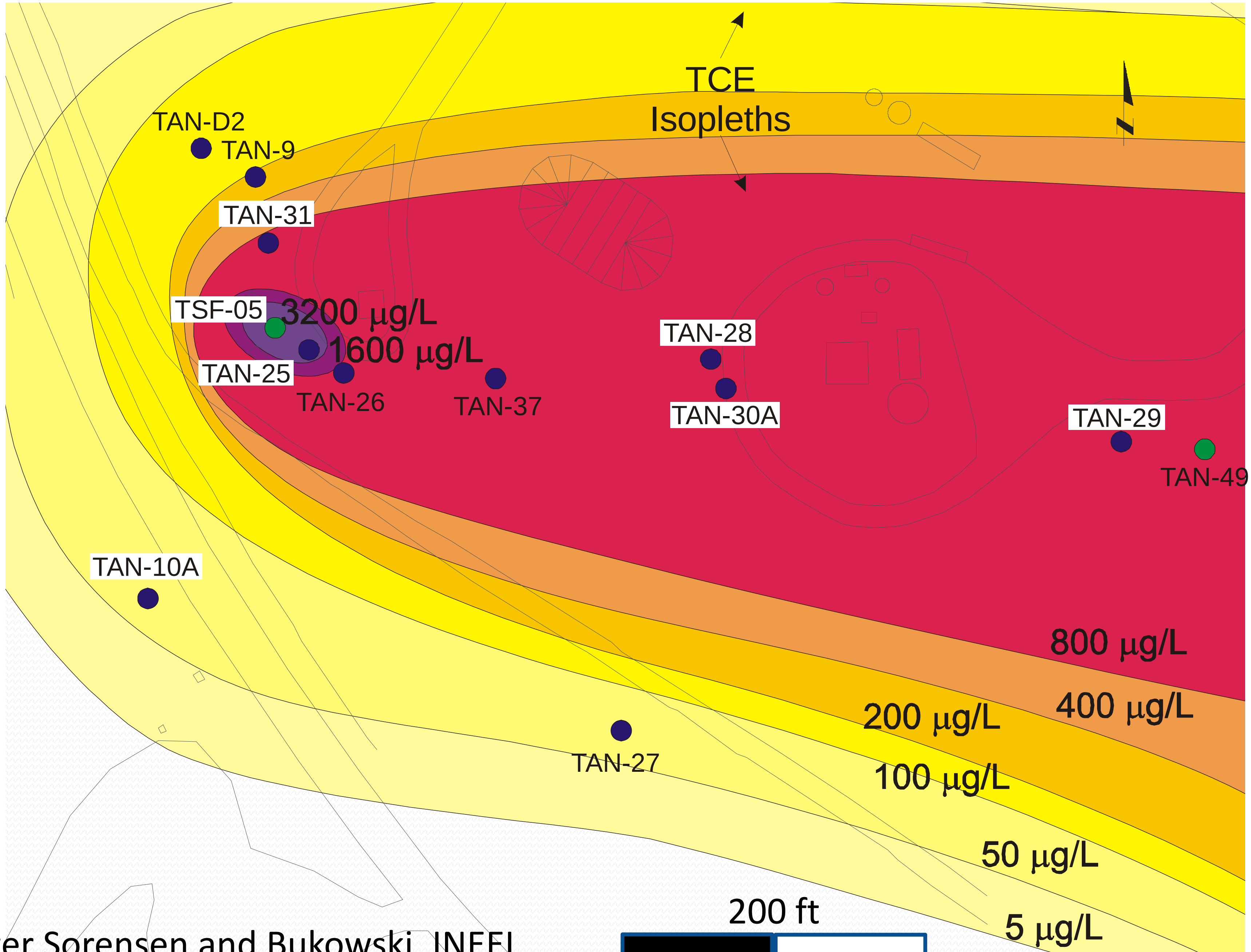
Example: Idaho National Engineering Lab

- Biostimulation used to reduce TCE in fracture basalt of Snake River Plane
- Lactate injected as an electron donor
- Objective was to create a treatment cell to reduce TCE source



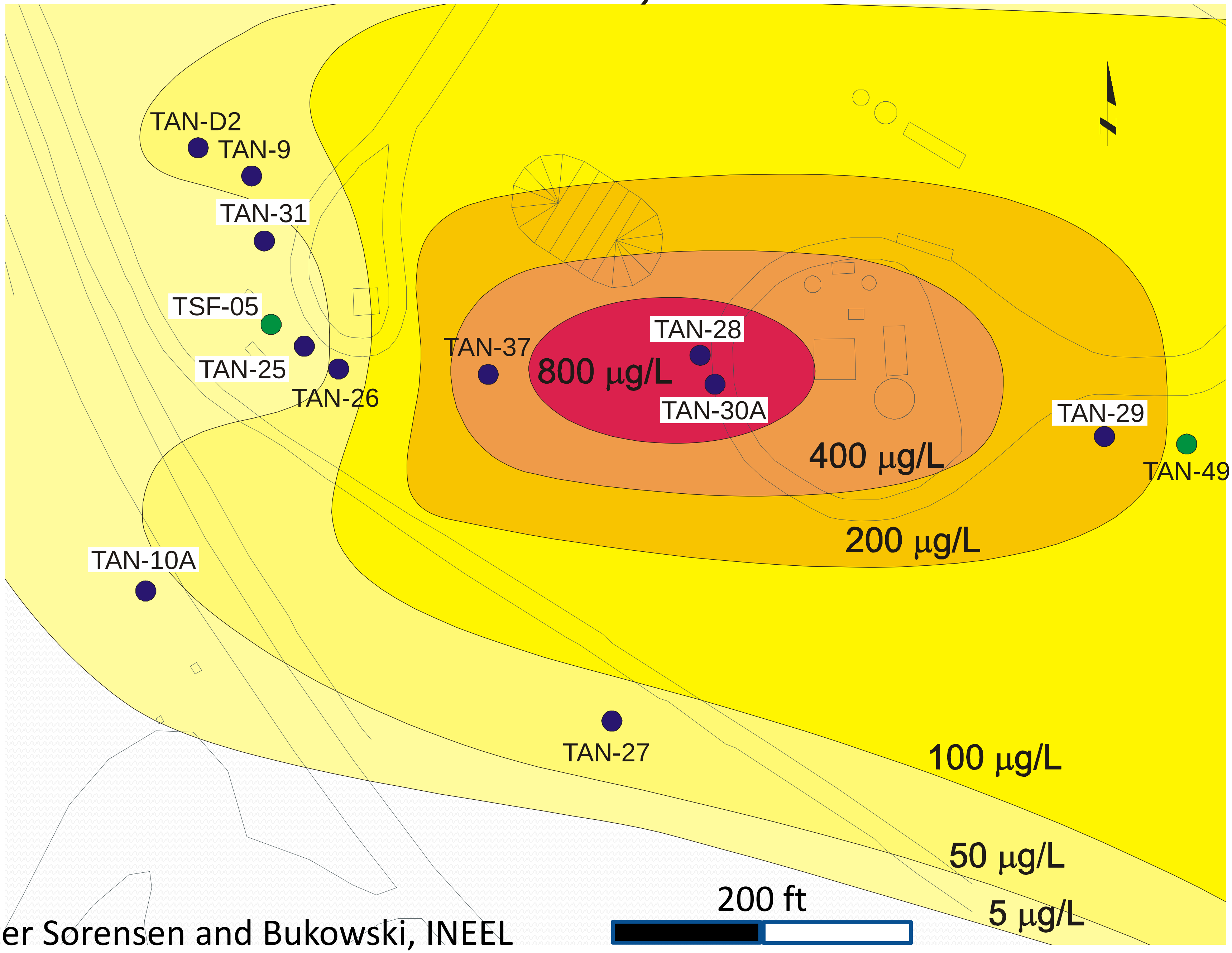
After Sorensen and Bukowski, INEL

Pre-Lactate



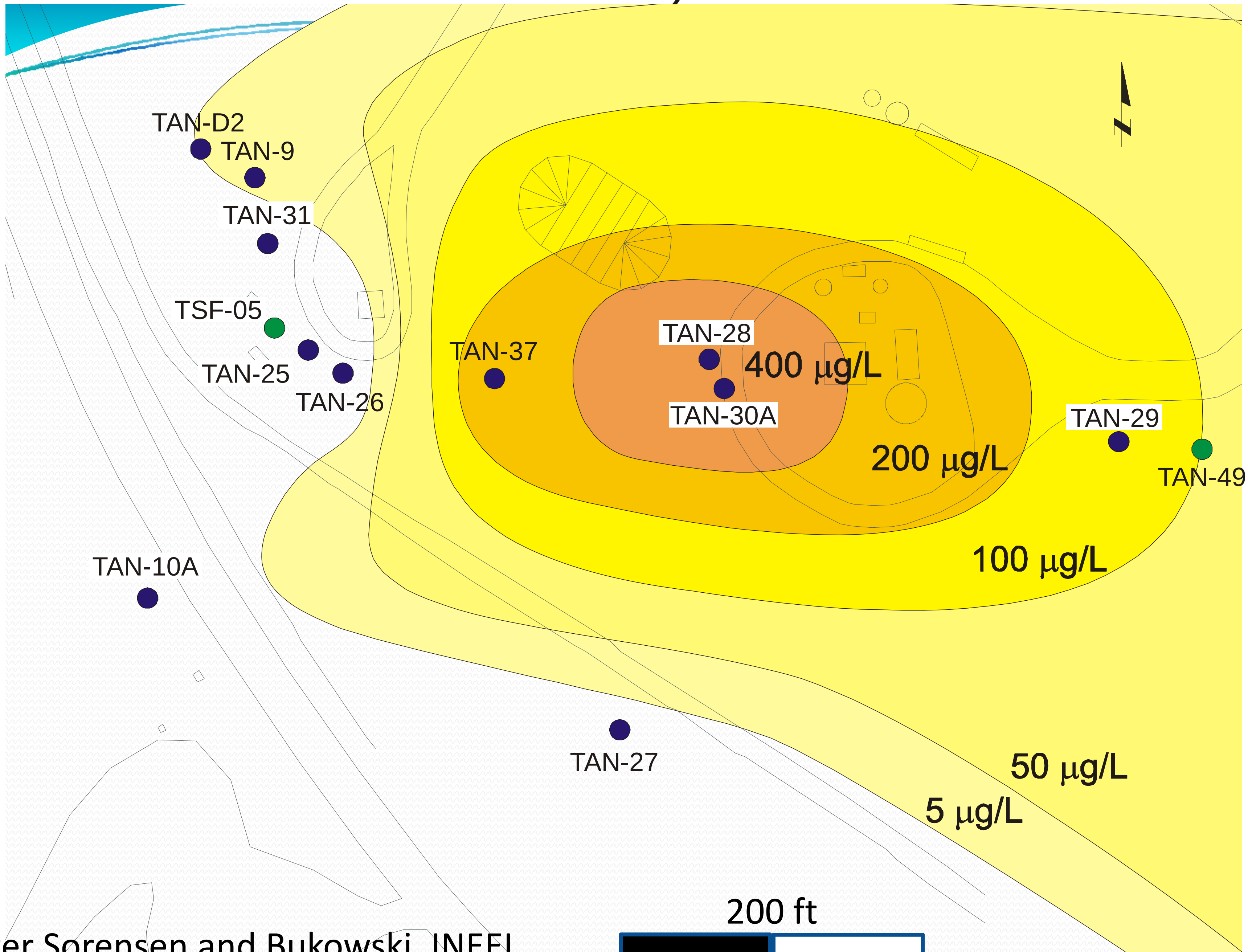
After Sorensen and Bukowski, INEEL

March 29, 1999



After Sorensen and Bukowski, INEEL

October 23, 2000

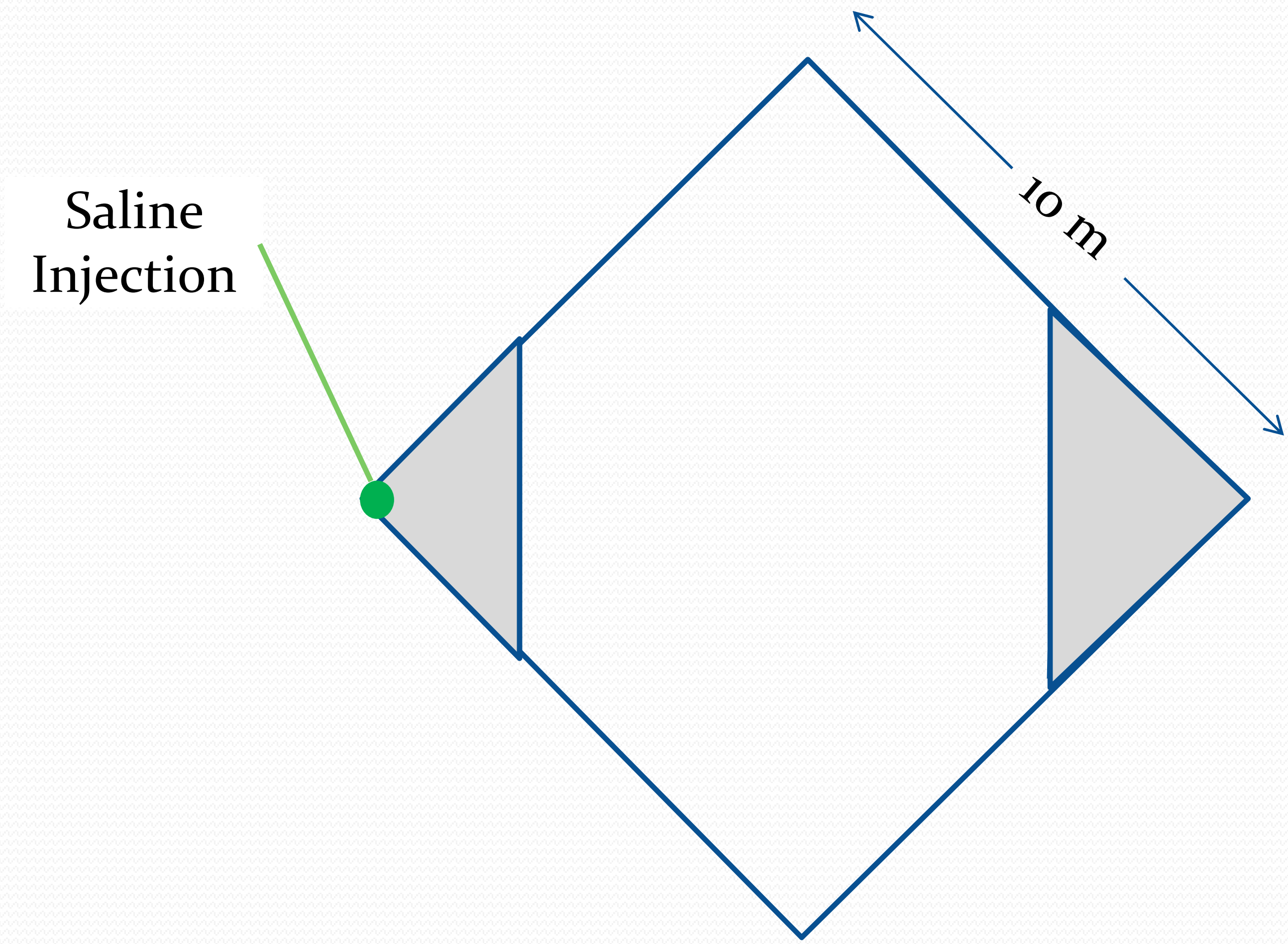


After Sorensen and Bukowski, INEEL

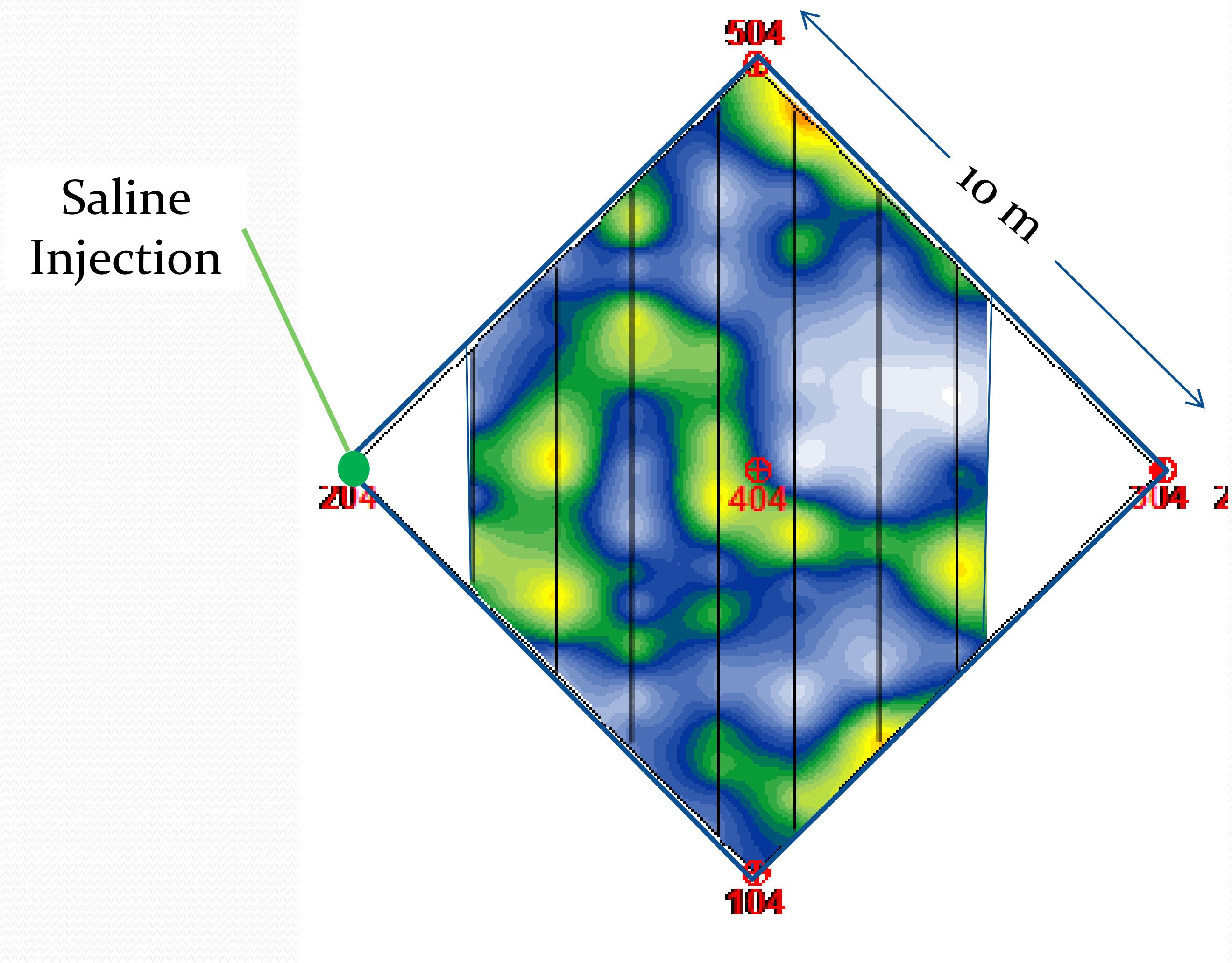
Monitored Natural Attenuation

- Not a “do nothing approach”
- Given the right elements, nature will take care of itself
- The key is the word “monitored”, must have confidence that offsite migration can be detected
- Confident monitoring not a given in fractured bedrock.

Pin the Monitoring Well on the Bedrock!

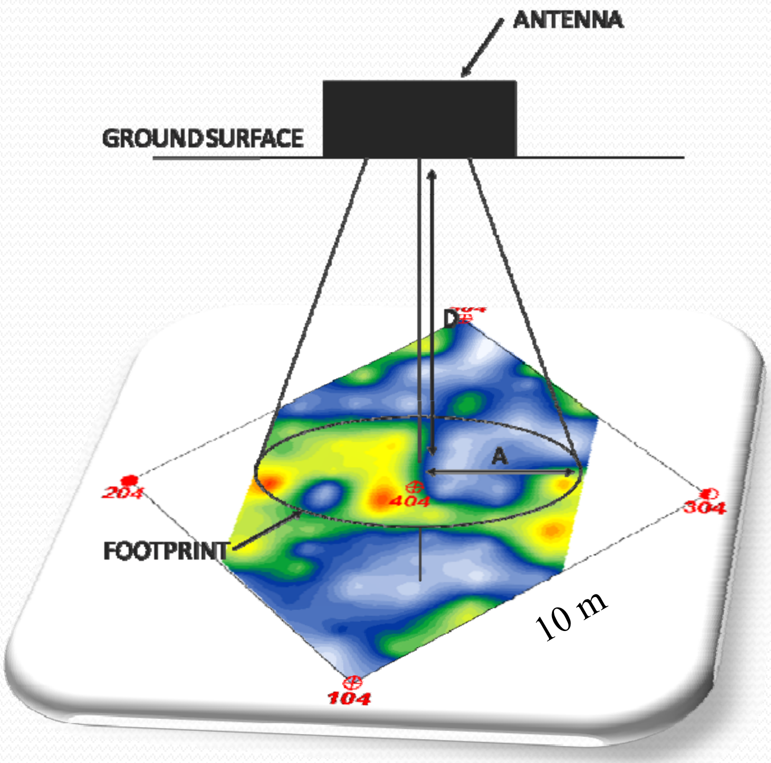


Did you catch the “plume”?

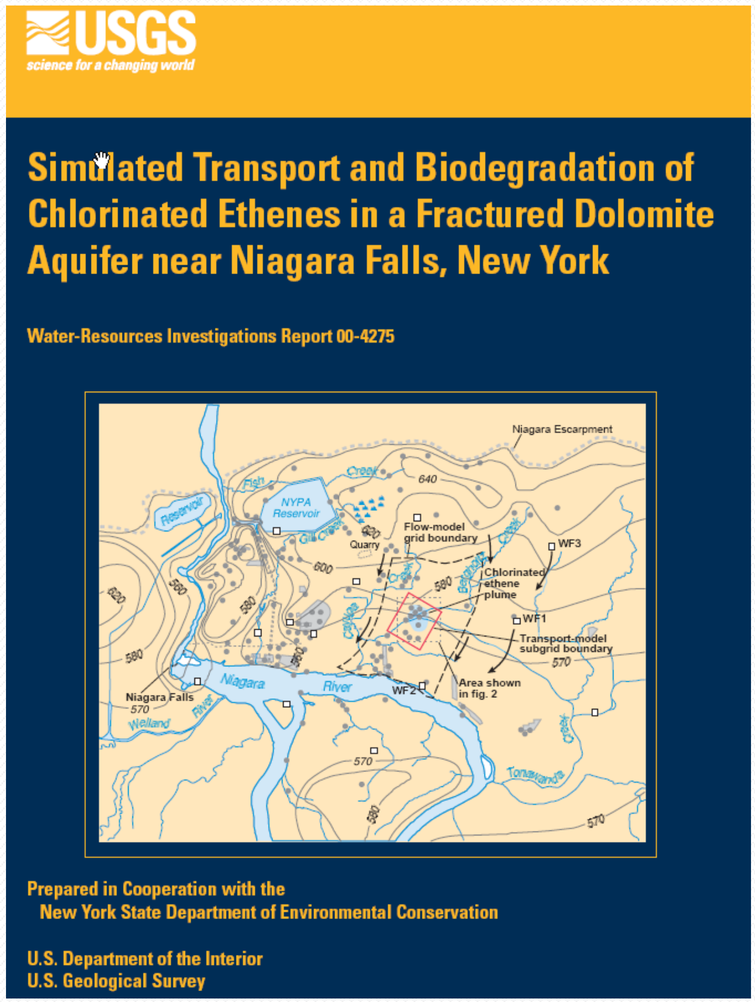


How do we know? Radar!

- We imaged saline tracer in a sandstone bedrock fracture using ground penetrating radar.
- We could see the saline “contamination” move in channels in a single 0.5 mm aperture fracture



Example: Bell Textron Aerospace



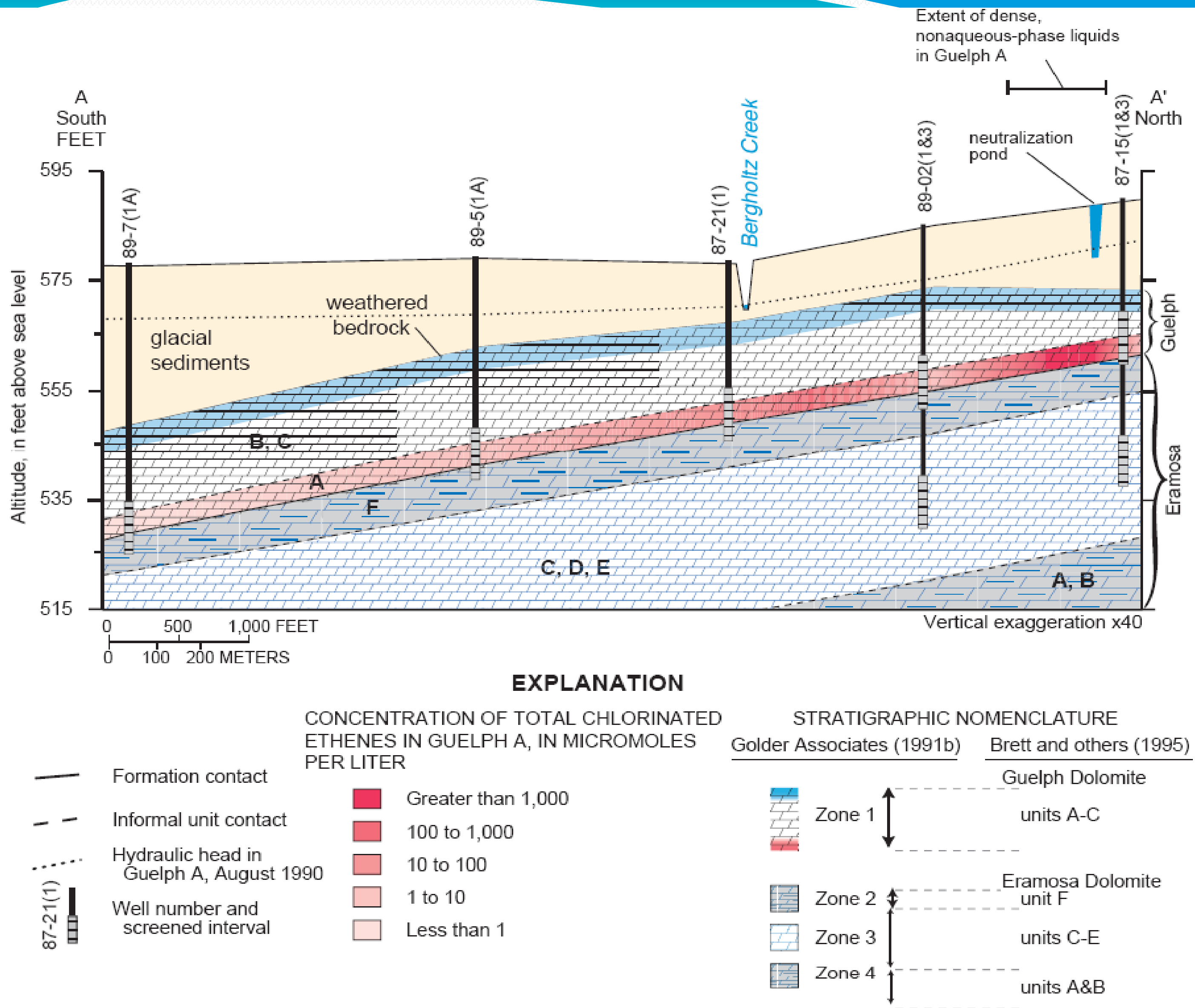
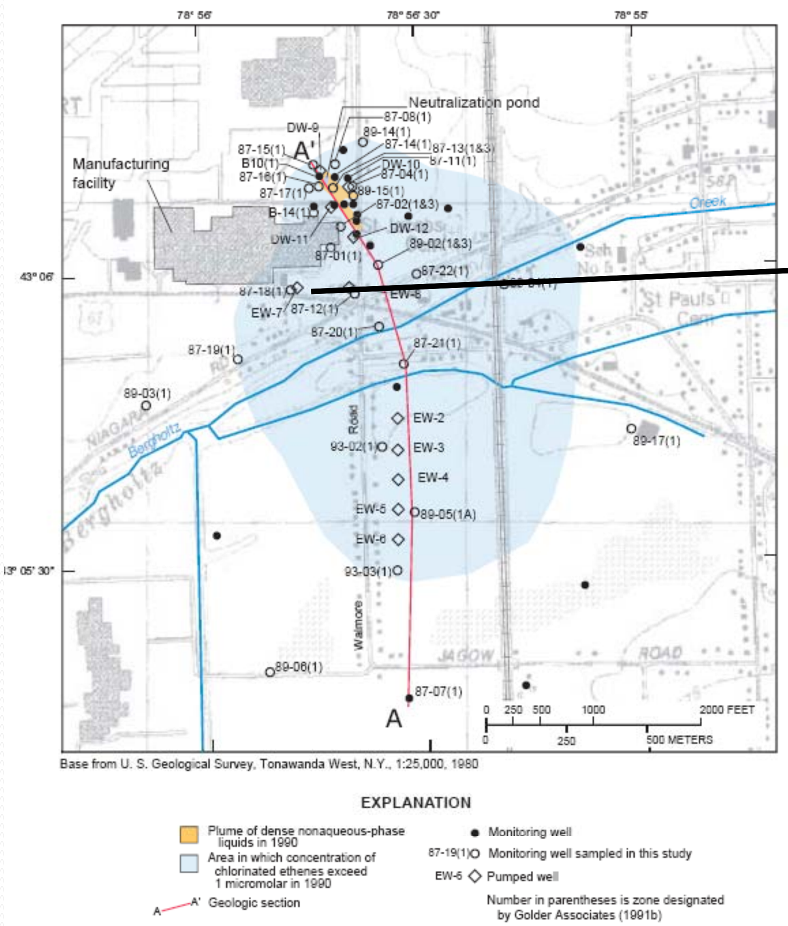
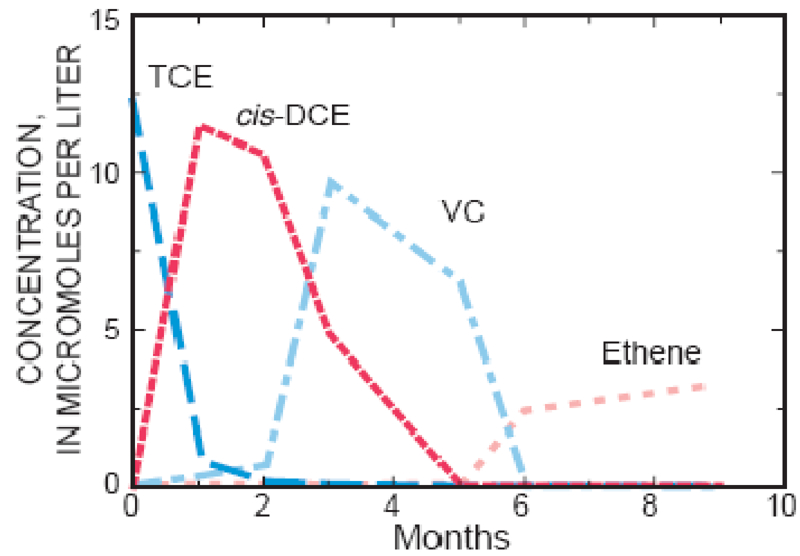


Figure 3. Vertical section A-A' through chlorinated ethene plume at study site near Niagara Falls, N.Y., 1990. (Location of section is shown in fig. 2).

Reductive Dehalogenation



Microcosm with native waters



Plume Evolution

- Chlorinated degradation daughter products of TCE (cDCE and VC) monitored in the plume
- Ethene (non-toxic) also detected in the plume indicating complete degradation

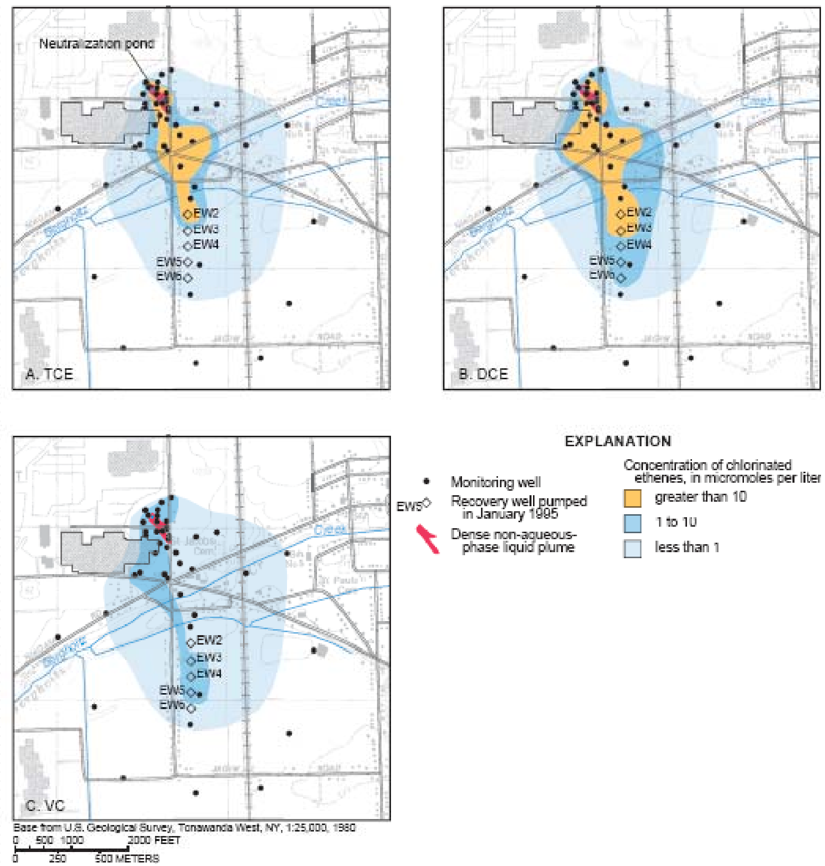
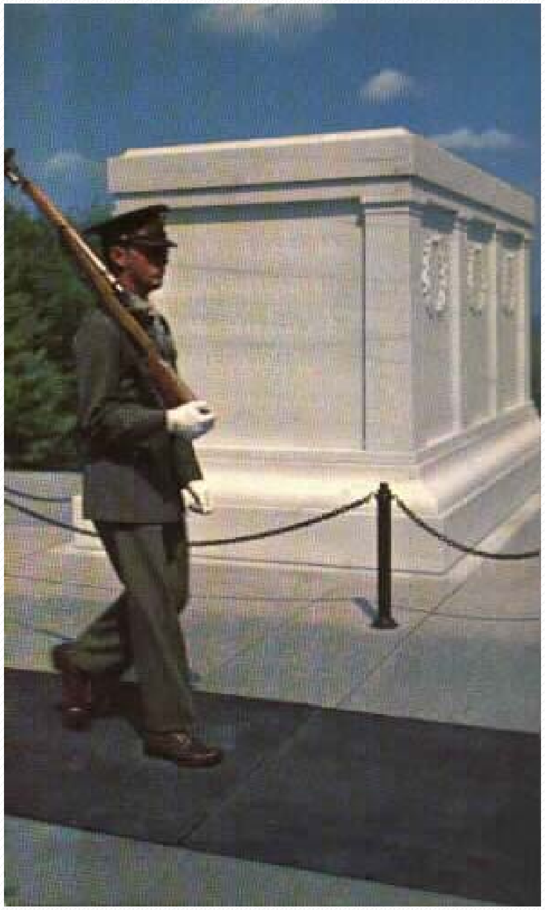


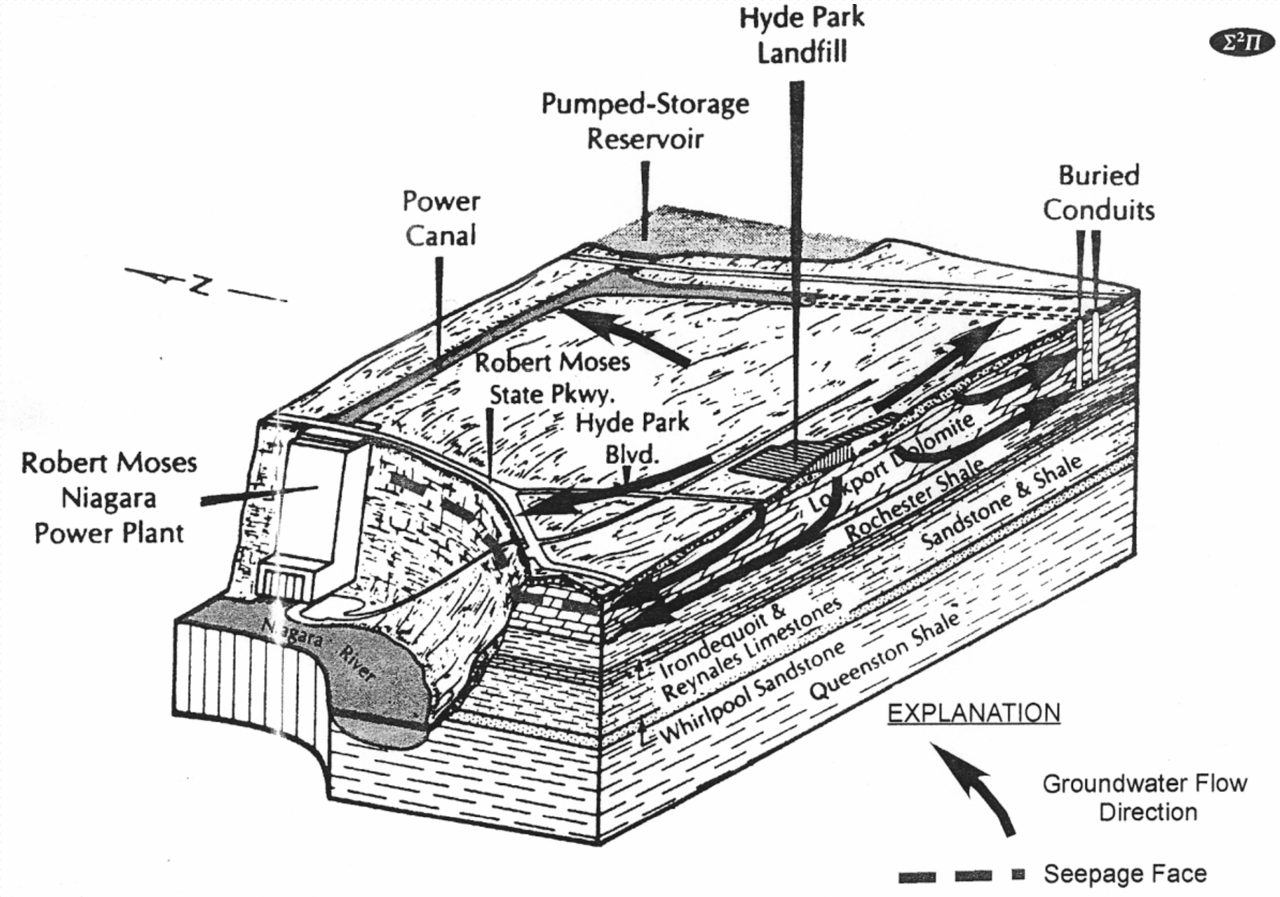
Figure 10. Distribution of chlorinated ethenes in Guelph A beneath the manufacturing facility at study site near Niagara Falls, N.Y., January 1995. A. Trichloroethene (TCE). B. cis-1,2-Dichloroethene (DCE) C. Vinyl chloride (VC).

Perpetual Containment

- If all else fails, one can try to entomb the contamination in place *forever.*
- Responsible companies don't like this any better than neighbors.
- In bedrock this usually means "hydraulic" rather than physical containment



Example: Hyde Park Landfill

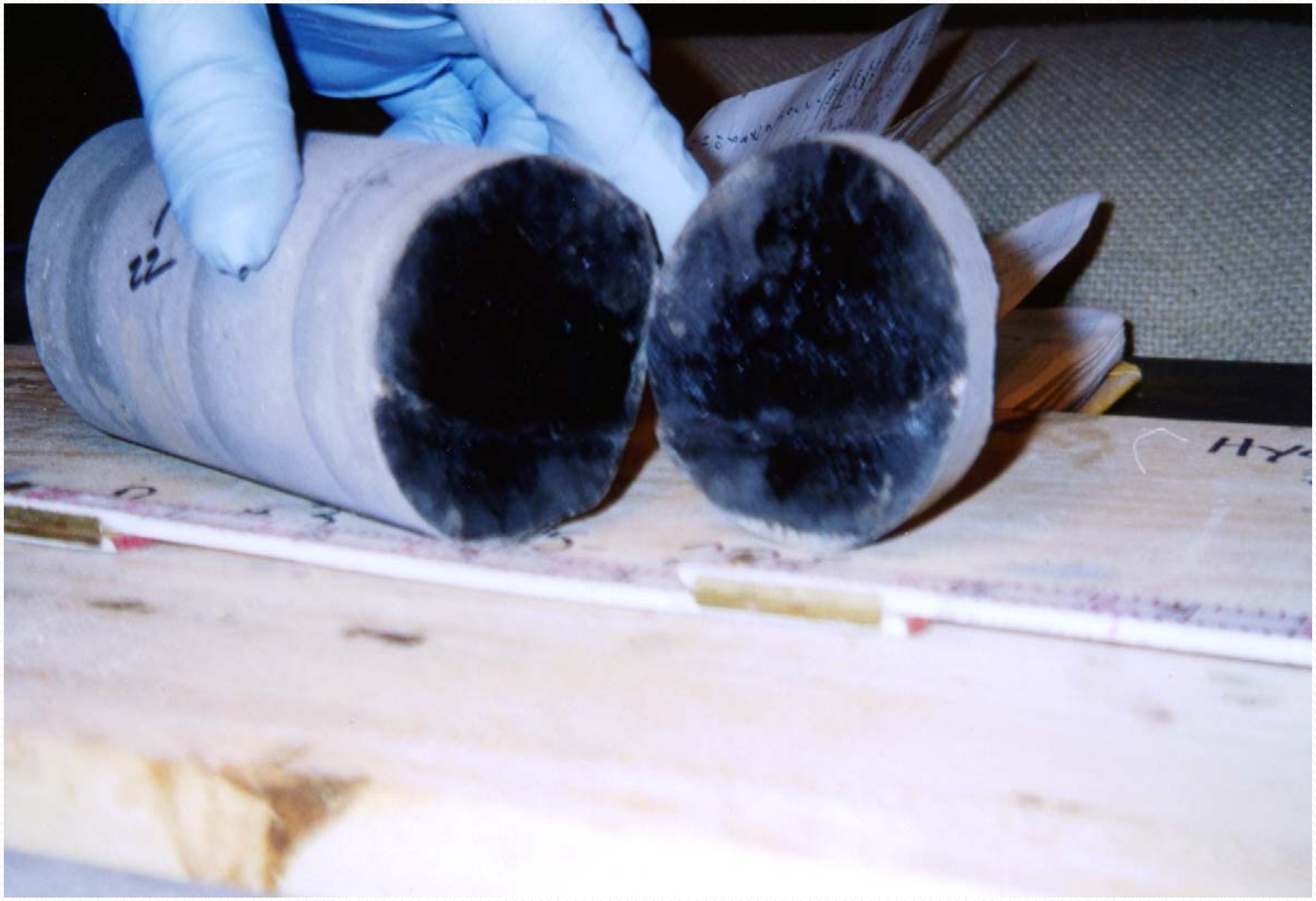


Conceptual sketch of ground-water flow patterns from the Hyde Park Landfill (S.S. Papadopulos & Associates, 2001)

Hyde Park: 80,000 Ton (13 Mgal) of DNAPL

DNAPL Viscosity

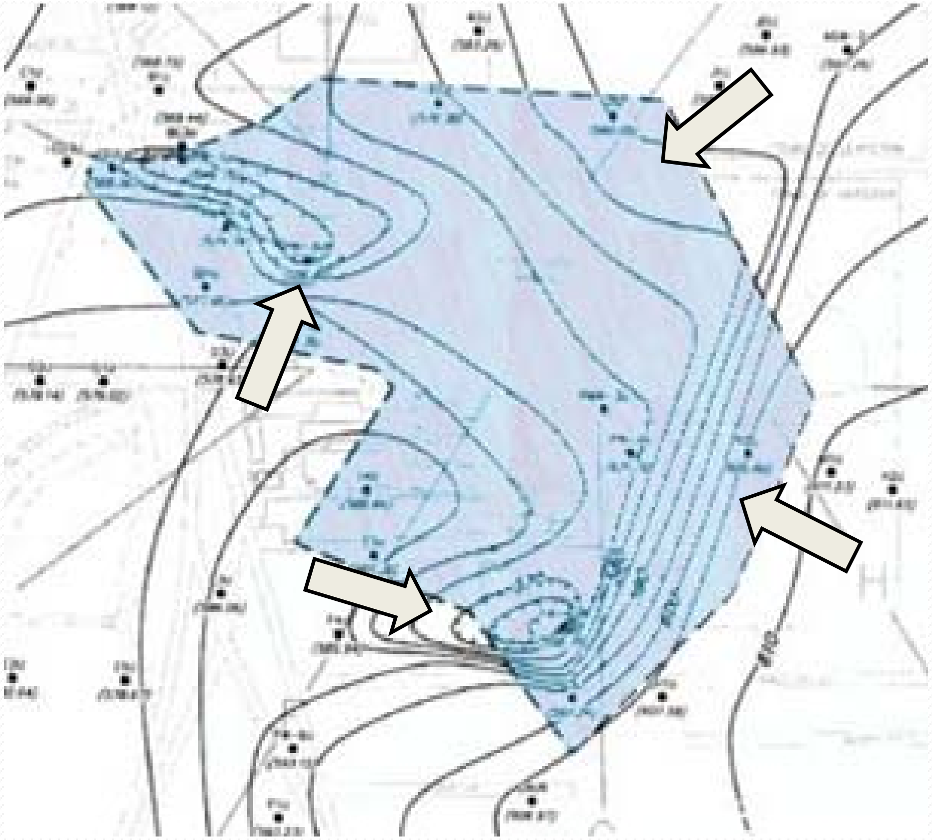
DNAPL on Bedding Plane Fracture



Seepage at the Niagara Gorge

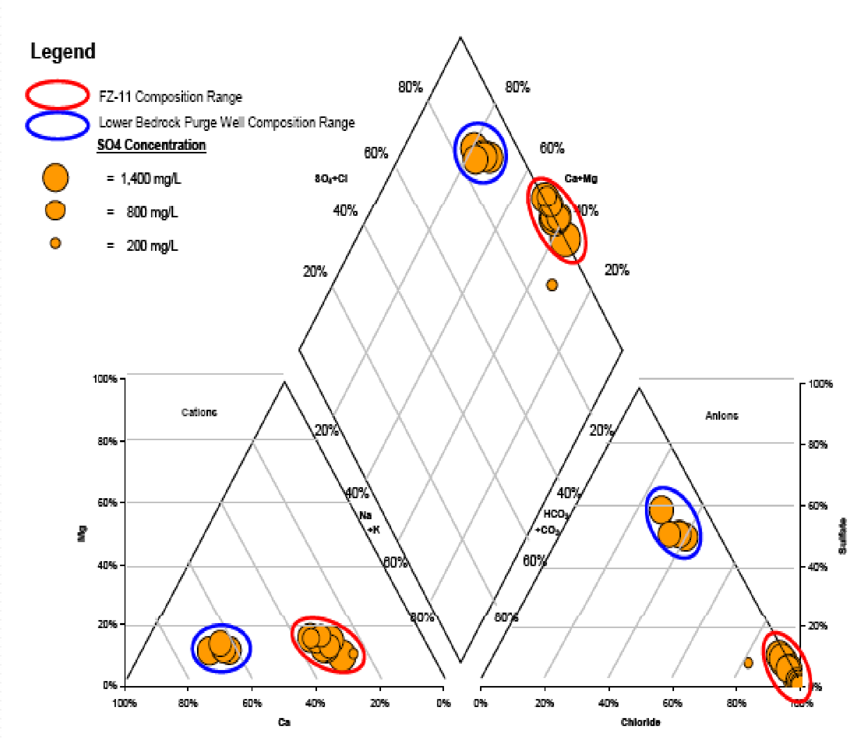
Hydraulic Containment

- To contain plume all water must flow inward toward pumping wells
- Flow direction very difficult to establish in fractured bedrock due to complex flow paths



Hydraulic Containment

- Ended up using chemistry to show containment
- Major ions show "old" versus "new" groundwater



After Sayko et al., 2004

Remedial “Solution”

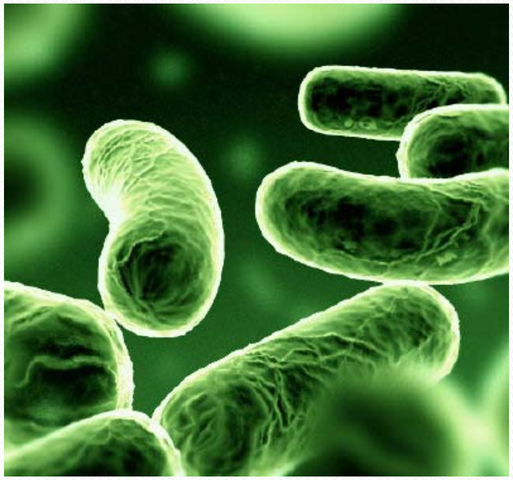
- Recover DNAPL through sumps and drains
- Pump and treat dissolved phase
- Maintain inward flow to prevent seepage to Niagara River

Remediation of Perchlorate

- **Technically easy but expensive**
- **Some popular choices are:**
  - **Ion Exchange - concentrate in a brine and dispose offsite (e.g. San Gabriel Valley Superfund Site)**
  - **Reverse Osmosis – use semi-permeable membrane**
  - **Electrodialysis – membrane with electrical gradient**

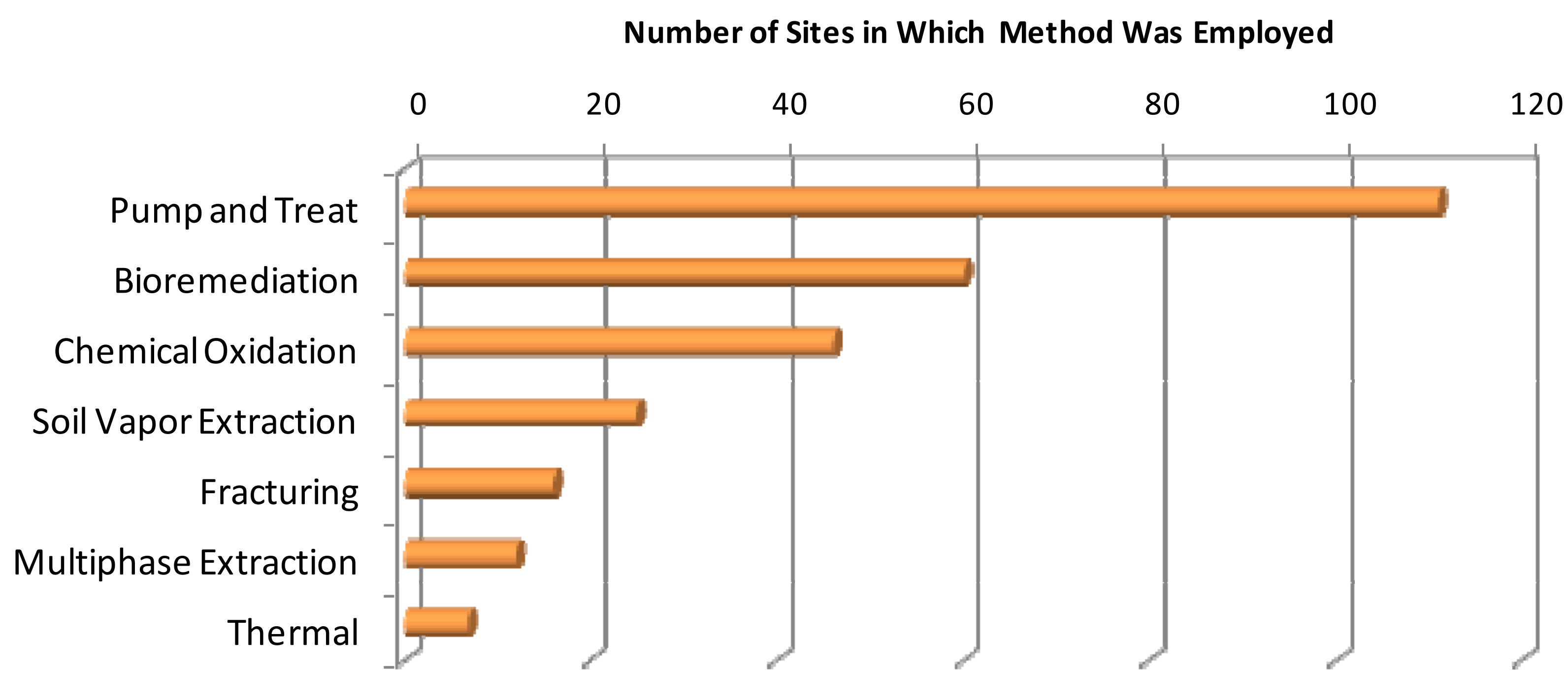
Bioremediation of Perchlorate

- **Can be biodegraded**
- **Necessary microbes appear to be widespread**
- **Nitrate tends to block biodegradation**
- **Reduction rates highly variable and site specific**
- **Possible but no guarantees…**



Popular Remedial Methods for Bedrock

- From EPA CLU-IN.org fractured rock data base (http://www.clu-in.org/products/fracrock/)



Summary

- Technologies exist for remediating contaminated bedrock
- Active methods work best on focused source zones
- Techniques that work in sediments are not necessarily applicable in bedrock
- Remediation goals have to consider the limits of technology