

Natural Attenuation in Fractured Rock Aquifers

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USEPA-USGS Fractured Rock Workshop

EPA Region 2

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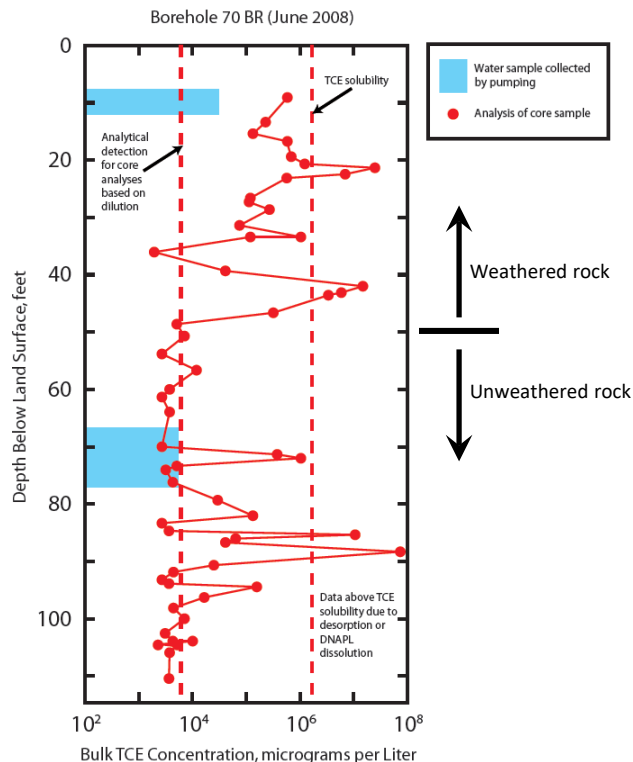


The Importance of Natural Attenuation in the Groundwater Management at Sites of Contamination in Fractured Rock Aquifers

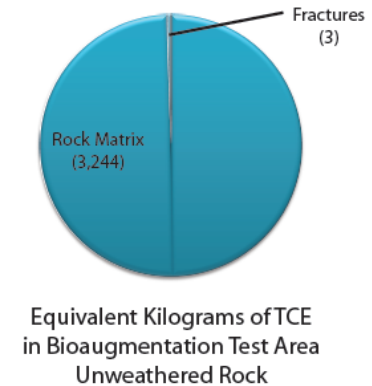
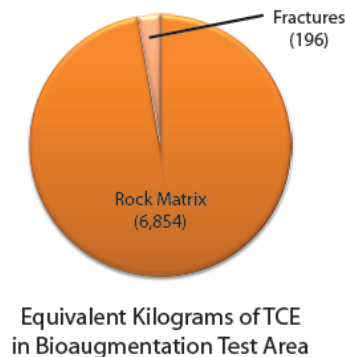
- Monitored Natural Attenuation (MNA) is currently evaluated as a groundwater remediation strategy, like other groundwater remediation strategies (e.g., Pump-and-Treat, Thermal Treatments, In Situ Chemical Oxidation, etc.)
- If the Remedial Action Objective is to restore groundwater, remediation strategies are evaluated on achieving ARARS (Applicable or Relevant and Appropriate Requirements) in a “Reasonable Time Frame”
- MNA has been successfully applied at a large number of sites of groundwater contamination over the past 15 years, including some sites in fractured rock
- There are many (federal, industrial, and state) sites, where achieving ARARs in a “Reasonable Time Frame” is unlikely in fractured rock

Technical Challenges to Remediation in Fractured Rock in a Reasonable Time Frame

- Difficulties in characterizing complex distribution of contaminants (e.g., source zone, flow paths, contaminant mass in flow-limited regions of the aquifer)
- Long-residence times of contaminants in flow-limited regions of the aquifer
- Challenges to remedial technologies in transforming/destroying contaminant mass in source zone and dissolved-phase plume in flow-limited regions of the aquifer



Estimate of TCE Mass in Fractures and Rock Matrix



Naval Air Warfare Center, West Trenton, NJ

The Magnitude of the Problem

Program/Agency	Number of Contaminated Facilities	Number of Sites	Estimated Cost Complete (\$B)
DoD		4,329	\$12.8
CERCLA	1,364		\$16 - \$23
RCRA	2,844		\$32.4
UST		87,983	\$11
DOE		3,650	\$17.3 - \$20.9
Other Federal Sites		>3,000	\$15 - \$22
State Sites		>23,000	\$5
TOTAL		>126,000	\$110 - \$127

National Research Council, 2013

The Magnitude of the Problem

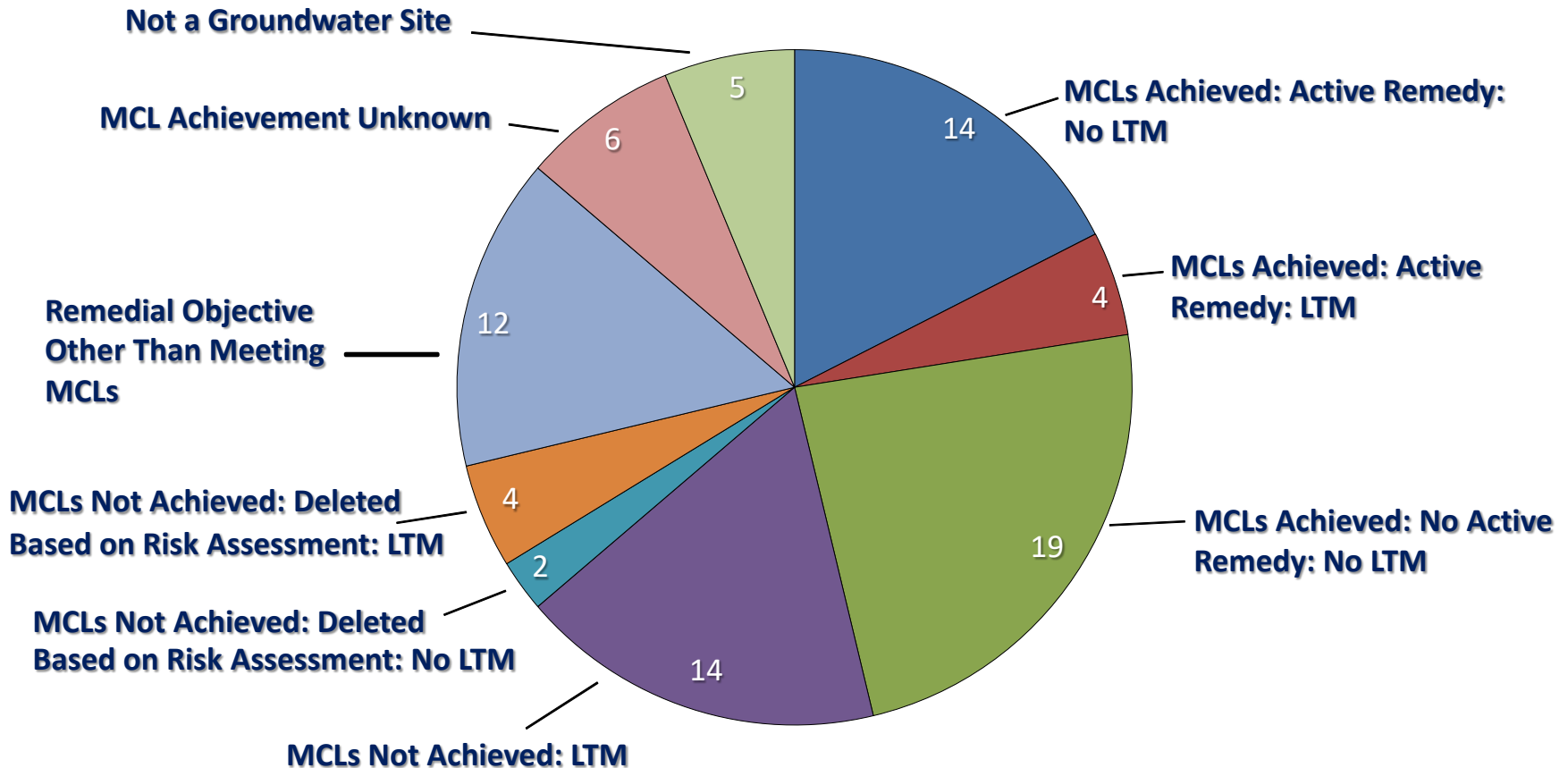
- ❑ **>126,000 sites have residual groundwater contamination that prevents “closure” . . . likely an underestimate. . .e.g., counting of “facilities” and “sites” differ between programs, does not include DoD facilities with Remedy in Place (RIP) or Response Complete (RC), etc.**
- ❑ **Cost of remediation \$110 - \$127 Billion. . .likely an underestimate given technical limitations of achieving Unlimited Use/Unrestricted Exposure (UU/UE). . .**
- ❑ **Estimated ~10% of sites (~12,000 sites) are “complex” . . . restoration unlikely for decades or centuries. . . ~10% of all sites will account for ~70% of total cleanup costs [Ehlers and Kavanaugh, 2013] . . .**

National Research Council, 2013

Are “Closed” Sites “Closed” ?

Analysis of 80 Delisted NPL Groundwater Sites

MCL Characterization



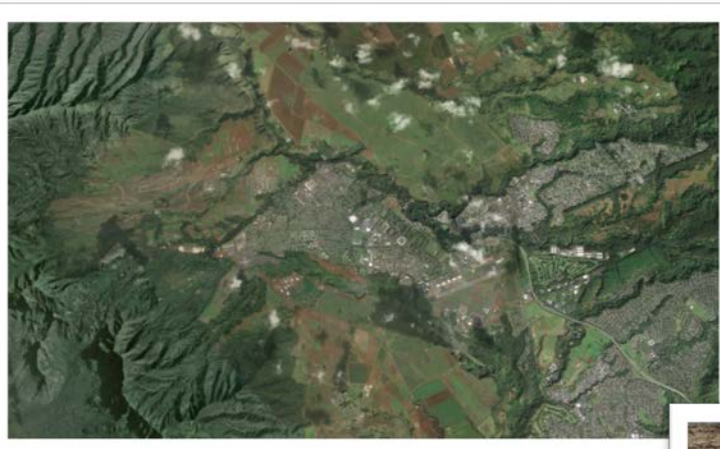
National Research Council, 2013

ARARs Waiver – Technical Impracticability

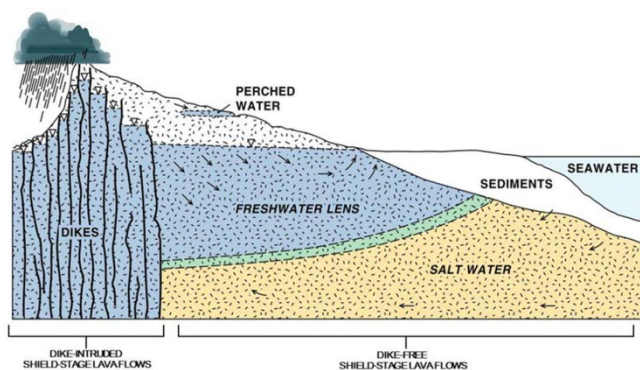
Schofield Barracks (U.S. Army), Oahu, Hawaii



17,000 acre facility
Land fill, sewage, industrial and vehicle waste, explosives
Water supply well impacted by TCE (100 ppb)



- Basaltic rock
- Thin, horizontal lava flows (hydraulic conductivity 100's to 1,000's ft/day)
- Intrusive dikes compartmentalize groundwater
- Groundwater 500-600 ft below land surface

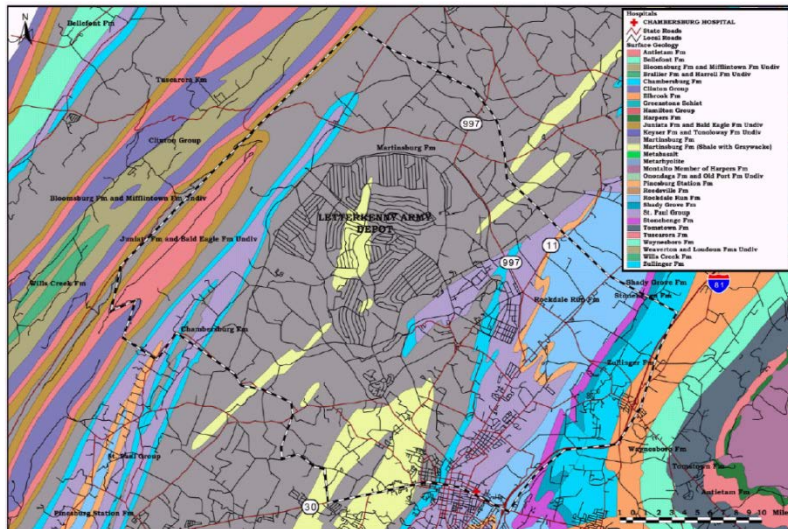


- U.S. Army applied for upfront TI Waiver as part of ROD, 1996
- Air strippers on drinking water wells, 1986
- Monitoring wells
- Delisted from NPL, 2000
- 5-year reviews

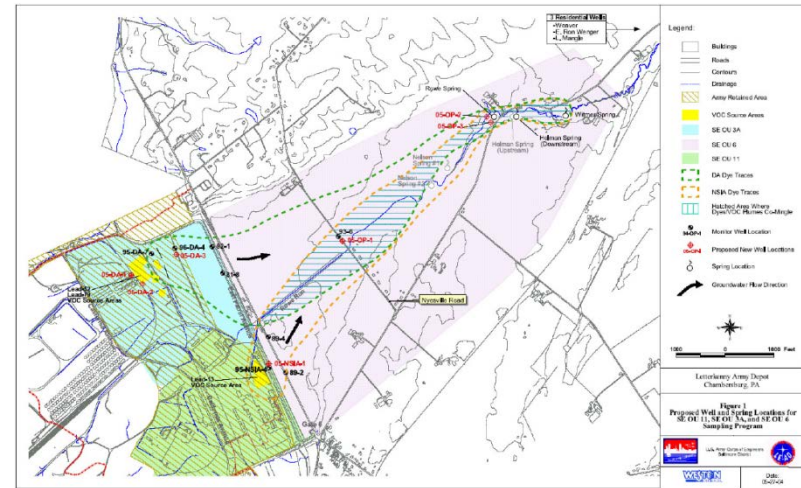
ARARs Waiver – Technical Impracticability (?)

Letterkenny Army Depot, Chambersburg, PA

- Testing, storage, overhaul of track vehicles
- Storage, transportation of industrial chemicals, petroleum
- Storage, modification of ammunition
- Groundwater contaminated with TCE, PCBs
- Soils contaminated with heavy metals, VOCs
- Facility divided into 7 Operable Units (OUs)
- Facility overlies limestone and dolomite
- Structural faulting in the area
- Karstic features (sink holes, caverns, springs)



- U.S. Army has been unable to obtain a TI waiver for selected OUs

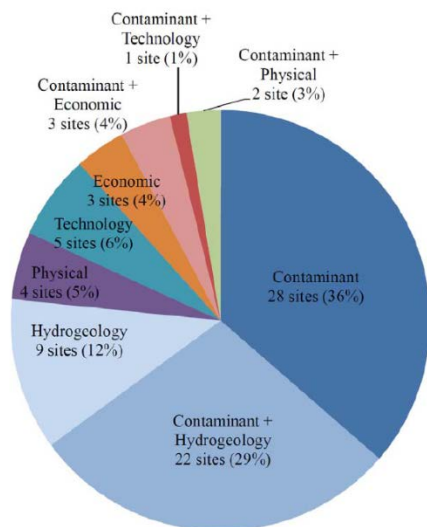


- In Situ Chemical Oxidation (ISCO) applied to VOC contamination in groundwater without success



ARARs Waiver – Technical Impracticability

77 TI waivers (up through November 2010)



~3/4 of TI waivers attributed to hydrogeology or nature of contamination

Hydrogeologic Setting

Hydrogeologic Setting	# Sites	# Sites where hydrogeology led to TI	Percent of Total
Fractured rock/karst/mining voids	36	21	47%
High heterogeneity	10	2	13%
High heterogeneity overlying bedrock	4	-	5%
Layered high- and low-permeability	9	2	12%
High-permeability sands and gravels	7	-	9%
High-permeability sands and gravels overlying bedrock	2	-	3%
Low-permeability silts and clays	6	6	8%
Low-permeability silts and clays overlying bedrock	3	-	4%
TOTAL	77	31	100%

Type of Contaminant

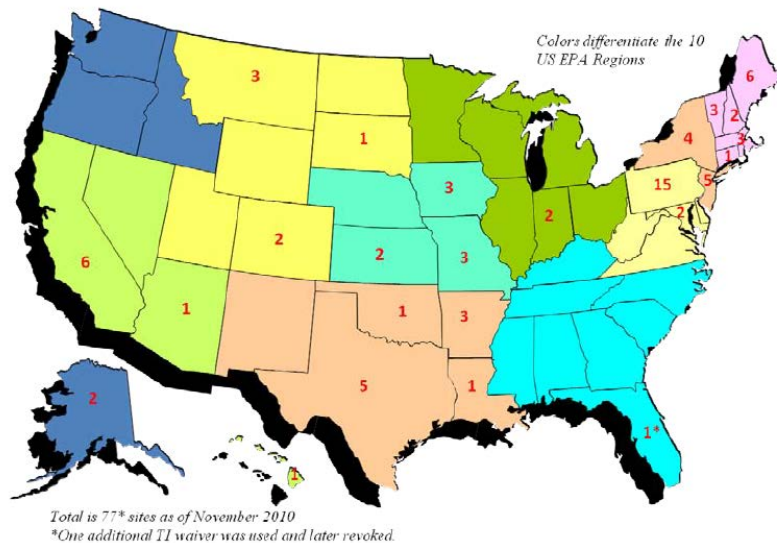
Compounds	Number of Sites
Chlorinated solvents, VOCs	16
Coal tar, PAHs, creosote	11
Metals	14
BTEX	1
PCBs	2
Pesticides	2
Mixture (2 or more types)	20
Mixture (3 or more types)	11
TOTAL	77

Deeb et al., 2011

ARARs Waiver – Technical Impracticability

77 TI waivers (up through November 2010)

Distribution of TI Waivers by EPA Regions



EPA Region	# Sites	# Post-1993 Sites
Region 1	14	11
Region 2	9	7
Region 3	18	9
Region 4	1*	0
Region 5	2	2
Region 6	10	9
Region 7	8	7
Region 8	6	3
Region 9	8	7
Region 10	2	2
TOTAL	77*	57

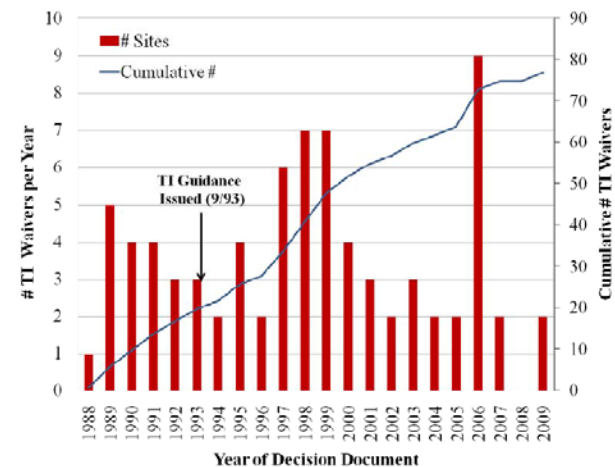
*One additional TI waiver was used and later revoked.

Approximately ½ of states have not had a TI waiver

Distribution of CERCLA sites is not evenly distributed over EPA regions

Hydrogeologic conditions differ from region to region

TI Waivers Granted Over Time




Deeb et al., 2011

The Importance of Natural Attenuation in the Groundwater Management at Sites of Contamination in Fractured Rock Aquifers

- Large number of sites are characterized as “complex”. . .ARARs unlikely to be achieved in decades to centuries. . .
- Unlikely that stakeholders will accept wide spread application of ARARs Waivers (Technical Impracticability) at fractured rock sites
- Need to consider longer time frames of remediation and remedial strategies that may evolve over time, recognizing that some active remedies may reach a point of diminishing returns. . .Natural Attenuation will likely be a component in the management of a large number of fractured rock sites. . .
- There is a need to document the existence of Natural Attenuation and understand the long-term prospects for continued Natural Attenuation

Monitored Natural Attenuation EPA Protocol (1999)

- MNA – encompasses all natural attenuation processes (not just biological) – preference for those processes that degrade or destroy contaminants
- Conditions at each site are unique, but common framework is applied in documenting natural attenuation

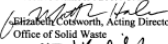
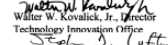
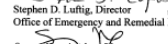
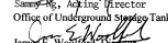

 UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 21 1999

OFFICE OF
SOLID WASTE AND EMERGENCY
RESPONSE

MEMORANDUM

SUBJECT: Final OSWER Directive "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites" (OSWER Directive Number 9200.4-17P).

FROM: 
Elizabeth Cotworth, Acting Director
Office of Solid Waste

Walter W. Kovalek, Jr., Director
Technology Innovation Office

Stephen D. Luftig, Director
Office of Emergency and Remedial Response

Sandra M. Smith, Acting Director
Office of Underground Storage Tanks

James E. Woodford, Director
Federal Facilities Restoration and Reuse Office

TO: Addressees

Purpose

This memorandum accompanies a copy of the Final OSWER Directive regarding the use of monitored natural attenuation for the remediation of contaminated soil and groundwater at sites regulated under all Office of Solid Waste and Emergency Response (OSWER) programs. A draft Interim Final version of this Directive was released on December 1, 1997 for use, and for general public review and comment. In response to comments received on that draft, EPA has incorporated several changes in this final version dealing with topics such as contaminants of concern, cross-media transfer, plume migration, and remediation time frame.

- Lines of evidence (1999)
 - Historical chemical data indicating decrease in contaminants of concern along flowpaths
 - Hydrogeological and geochemical data to demonstrate (indirectly) types of natural attenuation processes and rates
 - Field or microcosm studies

Monitored Natural Attenuation

Recent Advances

- Development of microbiological tools. . Polymerase Chain Reaction (PCR) . .
.explicitly identify presence of *Dehalocoides (Dhc)* species in groundwater
known to carry out reductive dechlorination
- Compound Specific Isotope Analysis (CSIA) . . .ratio of carbon isotopes. .
.dechlorination preferentially metabolizes ^{12}C in comparison ^{13}C , changing the
isotope ratio of TCE, *cis*-DCE, VC, and ethene as reductive dechlorination
continues. . .clearly identifies that decreases in concentrations of chlorinated
ethenes are a product of dechlorination rather dilution. . .
- Statistical model correlating presence of *Dhc* with geochemical parameters . .
.oxidation-reduction potential (ORP), methane, and nitrate + nitrite
- Recent advances provide quantitative (lines of) evidence for reductive
dechlorination

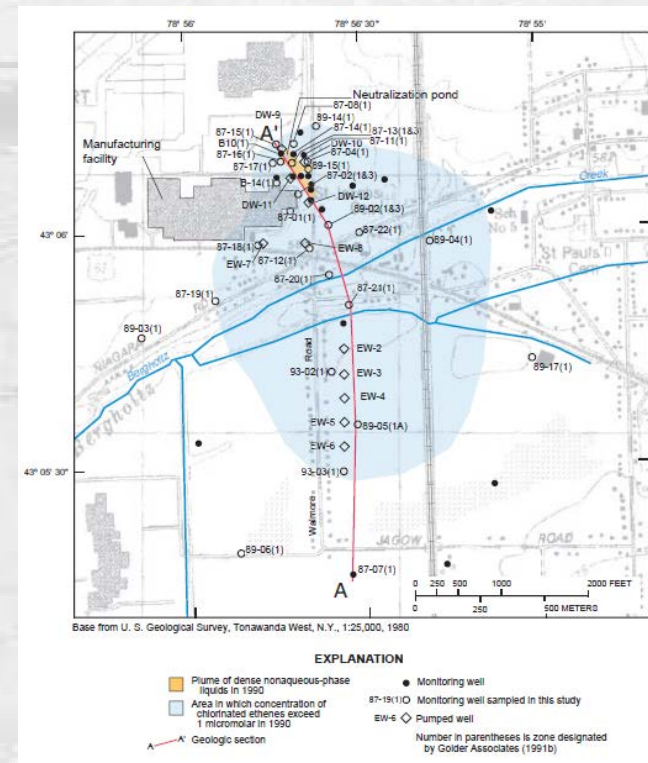
Wilson 2010

Monitored Natural Attenuation Attributes that Lead to Success

- Detailed understanding of flowpaths from source to receptors – design of monitoring well network – a challenge in fractured rock
- Source zone control – to prevent further downgradient contamination – remediation or containment
- Monitoring that demonstrates substantial reduction in contaminant concentration over a decade or more – reductions in concentrations by order of magnitude
- Monitoring includes geochemical and microbial parameters that document groundwater is an appropriate habitat for attenuation
- Quantitative evaluation of spatial distribution of contaminants and their degradation products (usually through mathematical modeling tools)

Monitored Natural Attenuation Application to Fractured Rock

- Successful applications of MNA in dissolved phase plume in fractured rock document for selected areally extensive plumes . . .1000's of feet. . . see, e.g., Twin Cities Army Ammunition Plant (MN) - sandstone, Bell Aerospace Textron Wheatfield Plant (NY) - dolomite
- Plumes over 1000's of meters – monitoring wells interpreted as if along a single flow path
- Current struggle to interpret MNA in fractured rock over dimensions where flowpaths are convoluted (10's -100's of meters)
- “Flowpath-independent” interpretation of MNA (see, e.g., Bradley et al., 2009) - an attempt to address this issue at discrete monitoring locations



Monitored Natural Attenuation in Fractured Rock Observations

- Natural attenuation (biotic and abiotic processes) will likely become an issue at some point in the life span of remedial activities at fractured rock sites
- Estimates of attenuation will to change over time. . .one cannot expect degradation rates to remain constant. . .for long time frames, one will need to document the processes and conditions that will maintain natural attenuation
- Over dimensions of 10's – 100's of meters, monitoring wells may not characterize representative flowpaths . . .under such conditions in fractured rock, it is difficult to infer if attenuation will reduce (spatially distributed) concentrations and contaminant mass

Suggested References

Bradley, P. M., Lacombe, P. J., Imbrigiotta, T. E., Chapelle, F. H., and Goode, D. J., 2009, Flowpath independent monitoring of reductive dechlorination potential in a fractured rock aquifer, *Ground Water Monitoring and Remediation*, v. 29, no. 4. P. 46-55.

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Yager, R. M., Bilotta, S. E., Mann, C. L., and Madsen, E. L., 1997, Metabolic adaptation and in situ attenuation of chlorinated ethenes by naturally occurring microorganisms in a fractured dolomite aquifer near Niagara Falls, New York, *Environmental Science and Technology*, v. 31, p. 3138-3147.