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ITRC's Internet-based Training Program

In Situ Bioremediation of Chlorinated Ethene – DNAPL Source Zones

Technical & Regulatory Guidance for *In Situ* Bioremediation of Chlorinated Ethene – DNAPL Source Zones (BioDNAPL-3, June 2008)

Sponsored by: Interstate Technology and Regulatory Council (www.itrcweb.org)
Hosted by: US EPA Clean Up Information Network (www.cluin.org)

Presentation Overview: Treatment of dissolved-phase chlorinated ethenes in groundwater using in situ bioremediation (ISB) is an established technology; however, its use for DNAPL source zones is an emerging application. This training course supports the ITRC Technical and Regulatory Guidance document In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones (BioDNAPL-3, 2008). This document provides the regulatory community, stakeholders, and practitioners with the general steps practitioners and regulators can use to objectively assess, monitor, and optimize ISB treatment of DNAPL source zones. The objective is to provide adequate technology background for the user to understand the general and key aspects of ISB for treatment of chlorinated ethene DNAPL source zones. It is not intended to be a step-by-step instruction manual for remedial design, but describes technology-specific considerations for application of ISB of DNAPL source zones.

For this training and guidance document, a DNAPL source zone includes the zone that encompasses the entire subsurface volume in which DNAPL is present either at residual saturation or as "pools" that accumulate above confining units. The DNAPL source zone includes regions that have come into contact with DNAPL and may be storing contaminant mass as a result of diffusion of DNAPL into the soil matrix. Even though DNAPLs may be present in both the unsaturated and saturated zones, the discussion of ISB of DNAPL source zones in this training and guidance document focuses on treatment of DNAPL source zones within the saturated zone.

Two goals of any DNAPL source treatment technology are to 1) reduce the mass of contaminants within the source area and 2) prevent migration of contaminants above unacceptable levels. The enhanced ISB technology reduces source mass and controls flux through the enhanced dissolution and desorption of DNAPL constituents into the aqueous phase, and subsequent microbially mediated degradation processes. Although enhanced ISB of DNAPL source zones has been demonstrated in the field at a few chlorinated solvent sites, expectations for rapid depletion of the source zone must be realistic. This training and guidance provide detailed requirements necessary to support the realistic determination of goals for ISB of a DNAPL source zone.

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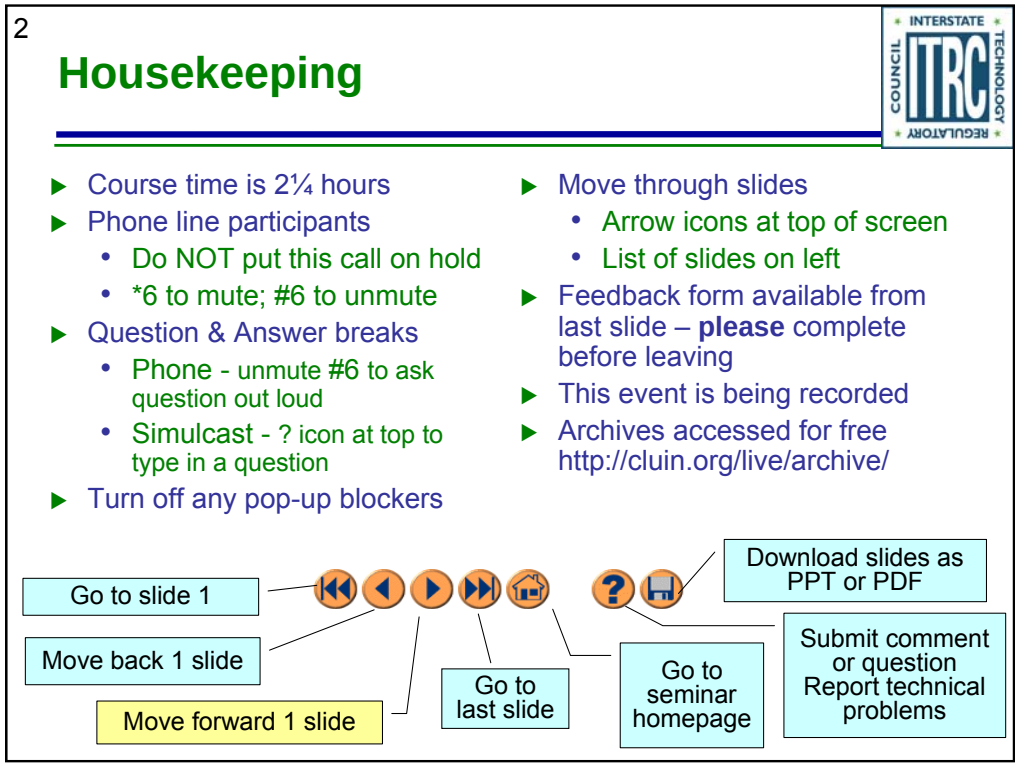

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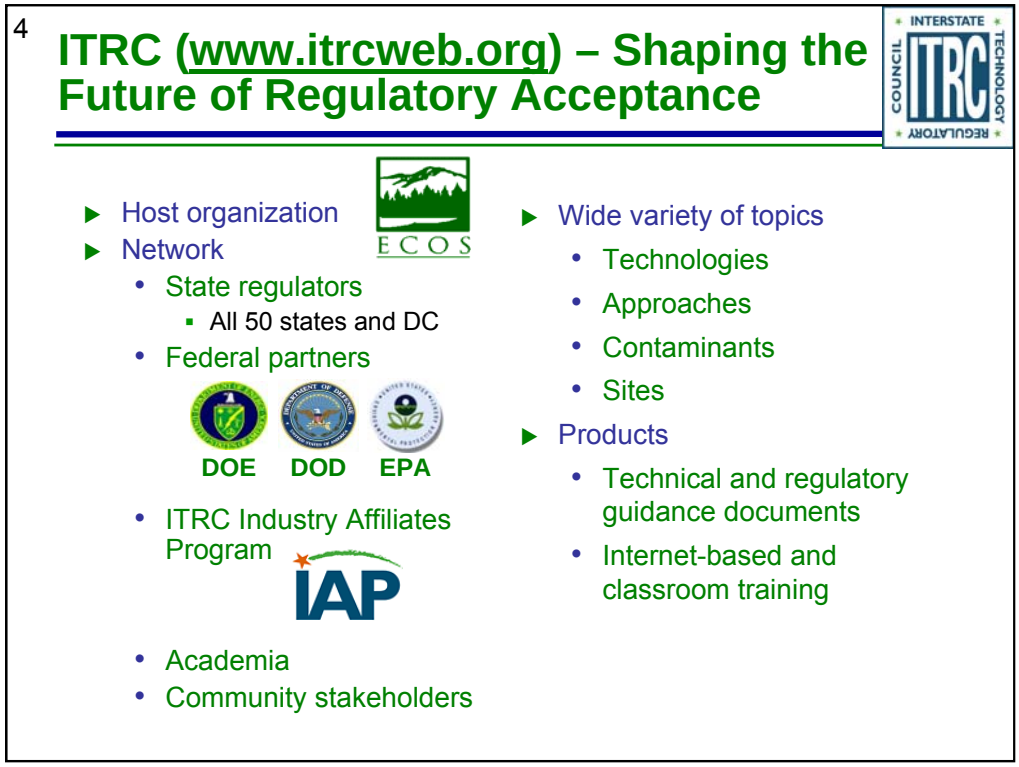

The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition of regulators, industry experts, citizen stakeholders, academia and federal partners that work to achieve regulatory acceptance of environmental technologies and innovative approaches. ITRC consists of all 50 states (and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and advance the regulatory acceptance of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision making while protecting human health and the environment. With our network of organizations and individuals throughout the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

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ITRC Course Topics Planned for 2010 – More information at www.itrcweb.org

Popular courses from 2009

- Decontamination and Decommissioning of Radiologically-Contaminated Facilities
- Enhanced Attenuation of Chlorinated Organics
- In Situ Bioremediation of Chlorinated Ethene - DNAPL Source Zones
- LNAPL Part 1: An Improved Understanding of LNAPL Behavior in the Subsurface
- LNAPL Part 2: LNAPL Characterization and Recoverability
- Perchlorate Remediation Technologies
- Performance-based Environmental Management
- Phytotechnologies
- Protocol for Use of Five Passive Samplers
- Quality Consideration for Munitions Response
- Survey of Munitions Response Technologies
- Determination/Application of Risk-Based Values
- Use of Risk Assessment in Management of Contaminated Sites

New in 2010

- Use and Measurement of Mass Flux and Mass Discharge
- LNAPL Part 3: Evaluating LNAPL Remedial Technologies for Achieving Project Goals
- Mine Waste Treatment Technology Selection

ITRC 2-day Classroom Training: Vapor Intrusion Pathway

More details and schedules are available from www.itrcweb.org under “Internet-based Training” and “Classroom Training.”

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Meet the ITRC Instructors

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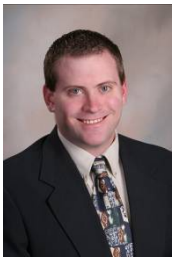

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Larry Syverson is a groundwater remediation specialist for the Virginia Department of Environmental Quality in Richmond, Virginia. Larry has worked at the Department for since 1991: five years in the underground storage tank section and since 1996 in the solid waste section. Larry issues solid waste groundwater permits, reviews post-closure care applications and oversees corrective action projects for the Department's Northern Regional Office. Prior to the Department, Larry worked for 16 years in Texas and Oklahoma has a petroleum geologist and in Virginia as an environmental consultant. Larry is currently the ITRC's point of contact for Virginia and is a member of the BioDNAPL team. Larry earned a bachelor's degree in geology in 1972 and a master of environmental science in 1988 from The University of Oklahoma in Norman, Oklahoma. Larry is a Certified Professional Geologist by the Commonwealth of Virginia.

Dr. David Major, Ph.D., is a Principal and a Vice President of Geosyntec Consultants Inc., Associate Editor of Ground Water Monitoring and Remediation, and an Adjunct Professor at the Department of Chemical Engineering and Applied Chemistry, University of Toronto and Department of Earth Sciences, University of Waterloo (UW). He has worked for Geosyntec Consultants Inc. in Guelph, Ontario, Canada since 1998. He has helped various researchers to develop and commercialize new environmental technologies such as zero-valent iron (ZVI) permeable reactive barriers, molecular biomarkers, and bioaugmentation cultures. David was recently inducted into the Space Hall of Fame® in 2007 in recognition for his role in commercializing NASA's Emulsified ZVI to treat DNAPLs. He received one of 50 Science's Alumni of Honor Awards from the University of Waterloo, in celebration of 50 years of success and accomplishments of UW alumni and the university. David also serves on various national scientific and regulatory advisory boards. He is a member of the Remediation Technologies Development Forum, served on a U.S. EPA Expert Panel to address the benefits of partial source treatment of DNAPLs, and on the U.S. National Research Council Committee on Geological and Geotechnical Engineering in the New Millennium. He has been active in ITRC since 1996. He co-developed and taught two ITRC courses (monitored natural attenuation [MNA] and accelerated anaerobic bioremediation of chlorinated solvents) and is currently an instructor on ITRC's BioDNAPL training course. David earned his bachelor's and master's of science, and doctoral degrees in biology from the University of Waterloo, Waterloo Ontario in 1981,1984, 1987 respectively.

Dr. Wilson S. Clayton, Ph.D., P.E., P.G., is a co-founder and Vice President of Aquifer Solutions, Inc., a small woman-owned business specializing in vadose zone and groundwater hydrology and in-situ remediation founded in 2001. Wilson was previously employed with Groundwater Technology Inc., and then by acquisition with Fluor Daniel GTI, and IT Corporation. Wilson held positions including Territory Manager, Treatability Laboratory Director, and National Practice Leader for in-situ chemical oxidation. He has been a member of ITRC since 2001, and has worked with ITRC teams on chemical oxidation and bioremediation of DNAPLs, and was an instructor on the ITRC in-situ chemical oxidation Internet-based training course. Wilson earned a bachelor's degree in geology from Clemson University in Clemson, South Carolina in 1984, a master's degree in geology from University of Connecticut in Storrs, Connecticut in 1986, and a doctoral degree in geological engineering from Colorado School of Mines in Golden, Colorado in 1996. He is a professional engineer in Texas and Colorado and a professional geologist in Texas, Colorado, and Wyoming.

Ryan A. Wymore, P.E., is with CDM in Denver, Co, where he serves as a national resource for evaluation, selection, and implementation of remediation strategies and solutions. Since 1998, he has specialized in innovative groundwater remediation technologies, particularly bioremediation, monitored natural attenuation and chemical oxidation. He also serves as the administrator for CDM's Research and Development Program, where he coordinates all of the company's internally and externally funded research. He has worked for the Idaho National Engineering and Environmental Laboratory, North Wind Inc., and is currently at CDM, where he has worked since 2005. He has given over sixty presentations at various local, regional, national, and international symposia and meetings. Since 2002, he has worked with ITRC teams on DNAPLS, Bioremediation of DNAPLS, and Enhanced Attenuation: Chlorinated Organics. He was an instructor on the ITRC DNAPL Performance Assessment Internet-based training course, which was delivered to more than 1,100 trainees. Ryan earned a bachelor's degree in Biological Systems Engineering from the University of Nebraska-Lincoln in 1997 and a master's degree in Civil/Environmental Engineering from the University of Idaho in Moscow, Idaho in 2003. He is a registered Professional Engineer in the state of Idaho and Colorado in the environmental discipline.

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Why *In Situ* Bioremediation (ISB) at DNAPL Source Zones?

- Problem
  - Tens of thousands DNAPL sites
  - Sites in every state
  - Low maximum contaminant levels (MCLs)
  - Long half-lives
  - Denser than water
- Solution
  - *In Situ* Bioremediation of Chlorinated Ethene DNAPL Source Zones
    - **Efficient**
    - **Cost-effective**

On this slide, we see a list of the problems associated with DNAPL source zones.

There are more than 10,000 DNAPL sites across the country, located in every state. These include many DOD and DOE sites as well as dry cleaner sites and various industrial and manufacturing properties

Due to the characteristics of DNAPL sites, many are considered high risk because they include cancer causing contaminants, such as PCE and TCE, which have low maximum contaminant levels (MCLs). Many of these contaminants have half-lives that are quite long. In addition, the sites are difficult to clean up because the contaminants are denser than water.

As a result, few remediation technologies are effective at cleaning-up DNAPL source zones.

In 2004, ITRC formed the Bioremediation of DNAPLs Team to investigate the use of In Situ Bioremediation at DNAPL source zone sites. Note: “In Situ Bioremediation” will be referred to simply as “ISB.”

ISB is an established technology; however, its use at DNAPL source zones is still an emerging application. The team determined that ISB is a viable technology for remediating DNAPLs at source zones because of its efficiency and cost effectiveness.

As a result, the team produced the technical and regulatory guidance upon which this training is based, to provide the know-how in utilizing ISB at DNAPL source zones.

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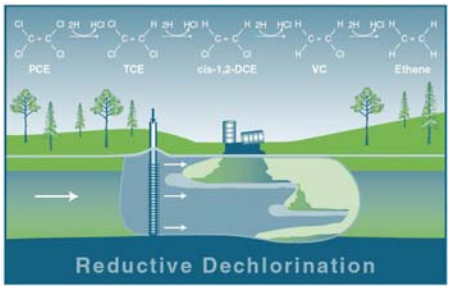
Why a Tech-Reg Guidance?



- ITRC Technical & Regulatory Guidance for *In Situ* Bioremediation of Chlorinated Ethene: DNAPL Source Zones (BioDNAPL-3, 2008)
  - Technology evaluation guide
  - Systematic understanding
    - Technical
    - Related regulatory consideration

So why a Tech-Reg Guidance?

It was the team's objective to provide the regulatory community, stakeholders, and consultants with a useful evaluation guide for ISB.

The document also provides a systematic understanding from both a technical and regulatory perspective.

Technical – The document describes technology specific considerations for source zone characterization, treatment application, and things to look for when designing the system. This allows ISB to be another remediation technology in your tool box.

The document also addresses **regulatory** concerns. It is imperative, however, that the user contact the regulators before applying this technology because regulations vary from state to state.

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You will learn…

- When and where to consider ISB of DNAPL source zones (the technology)
- Site's conditions affecting ISB performance
- How to monitor and evaluate ISB for source zones treatment performance
- The advantages and challenges

Not a detailed design manual!

Course only addresses the saturated zone!

Here are the key points you will learn from this course.

•You will gain insight as to when and where to consider this remedy for DNAPL source zones.

•Site conditions, both favorable and less favorable, that affect the performance of the technology.

•There will be a discussion on how to monitor and evaluate the performance of ISB.

•The course will discuss the advantages, as well as, the challenges of the technology at a DNAPL source zone.

You should be aware however that this Tech-Reg is not a detailed design manual and it will only address remediation of the saturated zone.

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What to Expect of ISB at DNAPL Source Zones

- Destroys contaminant mass
- Reduction in contaminant mass begins within months of implementation
- Increase the rate of dissolution and desorption
- May treat multiple chlorinated compounds
- Low maintenance

- Start-up costs may be lower than other technologies
- Time-frame is uncertain

This slide outlines what regulators and stakeholders can expect from the technology.

•ISB involves the mass removal of the contaminant.

•It is expected that this reduction in contaminant mass will occur within a few months of implementation. So you will see an immediate result.

•The technology, through microbial activities, increases the rate of dissolution and desorption of the DNAPLs.

•One other reason for the technology's success is that a multiple chlorinated compounds can be degraded at the same time.

•ISB requires low maintenance. Basically, microbes in the subsurface breakdown contaminants to less harmful compounds. However, it may require the introduction of additional microbes to increase the population and thereby enhance the degradation.

•The start-up costs may be considerably lower than other technologies particularly if the appropriate microbes are present in sufficient number and if the geochemical aspects of the site are suitable for biodegradation.

•The time frame is uncertain at this point because it is an emerging technology for DNAPL source zones and may vary from site to site.

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Course Roadmap

- What are DNAPL source zones?
- How ISB works
  - How to apply it
  - Operation and monitoring
  - Data evaluation and optimization of the treatment
  - How it's been used in the field

No associated notes.

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Overview of DNAPL Source Zones and ISB of DNAPL

- Source zone and its architecture
- Mechanisms of *in situ* bioremediation

No associated notes.

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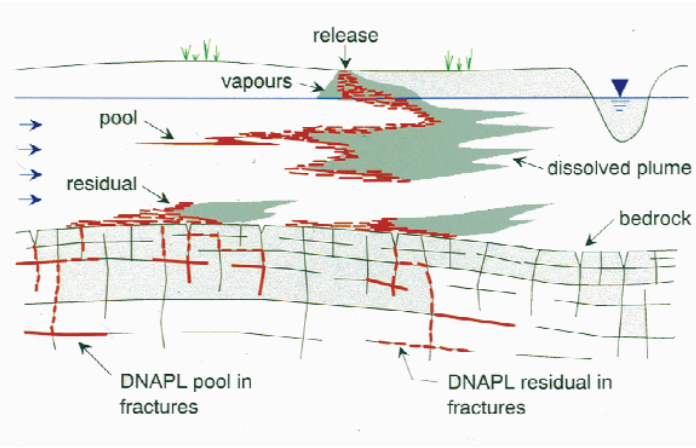
DNAPL Source Zone?

Taken from NRC, 2004



"A source zone is a saturated or unsaturated subsurface zone containing hazardous substances, pollutants or contaminants that acts as a reservoir that sustains a contaminant plume in groundwater, surface water, or air, or acts as a source for direct exposure. This volume is or has been in contact with separate phase contaminant (NAPL or solid). Source zone mass can include sorbed and aqueous-phase contaminants as well as contamination that exists as a solid or NAPL."

This section will provide an overview of how ISB for chlorinated ethene DNAPL works-refer to section 2 of the BioDNAPL guidance document.

DNAPL source zones do not necessarily have readily detectable free product. The NRC recognized that DNAPL would be present in a number of phases and therefore defined a source zone as…

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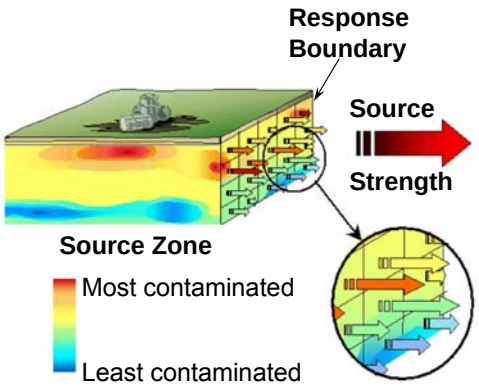
How ISB Works at DNAPL Source Zones

- Enhance the dissolution and desorption of DNAPL at the water/DNAPL Interface
- Stimulate microbial degradation of DNAPL to ethene
- Reduce the mass of DNAPL source



ISB works by enhancing the rate of dissolution of the various phases of DNAPL-degrade the parent compounds PCE or TCE to more soluble daughter products increasing the mass transfer of the DNAPL into solution.

Bacteria cannot directly degrade the free phase DNAPL, but can actively degrade at or close to the aqueous solubility of the chlorinated ethenes.

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Aqueous Solubility of Selected Chlorinated Solvents

Compound	Water Solubility*
Chlorinated Ethenes	(mg/L)
Tetrachloroethene (PCE)	200
Trichloroethene (TCE)	1470
cis-1,2-Dichloroethene (cDCE)	3500
trans-1,2-Dichloroethene (tDCE)	6300
Vinyl Chloride (VC or Chloroethene)	8800
Chlorinated Ethanes	
1,1,1-Trichloroethane (1,1,1-TCA)	1330
1,1,2-Trichloroethane (1,1,2-TCA)	4420
1,2-Dichloroethane (1,2-DCA or EDC)	8520
Chlorothane (Ethyl Chloride)	5680
Chlorinated Methanes	
Carbon Tetrachloride (CT)	793
Chloroform (CF or Trichlormethane)	7920
Dichloromethane (DCM or Methylene Chloride)	13000
Chloromethane (Methyl Chloride)	5330

Microorganisms that dechlorinate can function at or close to the chlorinated solvents' aqueous solubility limits

Lower chlorinated degradation products generally have higher aqueous solubility

Therefore, as dechlorination proceeds, more mass goes into solution

*Johnson and Ettinger (http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm (GW-SCREEN-FEB-04))

Lesser chlorinated compounds have higher water solubility.

Data on water solubility is available at http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm

From the "3-Phase System Models and Soil Gas Models" section, download the "Excel zip file (ZIP 282K)." From the zip file, open the "GW-SCREEN-Feb04.xls" Excel file. Information is listed on the "VLOOKUP" sheet.

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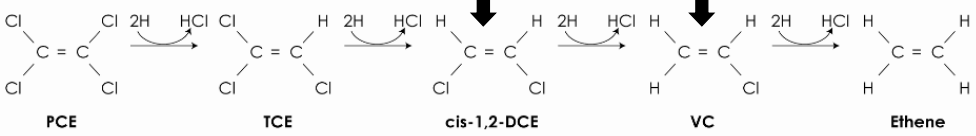
Reductive Dechlorination

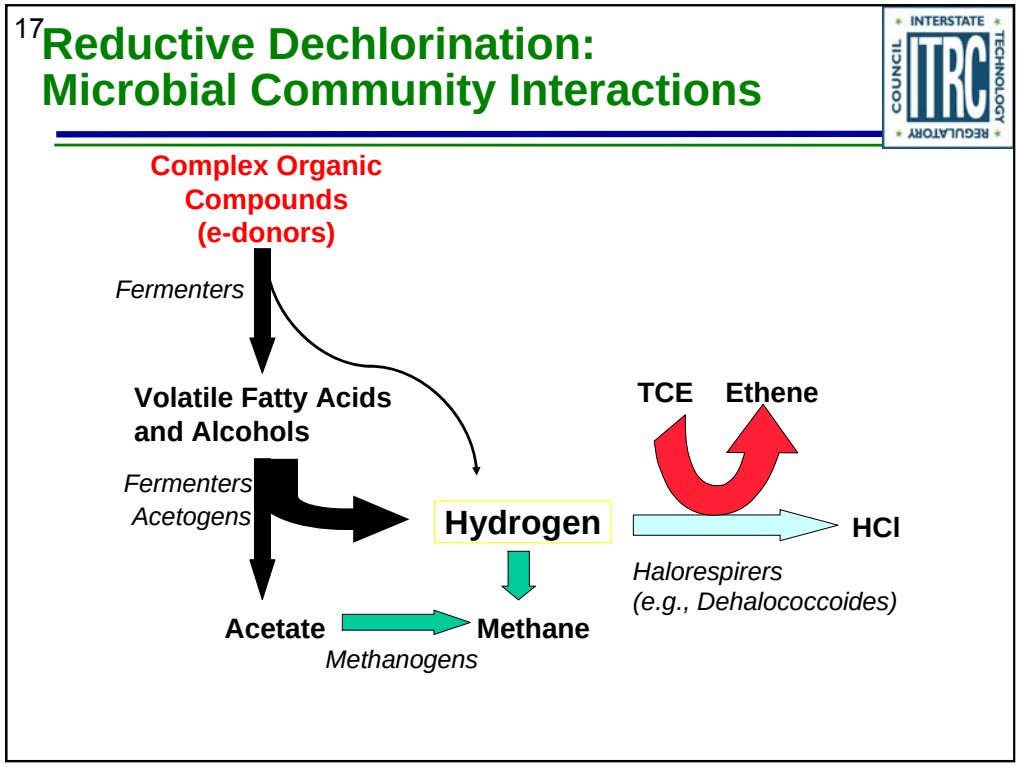
Can accumulate if requisite bacteria are absent



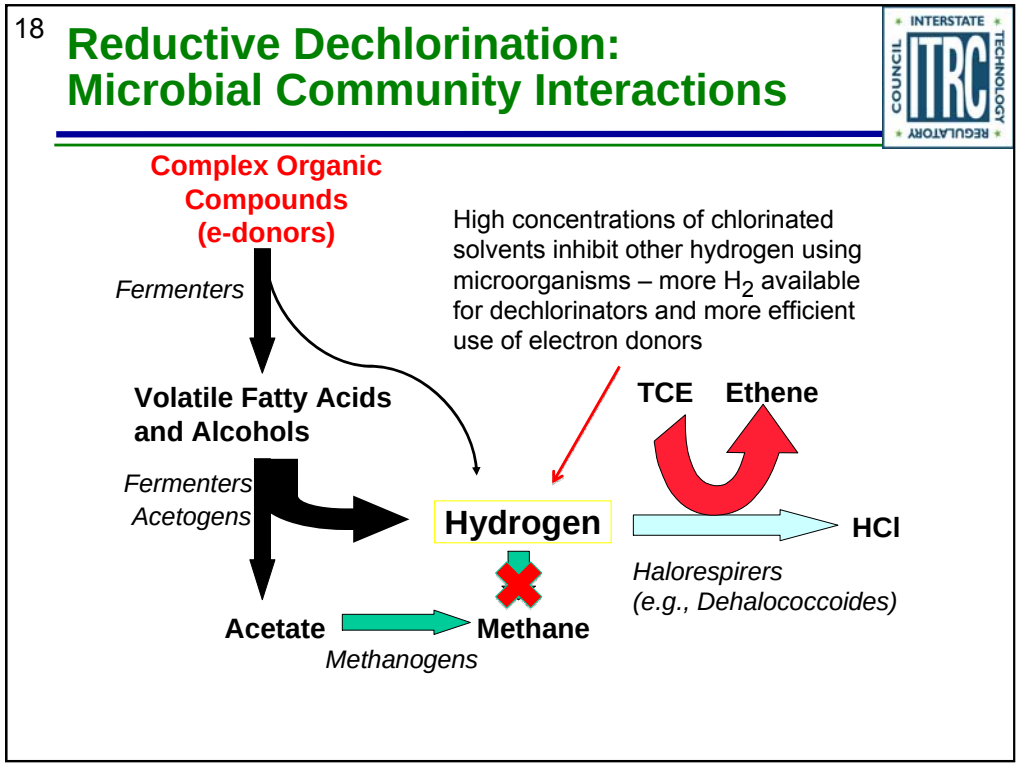
Dehalobacter
Dehalospirillum
Desulfitobacterium
Desulfuromonas
Dehalococcoides

Some strains within a single group *(Dehalococcoides)*

Many different types of bacteria can degrade PCE and TCE to cis-DCE, but only one group of bacteria (Dehalococcoides or DHC) has been identified that can dechlorinate completely to ethene. So if DHC are not present naturally they can be added – a process termed bioaugmentation. All strains of DHC bacteria cannot do the complete dechlorination-only those with the vcrA gene. There are molecular tests for the DHC bacteria and the vcrA gene.



Electron donors are the complex organic compounds that are added to 'feed' the bacteria during the reductive dechlorination process. Examples of electron donors are ethanol, lactate, molasses, emulsified soybean oil etc. – these compounds are broken down to hydrogen by fermentative bacteria. The hydrogen is the electron donor that the DHC bacteria use. DHC bacteria use the chlorinated ethene (TCE, PCE) itself as the electron acceptor-they 'breath' the chlorinated ethenes.



In addition to hydrogen, bacteria can produce acetate and methane from the addition of electron donors. High concentrations of chlorinated solvents in a DNAPL source zone can inhibit methanogens that produce methane and other hydrogen utilizing microorganisms. This has two positive effects-less methane production and more efficient use of the hydrogen produced-more available for the dechlorinating bacteria.

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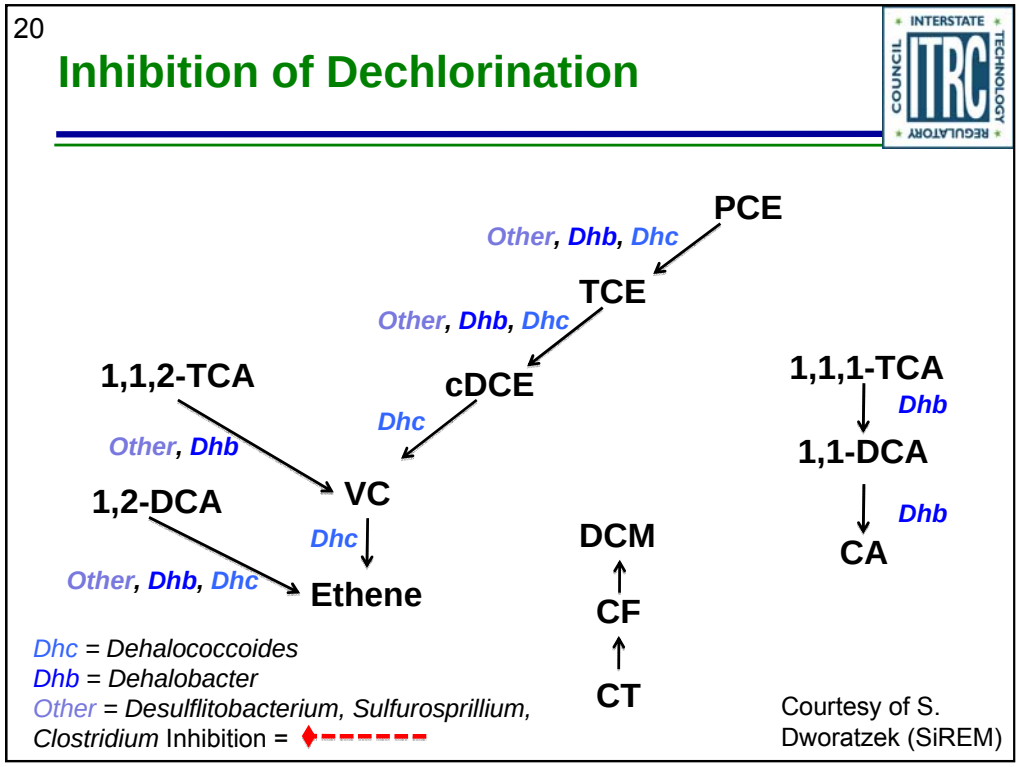
Biodegradation: Relevance to Source Zones

- Microorganisms that mediate reductive dechlorination can degrade chloroethenes at high concentrations
  - More efficient donor utilization because high VOC concentrations inhibit other microbes that use the hydrogen from the donor
- Faster degradation in source area
  - Increases the concentration gradient between free, sorbed or diffused DNAPL phases and groundwater
    - Promotes faster mass removal
- *Dehalococcoides* required to complete dechlorination of cis-DCE and VC to ethene
  - Bioaugment if they are…
    - Absent
    - Poorly distributed
    - Wrong strain
- Conclusion
  - Enhanced biodegradation is applicable to source areas with degradation rates that will enhance DNAPL removal

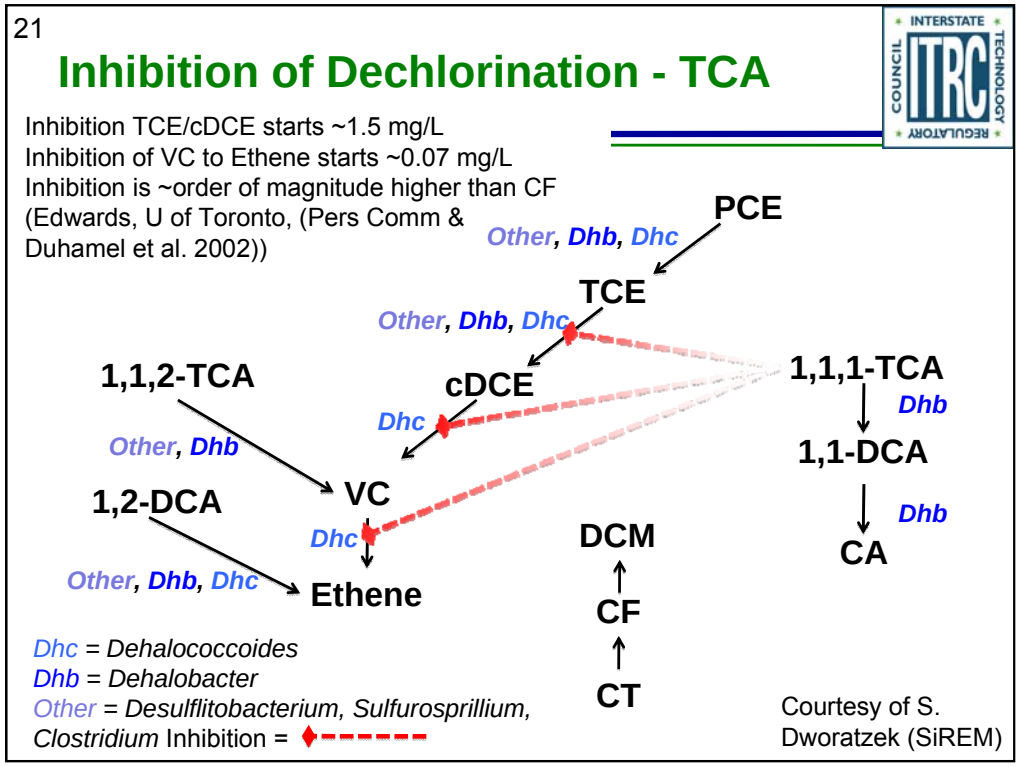
To sum up the last few slides:

Microorganisms can degrade chlorinated solvents at very high concentrations-to the limit of the solvents water solubility.

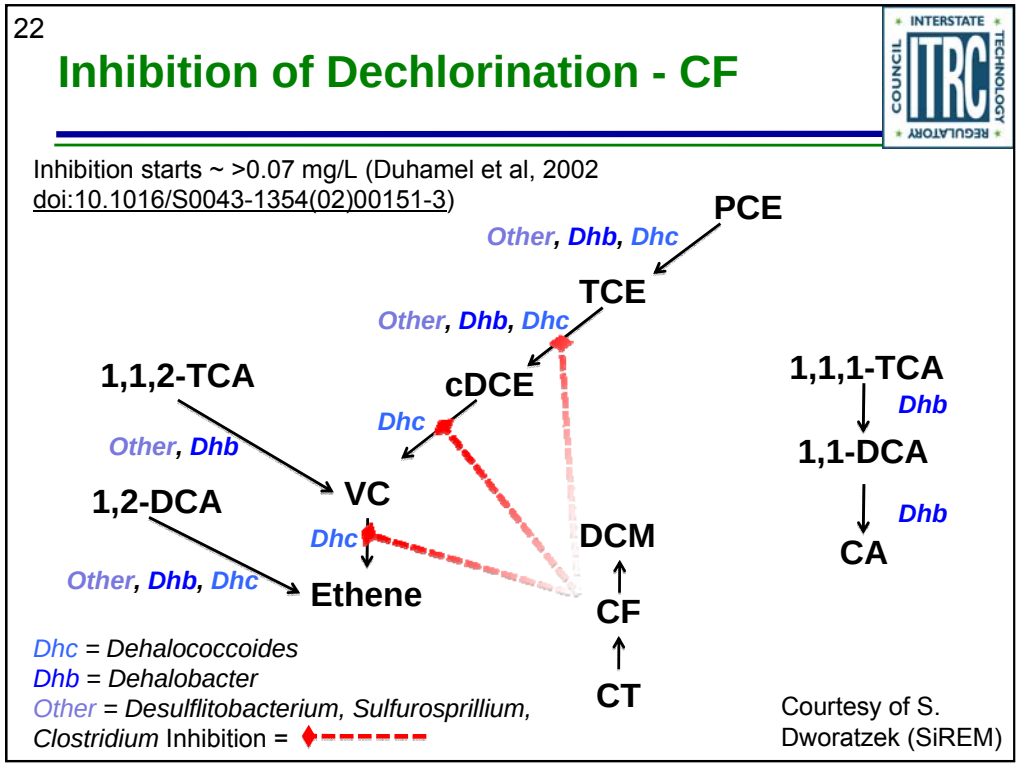
Degradation increases the concentration gradient between DNAPL and groundwater promoting faster mass removal. DHC bacteria are critical to complete dechlorination, but not critical in terms of enhancing dissolution in the source zone where the degradation of the parent compounds has the biggest impact.



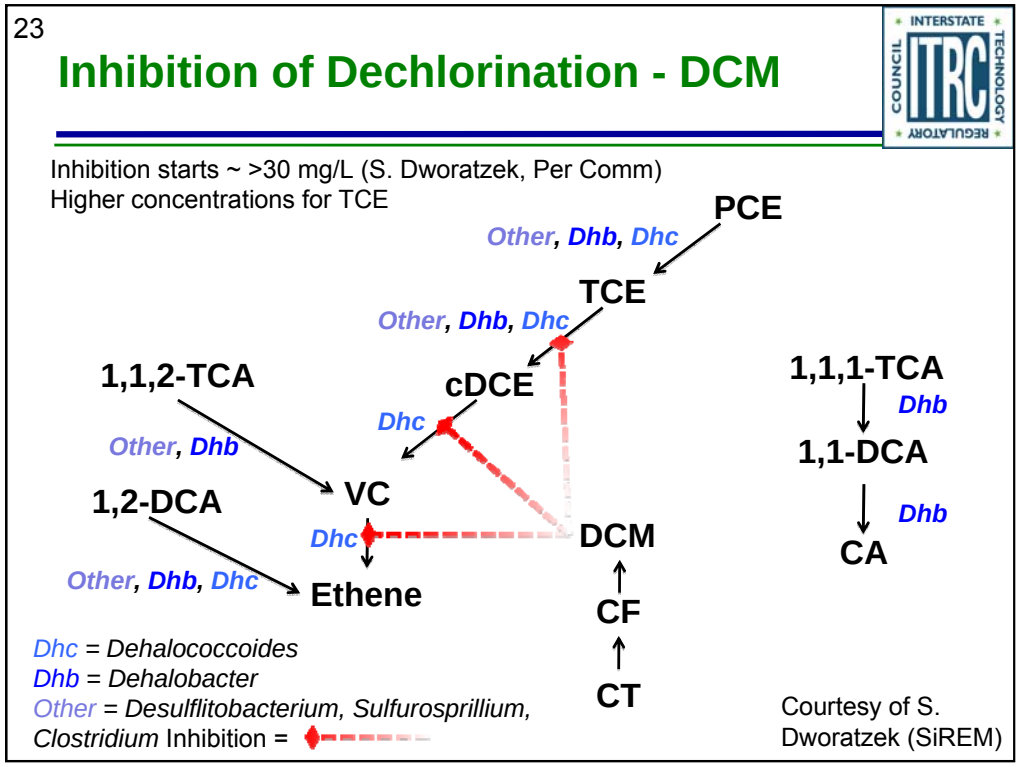
One of the complicating factors is working with mixed chlorinated solvents and the inhibition effects encountered. Inhibition is not the same as toxicity-it does not kill the organisms, just inhibits the degradative activity until the concentration is reduced or the compound removed. One thing to note here is the different groups of microorganisms associated with the different dechlorination steps.



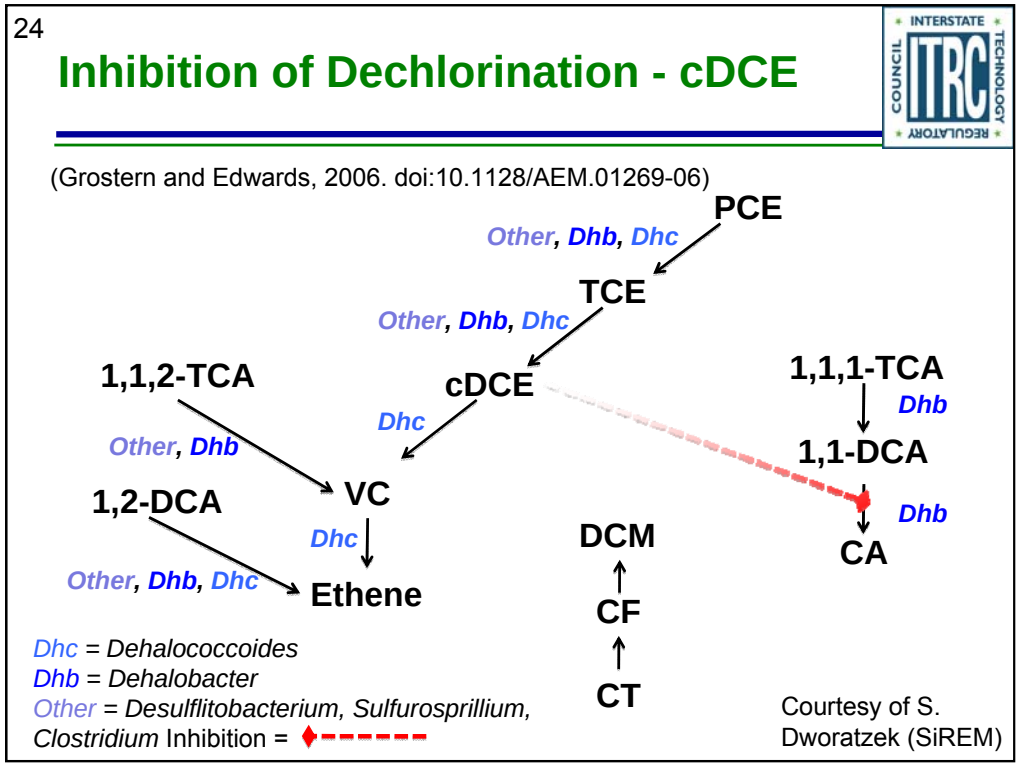
111 TCA can inhibit DHC and certain Dehalobacter bacteria that degrade TCE to cis DCE to VC to ethene.



Similarly chloroform at a relatively low concentration (70 ppb) can inhibit these dechlorination steps. In general with these compounds present above their inhibitory concentration we will see an accumulation of cis-DCE and or Vinyl chloride.



Much higher concentration of dichloromethane (aka methylene chloride) will also inhibit these dechlorination steps.



Cis-DCE can also inhibit further dechlorination of the chlorinated ethanes. In field studies inhibition has at some sites to occur at much higher concentrations. Bioaugmentation with mixed cultures that degrade different chlorinated VOCs can be used to overcome this inhibition.

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In Situ Bioremediation of DNAPL: Enhanced Reductive Dechlorination

- Creating conditions conducive to the anaerobic biodegradation of chlorinated solvents
- Hydrogen is the ultimate electron donor and used to sequentially replace chlorines atoms, eventually producing non-chlorinated end products (e.g., ethene)
- Dechlorinating organisms can withstand high concentrations of solvents and function at or near the water-DNAPL interface
- Mixed cVOC can inhibit different steps of dechlorination, but can be addressed through design

No associated notes.

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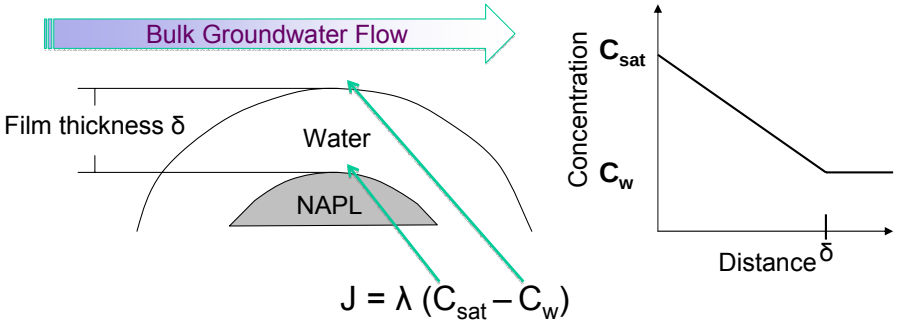
DNAPL Dissolution & Mass Removal



$$J = \lambda (C_{sat} - C_w)$$

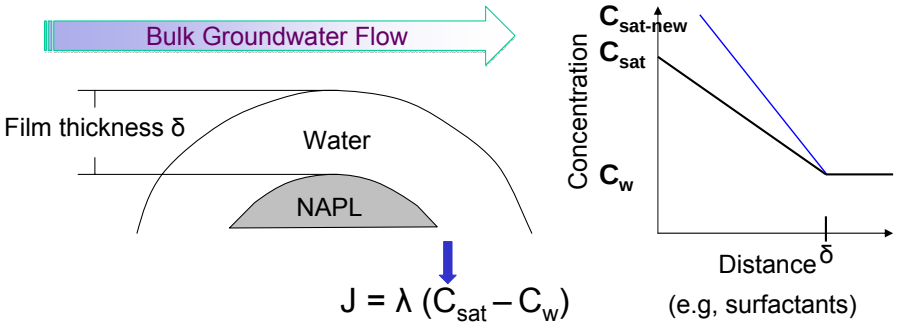
$$\lambda = f(\text{surface area, velocity})$$

- J = flux
- λ = mass transfer rate coefficient
- C_{sat} = saturated concentration at the DNAPL/water Interface
- C_w = bulk water concentration

The next set of slides shows the effect of biological degradation on DNAPL. This slide shows the DNAPL as a drop sitting on a surface surrounded by groundwater and the concentration with distance from that drop. The DNAPL exposed to flowing groundwater will dissolve into the groundwater right at the surface at its maximum water solubility called C sub sat and that concentration will decrease as a function of distance from the NAPL surface (C sub w) - the difference between C sat and Cw is the concentration gradient that drives the flux (J) or the mass transfer rate from the NAPL surface to the bulk groundwater. The gradient is show as the slope of the line on the graph to the right.

27

DNAPL Dissolution & Mass Removal



$J = \lambda (C_{sat} - C_w)$

(e.g, surfactants)

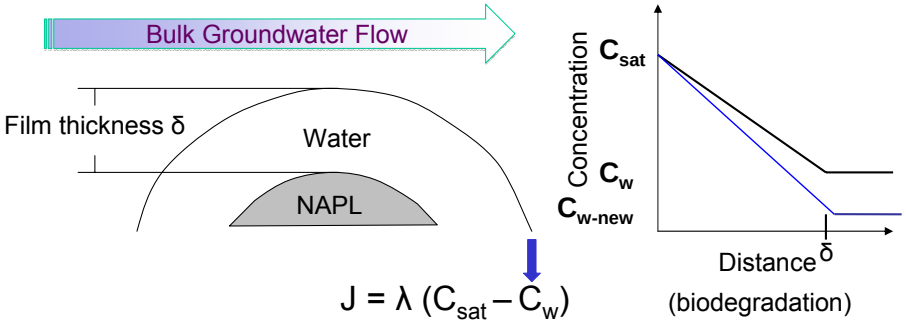
$\lambda = f$ (surface area, velocity)

- J = flux
- λ = mass transfer rate coefficient
- C_{sat} = saturated concentration at the DNAPL/water Interface
- C_w = bulk water concentration

Increases in the concentration gradient can be caused by the use of surfactant, co-solvents and heat.

28

DNAPL Dissolution & Mass Removal

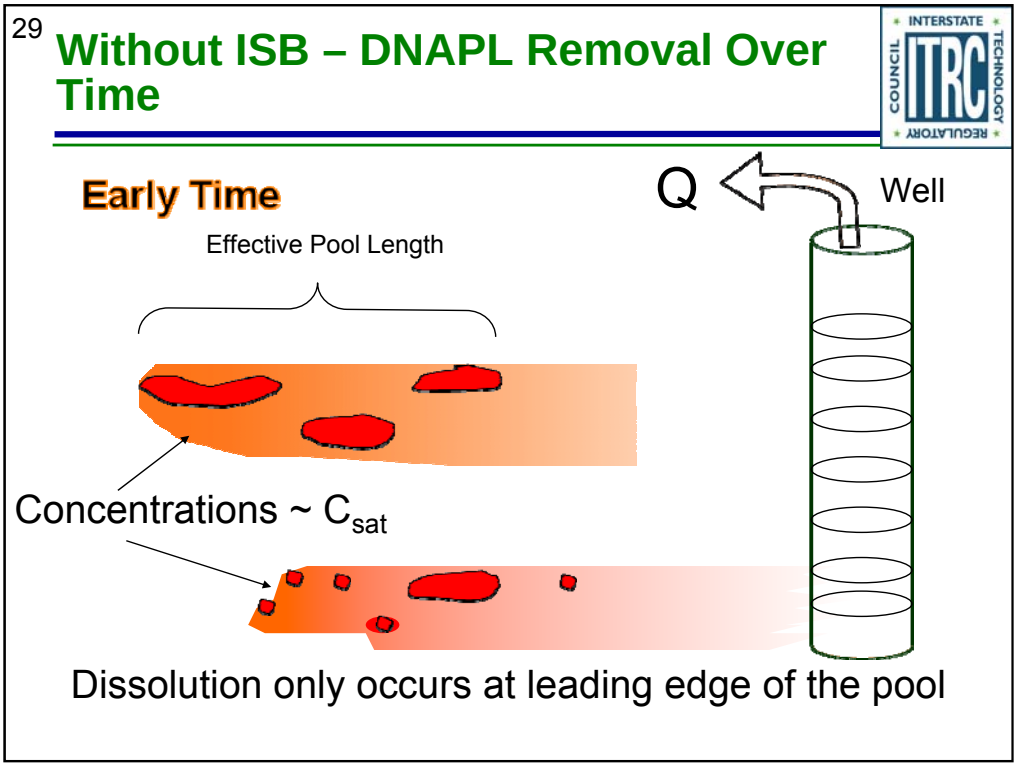


$$J = \lambda (C_{sat} - C_w)$$

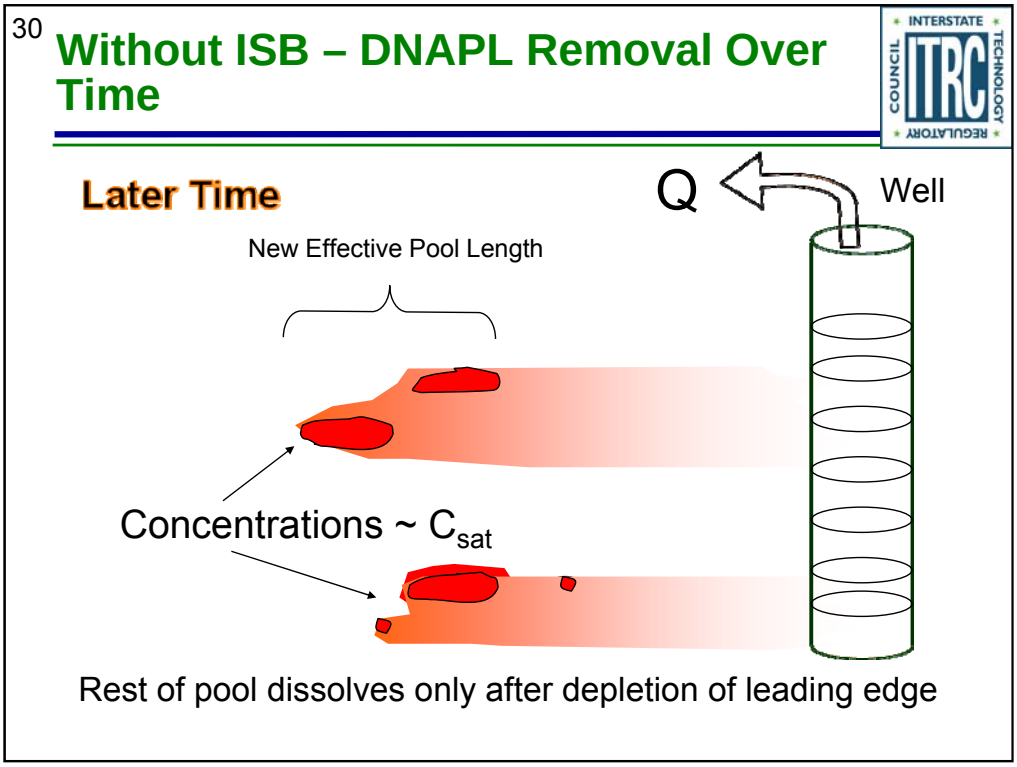
$$\lambda = f(\text{surface area, velocity})$$

- J = flux
- λ = mass transfer rate coefficient
- C_{sat} = saturated concentration at the DNAPL/water Interface
- C_w = bulk water concentration

Biodegradation lowers the concentration of the chlorinated compounds in the groundwater (C sub w) increasing the concentration gradient.



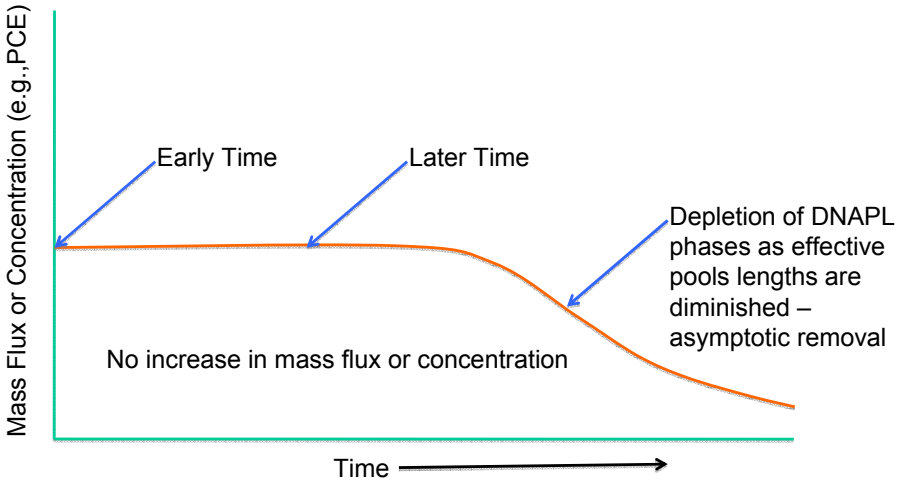
The DNAPL 'pool length' is typically made up of small residuals, droplets, and ganglia of DNAPL. The length of the pool has a direct effect on the remediation timeframe because the pool dissolves from the upgradient edge.



When only the leading or upgradient end dissolving there is little change in the concentration over time in the well.

31

Without ISB – Mass Removal Over Time

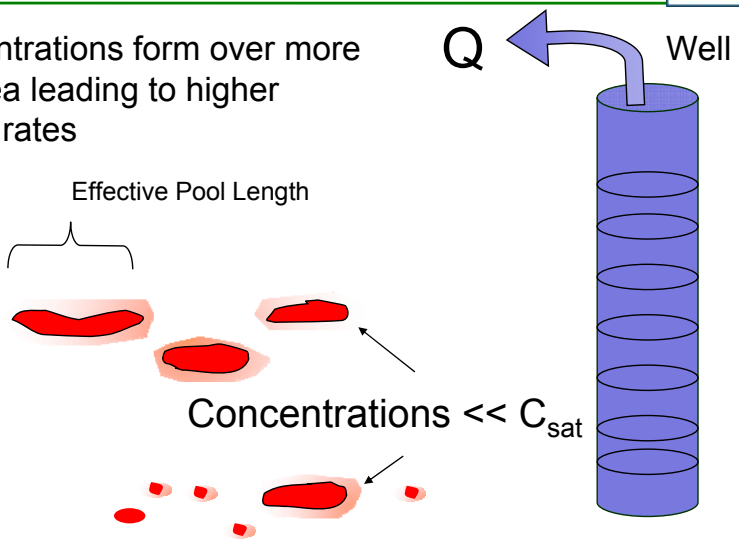


This shows the concentration of the chlorinated solvents with time without degradation

32

Impact of Biodegradation on Dissolution

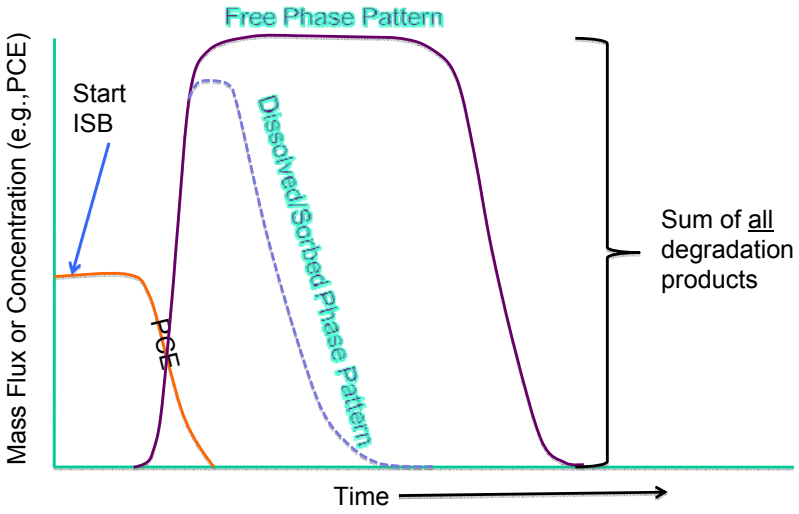
Low concentrations form over more surface area leading to higher dissolution rates



ISB overcomes this problem in two ways: Increasing the concentration gradient and therefore the dissolution rate and also by 'cleaning' water between the droplets allowing more mass to be impacted, not just the leading edge.

33

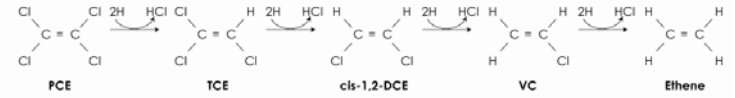
With ISB – Mass Removal Over Time



This slide shows the pattern of concentrations that you would observe if DNAPL ethenes were being treated by ISB. When ISB is working the concentration can increase due to enhanced dissolution and stay high for a long period of time until all of the mass is depleted.

34

Summing the Degradation Products



1 M of PCE to ethene yields 1 M of Ethene and 4 M of Chloride ion

If **NO** enhancement of PCE
(at max solubility of 200 mg/L=
1.2 M/L of PCE at steady state)

Complete dechlorination yields
1.2 moles of ethene = 34 mg/L
4.8 moles of chloride =171 mg/L
} **= 1.2 M/L PCE**

Partial dechlorination (e.g. to equal amounts of TCE and cDCE at steady state)
0.6 moles of TCE = 79 mg/L
0.6 moles of cDCE = 59 mg/L
1.8 moles of chloride = 64 mg/L
} **= 1.2 M/L PCE**

If PCE dissolution enhanced by **4 fold**
(800 mg/L= 4.8 M/L of PCE)

Complete dechlorination yields
4.8 moles of ethene = 135 mg/L
19 moles of chloride = 684 mg/L
} **= 4.8 M/L PCE**

Partial dechlorination (e.g. to 10% TCE and 90% to cDCE at steady state)
0.48 moles of TCE = 63 mg/L
4.3 mole of cDCE = 421 mg/L
9.1 moles of chloride = 325 mg/L
} **= 4.8 M/L PCE**

No associated notes.

35

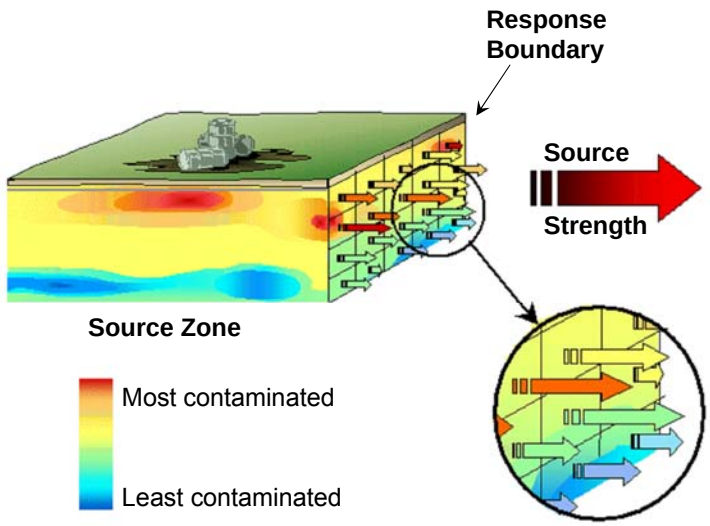
Challenges

- Low aquifer permeability or heterogeneity and preferential pathways
- Geochemical conditions outside optimal (e.g. low or high pH)
- Biofouling
- May take several months to years
- Monitoring and system maintenance
- Adequate microbial populations
- Decreases in pH and redox conditions during bioremediation may solubilize metals
- Very large source zones require a combination of methods/technologies
- Inhibition/toxicity of contaminants & of co-contaminants to dechlorinating microbes.

As with any technology there are challenges and limitations to its application….

36

Question and Answer



No associated notes.

37

Course Roadmap

- What are DNAPL source zones?
- How BioDNAPL works
- **How to apply it**
- Operation and monitoring
- Data evaluation and optimization of the treatment, and
- How it's been used in the field

No associated notes.

38

Fundamental Design Goals for ISB of DNAPL Source Zones

- Inject and distribute carbon donor into the target treatment area in order to
  - Control the aquifer's redox status
  - Expand populations of fermenting bacteria
  - Enhance early-stage dechlorination metabolism
  - Initiate (if necessary) and expand late-stage dechlorination
  - Dissolve and desorb DNAPL mass

Determine and control the aquifer's redox status – Oxidative bacteria dominate aquifers in which energetic electron acceptors (O2, NO3, Fe3+, Mn5+, for example) are abundant. Often these electron acceptors are available in the groundwater flowing into the DNAPL source zone and, in the case of iron and manganese, from the aquifer matrix, itself. The first task for enhanced reductive dechlorination treatment is to determine aquifer oxidation/reduction status.

Expand populations of fermenting bacteria – Late-stage dechlorinating bacteria (those that dechlorinate cis-DCE and vinyl chloride) depend on molecular hydrogen (H2) for reducing equivalents. As noted earlier, hydrogen is generated along with mixed organic acids during fermentation reactions. When the aquifer microbial community enters fermentative metabolism, many partial decomposition products can be observed, including alcohols, ketones, and volatile fatty acids (VFAs). These compounds are then metabolized during consumption of electron acceptors including chlorinated solvents.

Enhance early-stage dechlorination metabolism – Several bacterial genera are known to dechlorinate perchloroethene and trichloroethene to the cis-dichloroethene stage. This is referred to as the early-stage dechlorination. It is possible to dechlorinate the perchloro- and trichloroethene at a solvent contaminated site, without achieving significant reductions of the cis-dichloroethene that is produced.

Initiate (if necessary) and expand late-stage dechlorination – To date, one bacteria species has been identified that performs late-stage dechlorination reactions – the dechlorination of cis-dichloroethene and vinyl chloride. That species is *Dehalococcoides ethenogenes* and only some strains of that species produce vinyl chloride reductase, and the enzyme that completes the last step in dechlorination, reducing vinyl chloride to ethene.

Dissolve and desorb non-aqueous solvent mass – Only a small fraction of the solvent mass in DNAPL source zones resides in the aqueous phase. To achieve measurable reductions of DNAPL source mass, it is necessary to dissolve and desorb solvents that are stored in non-aqueous phase.

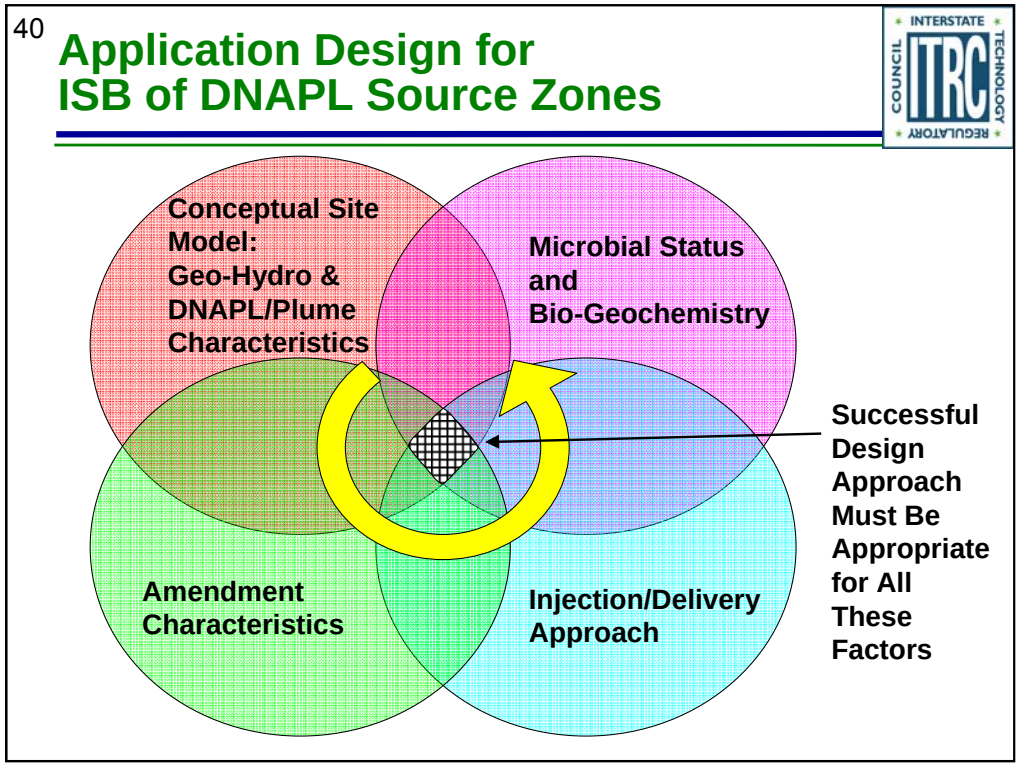
39

Baseline Design and Operational Optimization

- ISB is a dynamic process
  - Geochemical and microbial responses dictate process optimization
- Baseline design should incorporate flexibility
  - Frequency of carbon donor addition
  - Concentration/dose of carbon donor
  - Injection process and target areas
- Ongoing operational optimization is critical for success with ISB
  - Closely aligned with monitoring and evaluation

Refer to document

Ongoing optimization –later presenters discuss monitoring and evaluation



ISB design should be optimized to the site conditions.

As discussed in the first portion of the presentation, need to have a good Conceptual Site Model (CSM).

From the CSM, the amendment and delivery approach need to be appropriate to the site conditions (physical and chemical/biological).

For some sites, conditions may dictate that only a narrow range of the available approaches will be optimal.

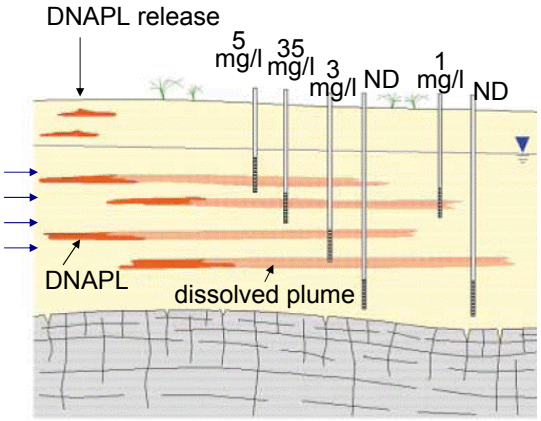
Transition to discussion of DNAPL source area CSM.

41

Effect of DNAPL Distribution / Architecture on Pre-Design Data

Design of ISB for source zones must account for:

- The delineation of the source mass
- The source area hydrogeology
- Context of monitoring data



Kueper, BH et al., 2003 – An illustrated handbook of DNAPL transport and fate in the subsurface

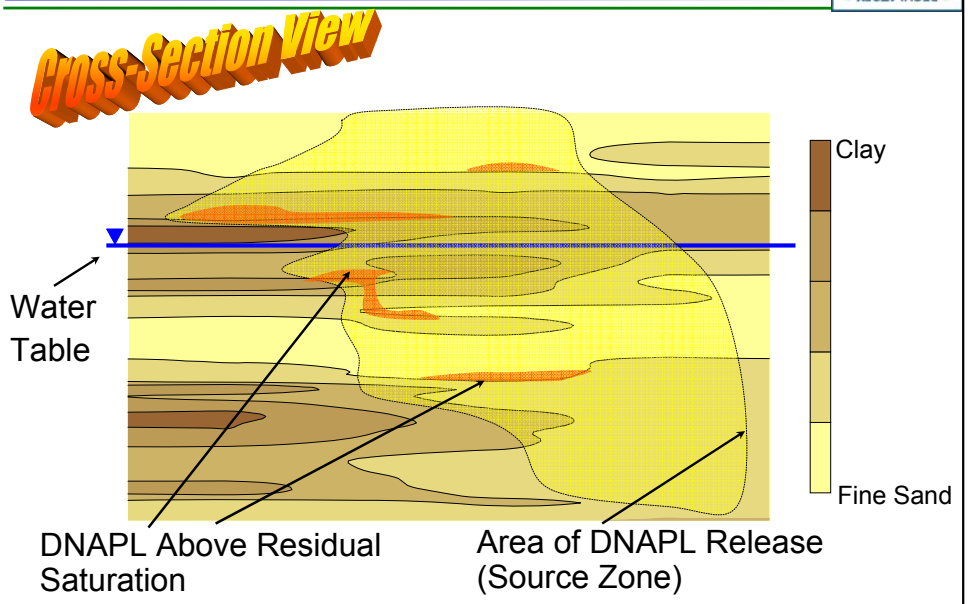
DNAPL source mass delineation – One of the very difficult problems for DNAPL treatment is the mapping of contaminant mass in the aquifer. There are no proven methods to remotely sense DNAPL source mass, so the only viable survey methods depend on direct contact with the contaminant – significant sampling is intensive in three dimensions.

DNAPL source area hydrogeology – The injection of electron donor solutions into an aquifer, to achieve placement in intended locations, is as challenging as any other element of the technology.

Transition to discussion of heterogeneity.

42

Effect of Source Zone Geologic Heterogeneity



Geologic Heterogeneity Effects Both DNAPL Distribution and Amendment Delivery.

Areas of DNAPL above residual saturation are notoriously hard to identify, and likely their presence/absence is unknown.

Think about how the depicted heterogeneity would effect the design approach.

Think about how it might vary as a function of scale. What if this cross-section were 3m. high and 5m. wide? What if it were 30m x 50 m?

At what point might you need multi-level injection wells to target specific injection intervals? Will all the injected fluid flow into the sand interval in the middle?

How will the treatment strategy deal with the source zone above the water table? Reductive dechlorination ISB will not work there, so probably a combined remedy is needed.

How might the scale effect the delivery strategy? As the scale becomes larger, the options narrow and developing a well integrated design becomes more critical. In general, the delivery strategy and the amendment selection have to go hand-in-hand.

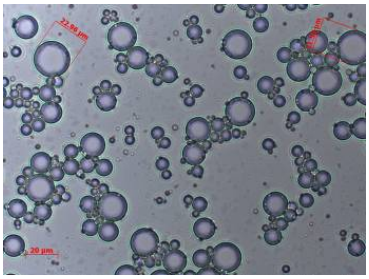
Transition to discussion of amendment alternatives and say we will talk about delivery strategy after amendment selection.

43

Carbon-Donor Amendment Characteristics

- Carbon donors provide a source of hydrogen
- Carbon donors vary in several properties
  - Manner of hydrogen production
  - Chemical composition
  - Electron equivalents released per unit mass of amendment
  - Microbiological responses
  - Geochemical impact
  - Chemical / physical properties
  - Transport characteristics
  - Longevity

Edible Oil Emulsions



The carbon donors are consumed by fermenting bacteria, and the fermentation process ultimately releases hydrogen that is used for electron transfer

Differences are primarily in chemical and physical properties and behavior in the subsurface.

The practical differences relate to injectability, persistence, and the specific fermentation process that is promoted.

For example, edible oils like soybean oil can be used, but they have to be made into an emulsion to be able to be transported in the subsurface, as shown in the lower corner.

Transition by looking at the fermentation process for edible oil emulsions.

44

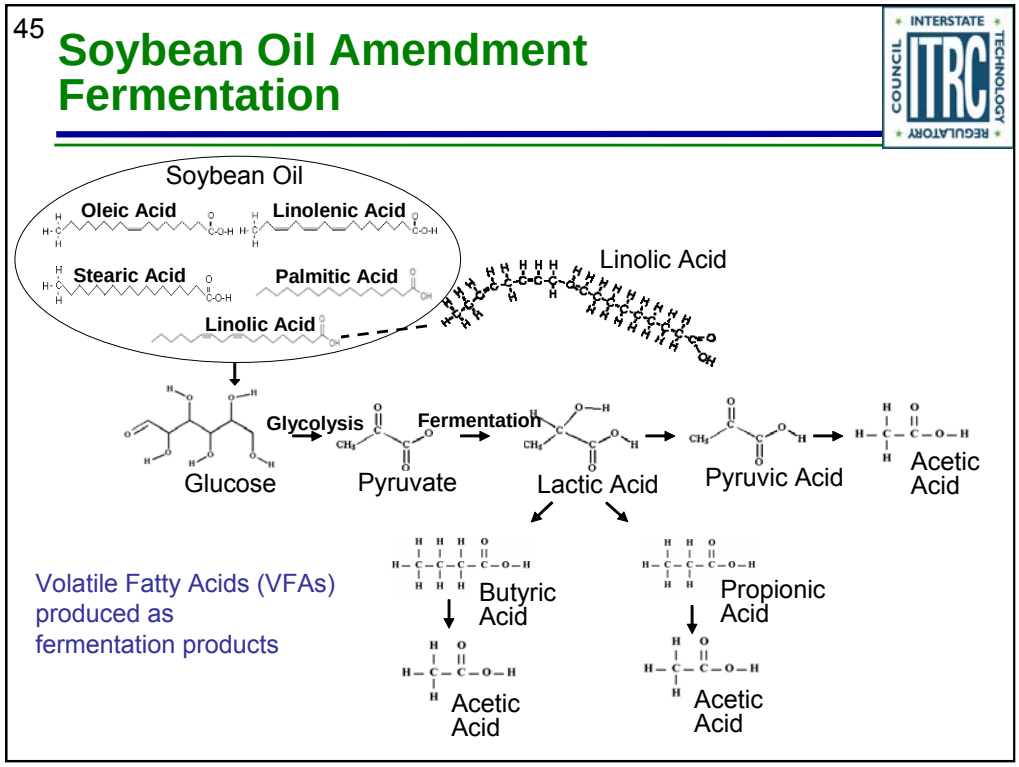
Electron Donor Amendments

- Soluble
  - Lactate / other organic acids
  - Methanol / ethanol
  - Molasses / other carbohydrates
  - Dairy whey
- Slow-release
  - Edible oils and oil mixtures
  - Chitin (glucosamine polymer)
  - Lactate polymers
  - Mixtures of lactate and fatty acids
  - Solids (mulch)
- **Key point: amendment choice and injection design are closely linked**

Increasing Product Development Creating a Continuum

Electron donors fall into two general classes, although in reality a continuum of behavior exists.

Transition by going back to the classes as useful distinctions, albeit not absolute characterization.



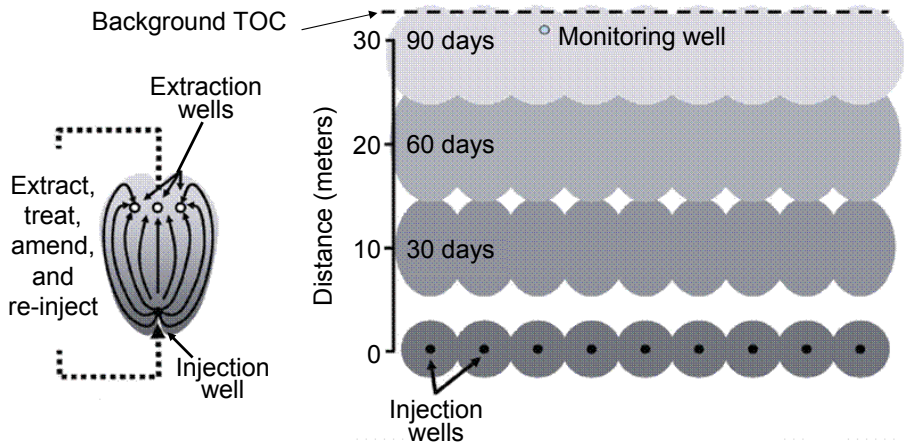
This slide shows the fermentation of soybean oil to volatile fatty acids (term – VFA).

Each step in the fermentation process releases hydrogen. Some VFAs are not very productive toward the desired microbial process, for example acetic acid.

Note that lactic acid VFA is a fermentation product of soybean oil. It is also used by itself as a highly soluble amendment, as shown in the next slide.

46

Transport Considerations for Highly Soluble Amendments



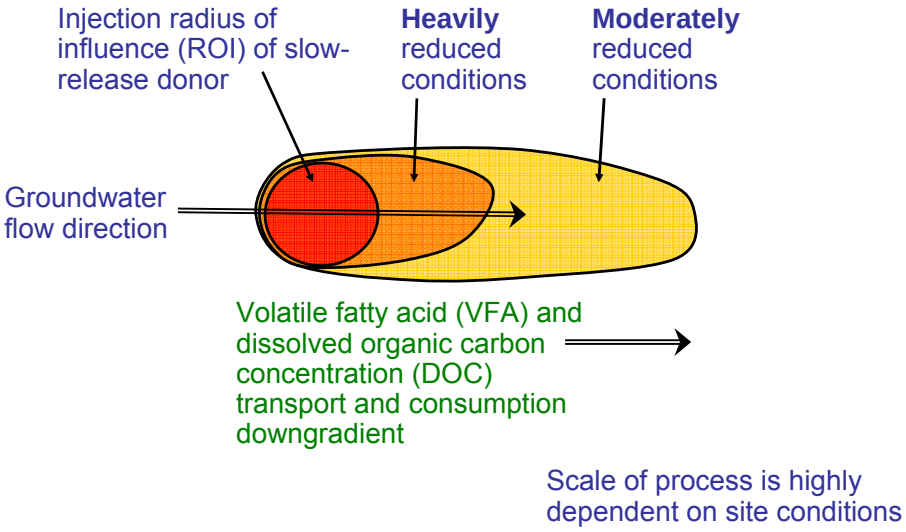
ITRC Technology Overview: In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones (BIODNAPL-1, 2005)

"Soluble amendments" are generally referring to a product that is highly mobile in the subsurface – fully miscible in water.

The slide shows two approaches to injection. The recirculation scenario on the left provides greater control and flexibility (e.g., allows changing the donor concentrations in real time), but will generally cost more than direct injection, which may be designed similar to the depiction on the right.

47

Transport Considerations for Slow Release Amendments

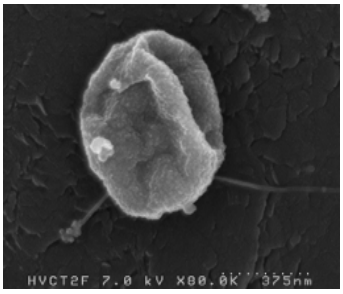


Slow release amendments are generally referring to a product that has some limitations on mobility in the subsurface, and that results in a residual capacity to release Volatile Fatty Acids (VFA) over time. With slow release donors, the area of influence may expand over time and then later contract as the donor is depleted.

48

Secondary Amendments

- pH buffers
  - Carbonate/bicarbonate
  - Offset the production of hydrogen ion (H+) and volatile fatty acids (VFAs)
- Nutrients
  - Nitrogen (N), phosphorus (P) and potassium (K)
  - Generally not needed for anaerobic bioremediation
  - Can compete as electron donors
- Bioaugmentation
  - May be needed if process is stalled at cis-DCE or VC
  - Not needed if appropriate microbial consortium is present
  - May accelerate process at some sites
- Chemical reagents
  - e.g., zero valent iron (ZVI), other reductants



Dehalococcoides

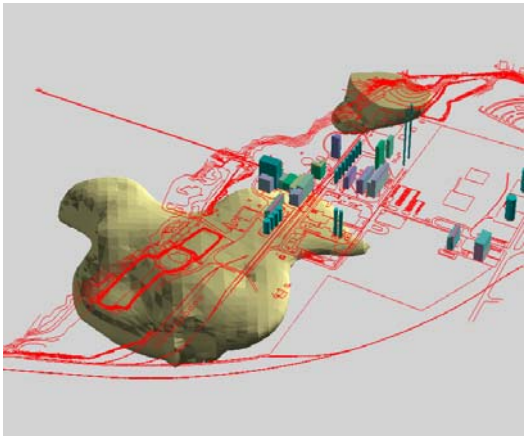
Secondary amendments can be used to help control geochemical or microbial conditions, if needed.

49

Treatment Zone Configurations

ISB is highly flexible. Selection of the treatment zone configuration deals with inter-related decisions

- Target area for treatment
- Amendment selection
- Delivery requirements and methods



After you understand the conceptual site model and choices of amendments, it is time to select an overall treatment configuration.

Treatment zone configuration, and differences in Injection Volume Dose delivery mode

Elements include:

The treatment zone configuration (i.e. barrier vs. areal treatment)

The hydrogeologic constraints and conceptual plan for amendment injection and subsurface distribution

A plan for monitoring, evaluating, and possibly modifying the treatment process over time

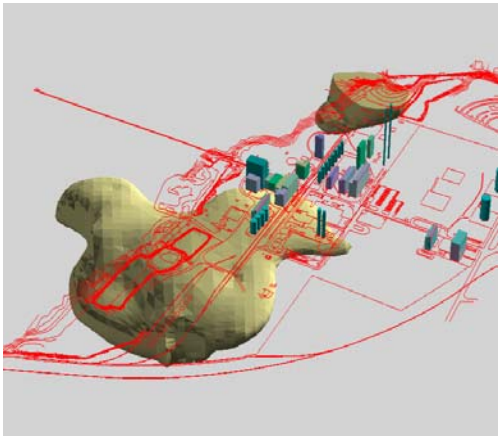
There is always more than one way to approach the design. The “art of practice” comes into play in choosing an optimal design.

Transition with site specific considerations.

50

Site Factors Affect the Treatment Zone Configuration

- Need for extraction
  - Attenuation rates
  - Distance to receptors
- Accessibility of target treatment zone
- Source zone size
- Surface or subsurface obstructions
- Groundwater flow rates
- Available time



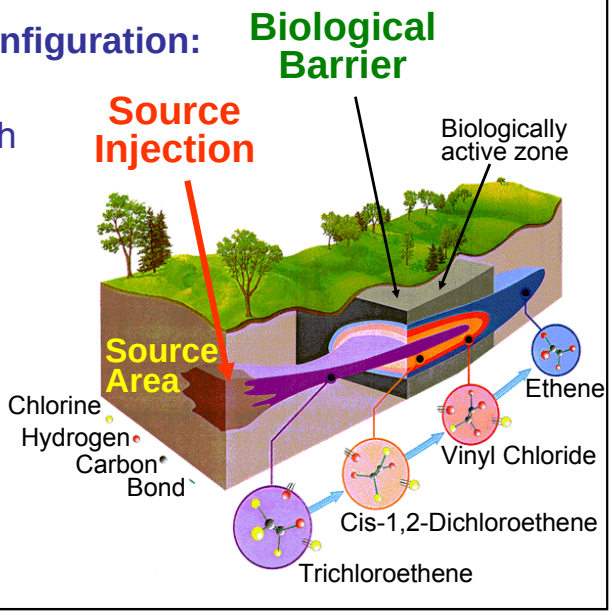
No associated notes.

51

Treatment Zone Configurations

Objectives impact configuration:

- Reduce plume length
  - Biological barrier
- Reduce longevity
  - Enhanced flushing
- Reduce mass flux
  - Sequestration

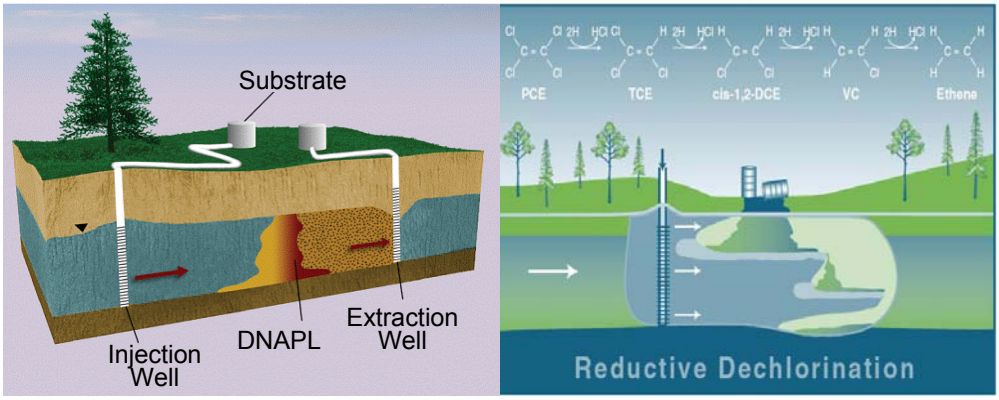


Example of source zone barrier configuration

52

Treatment Zone Configurations (continued)

Upgradient Injection
Downgradient extraction / Downgradient attenuation



Examples of source zone injection/extraction and “inject and drift”

53

Amendment Injection Design

Three fundamental questions:

1. How much amendment do we need?
2. How will we get it in the ground?
3. How often do we expect will we have to re-inject?

After you have selected an amendment and an overall treatment configuration, it is time to get the amendment into the ground.

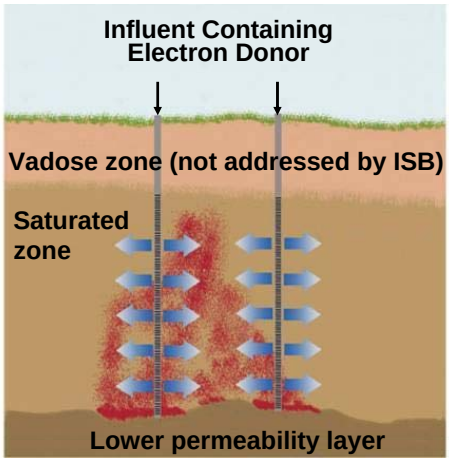
The tech-reg guidance document, and this presentation are not focused on providing a design cook book, but rather focused on educating folks on the technical issues and decisions that are faced.

We will only be able to address the injection design in an overview fashion.

54

Injection Design Goals

- **Achieve relatively uniform amendment distribution** throughout the target treatment zone
- **Deliver sufficient mass of amendment(s)** to ensure treatment goals are achieved
- **Ensure amendments remain present** long enough to attain treatment goals (by persistence or reinjections)



No associated notes.

55

Subsurface Conditions Affecting Injection Designs

- Heterogeneity and/or low permeability strata
- DNAPL distribution
  - Area
  - Volume
  - Depths below grade
  - Depths below water table
- Target treatment zone
  - Location
  - Extent
- Depth to groundwater
  - And other factors influencing injection well costs
- Groundwater flow rates
- Geochemical conditions affecting
  - Bioremediation
  - Groundwater quality

Site-specific factors strongly affect our ability to deliver amendments uniformly throughout the target treatment zone

56

Calculating the Dosage

- The goal is to account for the demand imposed by all of the electron acceptors in the system
  - There is uncertainty in accurately determining or estimating the native electron donor demand
  - Typical safety factors of 2-10 are commonly applied to the calculated dose to reflect the uncertainty
- Reasons for safety factors include
  - Unknown mass of electron acceptors (e.g., Fe3+) present within the treatment zone
  - Difficulty accurately predicting electron acceptor influx over time
  - “Wasteful” microbial activity (not linked to dechlorination)

The amount of the donor needed is determined by all of the electron acceptors in the system.

There are spreadsheets available that calculate donor demand based on electron acceptor concentrations and influx, but these still include safety factors.

57

Field Testing

- Field tests are often required to collect data necessary to finalize the full-scale design
- Key objectives
  - Determine the ability to deliver fluid to the subsurface
  - Determine the volume-radius relationships, to finalize injection well spacing
  - Confirm groundwater flow rates, to determine the necessary injection frequency

No associated notes.

58

Summary of Application

- ISB is highly flexible and adaptable
- Several alternatives
  - Remedial objectives
  - Electron donor formulations
  - Injection methods
  - Delivery strategies
  - Secondary amendments
- Design needs to fit goals and site constraints
- **Need to know goals and site conditions**
- **Need ongoing monitoring and optimizing**

No associated notes.

59

Course Roadmap

- What are DNAPL source zones?
- How ISB works
- How to apply it
- Operation and monitoring
- Data evaluation and optimization of the treatment
- How it's been used in the field

No associated notes.

60

Operation and Monitoring

- Process controls
  - Adjust
    - Carbon solution composition
    - Volume
    - Concentration and injection frequency
    - Aquifer pH
  - Inject bacterial cultures
- Monitor the treatment zone to determine
  - Is the organic carbon distribution is meeting design objectives?
  - Have the microbial populations developed as expected?
  - Have the expected contaminant reductions been achieved?

The process controls on this technology are simple:

Carbon solution composition, volume, concentration and injection frequency can all be adjusted

Aquifer pH may be adjusted through base or buffer addition

Bacterial cultures can be injected to augment natural aquifer populations

The process requires monitoring of the treatment zone to determine:

1) Is the organic carbon distribution is meeting design objectives?

2) Have the microbial populations developed as expected?

3) Have the expected contaminant reductions been achieved?

61

Operational Decision Making – Key Points from Figure 5-1

- Benchmark analyses
  - During remedy selection and pre-design studies, an extensive list of parameters is typically analyzed
- During pre-design and pilot testing
  - Are the critical design assumptions validated (e.g., fluid injectability, groundwater velocity, aquifer alkalinity)? If not, design modifications are needed.
- During operation
  - Operational decision-making is typically based on a short list of critical operating parameters
  - Are the key system operating parameters within accepted ranges? If not, operational adjustments are required.
  - It may be necessary to expand the system parameters that are sampled, to support troubleshooting

No associated notes.

62

Fluid Injection Consideration

- Injection pressure limits
- DNAPL mobilization
- Confined and semi-confined aquifers
- Groundwater displacement

No associated notes.

63

Performance Monitoring

- Parent chlorinated aliphatic hydrocarbons (CAH) compounds and their dechlorination products
  - e.g., cis-DCE, VC, and ethane
- Total organic carbon (TOC) or dissolved organic carbon concentration (DOC)
  - As an indication of substrate strength
- Indicators of prevailing geochemical conditions
  - Oxidation-reduction potential (ORP), dissolved oxygen (DO), ferrous iron, sulfate, methane, pH, and alkalinity
- Table B-1 Monitoring Metrics for Soil and Groundwater

No associated notes.

64

Using Optimization Parameters from Table 5-2

- Analyze delivery
  - Are you achieving desired distribution over the horizontal and vertical extent within treatment area?
  - Are you achieving desired contact with residual mass?
- Tracking contaminant fate
  - Are you achieving and maintaining efficient Enhanced Reductive Dechlorination (ERD) treatment area?
  - Are you achieving desired contaminant mass flux reduction downgradient of the treatment area?
  - Are you achieving desired mass removal rates (i.e., dissolution of residual mass)?
  - Can removal mechanisms be validated (i.e., biodegradation vs. sequestration of DNAPL)
- Managing secondary water quality impacts
  - Are there negative geochemical impacts within the treatment area?
  - Are you risking displacement or mobilization of residual mass?

No associated notes.

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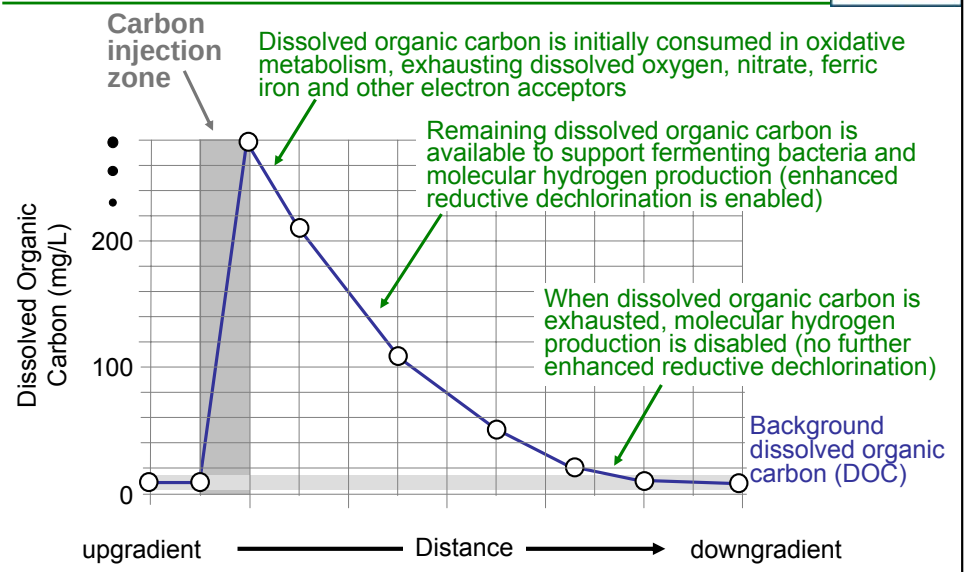
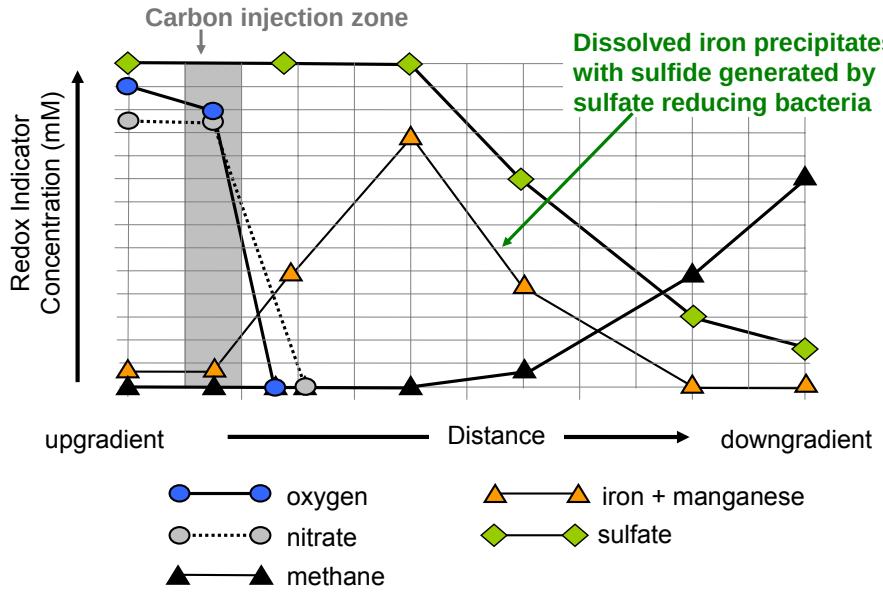
Data Evaluation – Electron Donor Loading Figure 5-2



No associated notes.

66

Data Evaluation – Redox Indicators
Figure 5-3



No associated notes.

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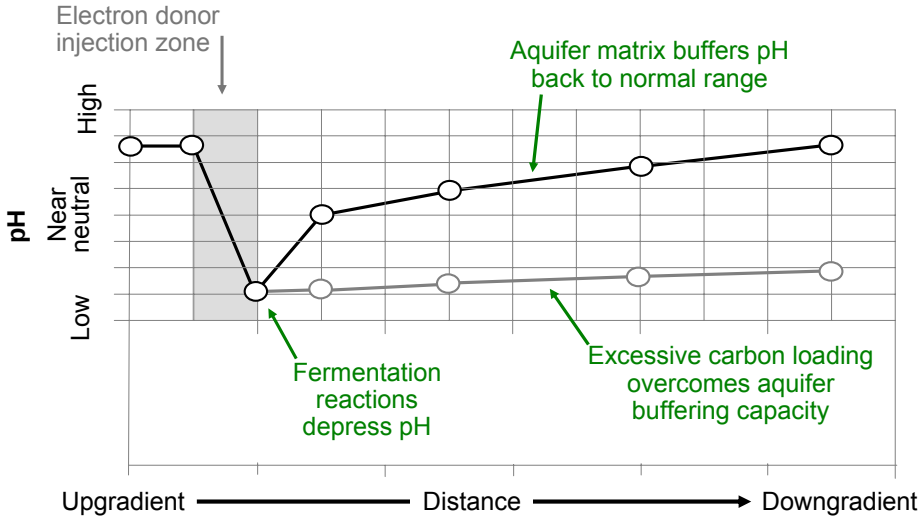
Data Evaluation – pH
Figure 5-4



No associated notes.

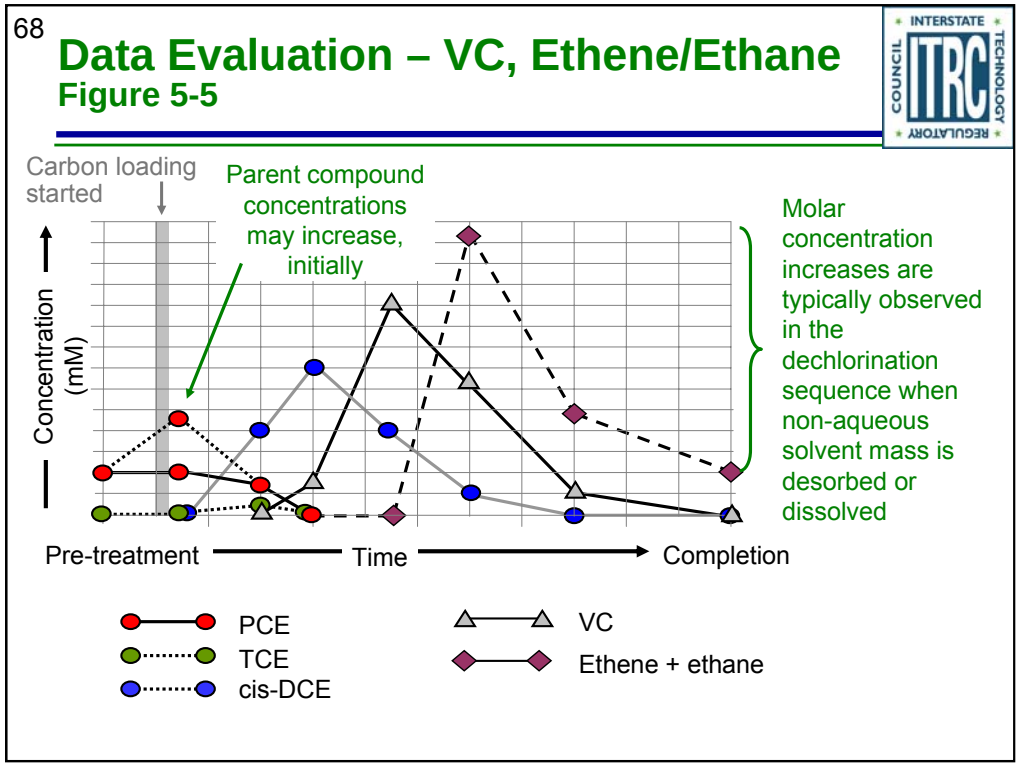


Figure 5-5 Concentration patterns in the chlorinated ethene dechlorination sequence that are typically observed when DNAPL source mass is dissolved or desorbed during enhanced reductive dechlorination.

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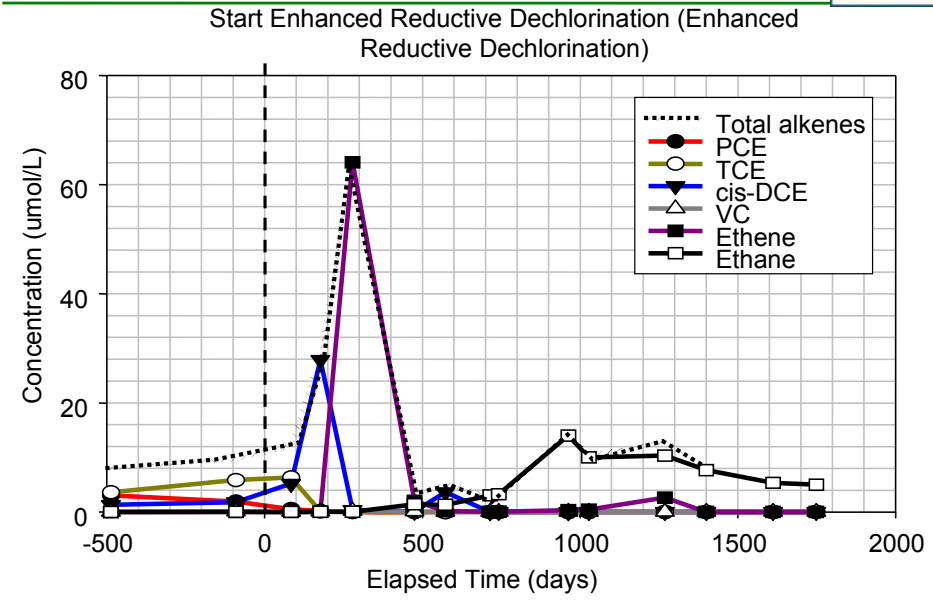
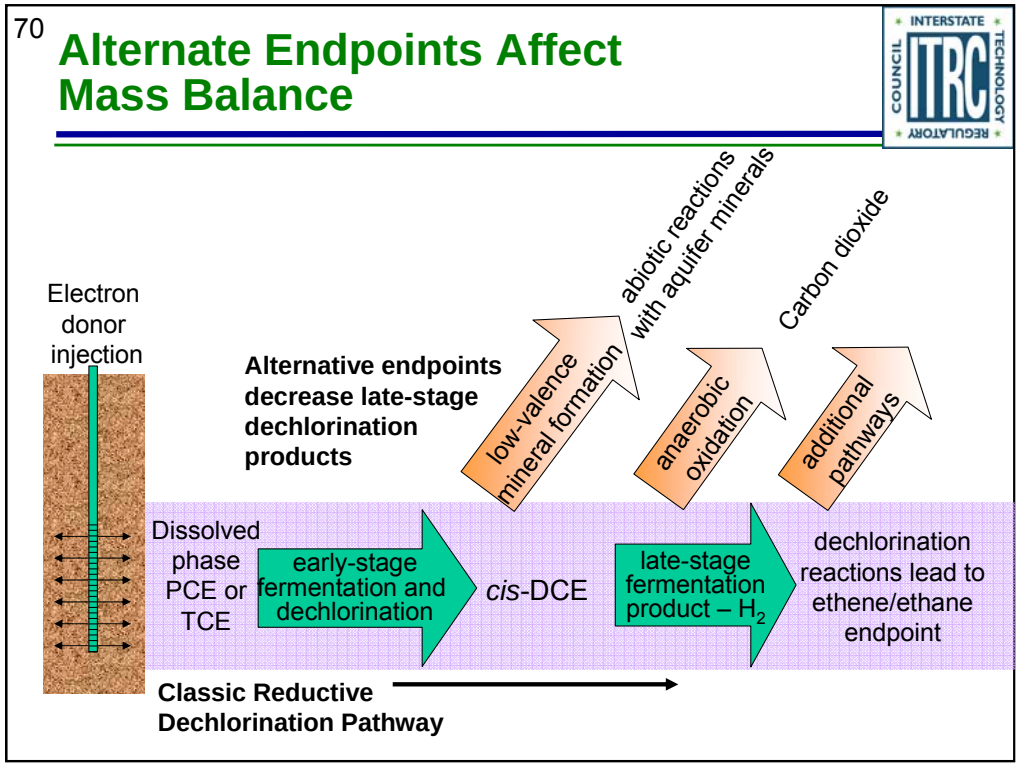
Mass Balance Examples



No associated notes.



No associated notes.

71

Effect of Red/Ox-Sensitive Metals

- Metals that tend to solubilize during ERD
  - Arsenic
  - Iron
  - Manganese
- Metals that tend to precipitate during ERD
  - Antimony
  - Chromium
  - Selenium
  - Vanadium
  - Uranium

Refer to Table 5-3 for additional information

No associated notes.

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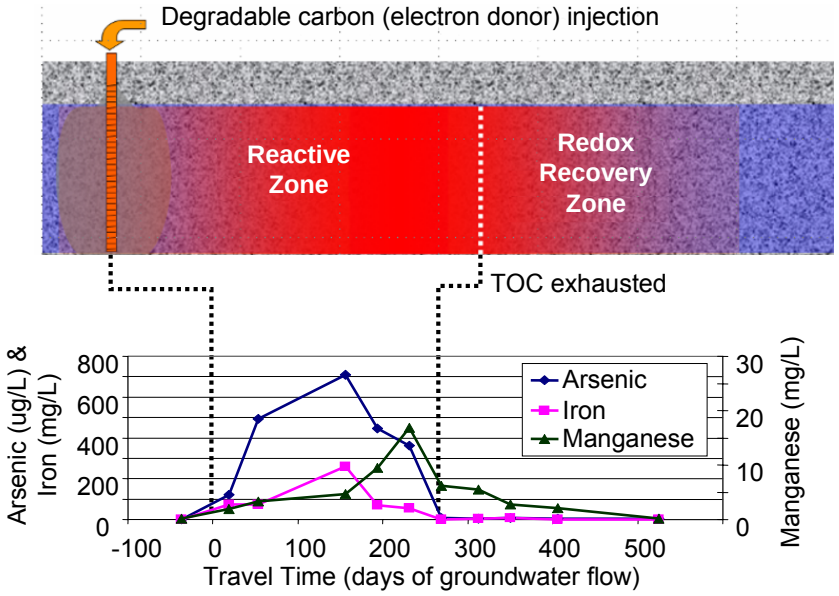
Reactive Zone Profiles –Water Quality Impacts Associated with ISB



No associated notes.

73

ISB at DNAPL Source Zones – In Summary

- Is a viable technology
- Can be stand-alone or paired with another technology
- Accelerates remediation through mass removal
- Degrades contaminants within months of implementation
- Treats multiple compounds simultaneously
- Is an efficient and cost effective technology

A summary of today's course is found on this slide. The important points to take away are:

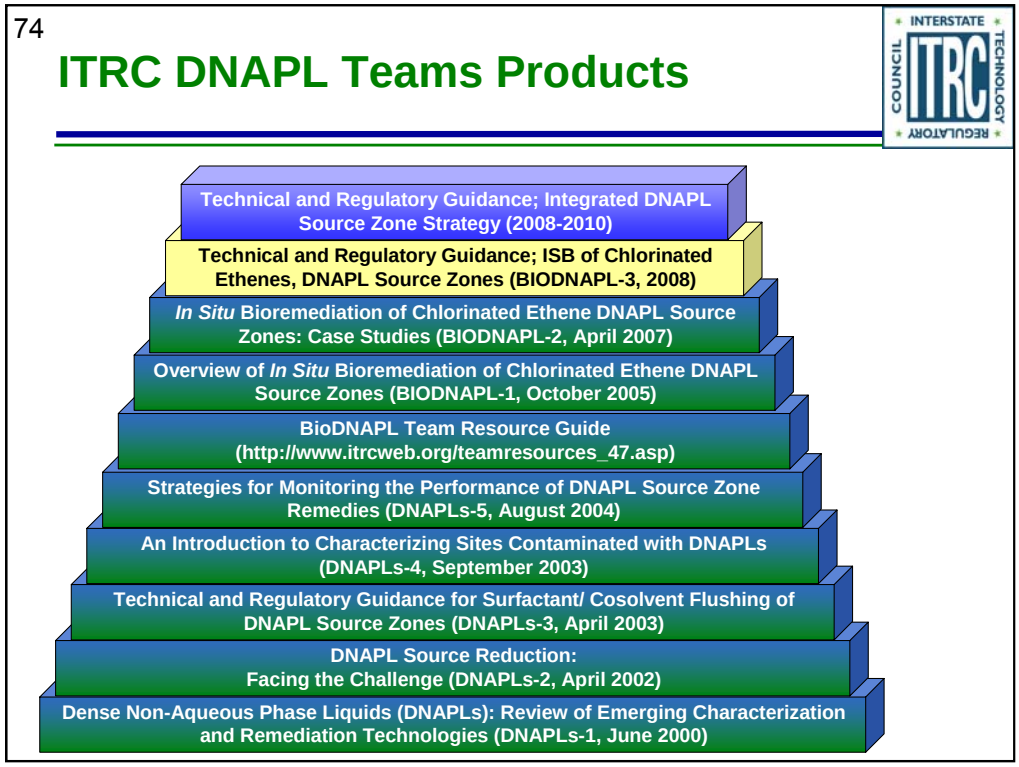
•ISB is a viable remediation technology for source zones. It can be a stand-alone remedy or combined with another technology.

•The technology accelerates mass removal.

•That degradation begins within a few months of implementation.

•The technology treats multiple compounds at the same time.

•ISB is an efficient and cost effective technology.



As you will see on this slide, there are seven other DNAPL-based documents (plus a resource guide) in addition to the document we discussed today (as seen in yellow). We encourage you to visit the ITRC website and download those documents that will assist you in implementing ISB.

The top block (in blue) refers to a new team forming this year to address combining technologies when remediating DNAPL source zones. It is anticipated that the team will produce a Tech-Reg document in 2010.

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Thank You for Participating

- **2nd question and answer break**
- **Links to additional resources**
  - http://www.clu-in.org/conf/itrc/bioDNAPL/resource.cfm
- **Feedback form – *please* complete**
  - http://www.clu-in.org/conf/itrc/bioDNAPL/feedback.cfm

Need confirmation of your participation today?

Fill out the feedback form and check box for confirmation email.

Links to additional resources:
http://www.clu-in.org/conf/itrc/bioDNAPL/resource.cfm

Your feedback is important – please fill out the form at:
http://www.clu-in.org/conf/itrc/bioDNAPL/feedback.cfm

The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

✓Helping regulators build their knowledge base and raise their confidence about new environmental technologies

✓Helping regulators save time and money when evaluating environmental technologies

✓Guiding technology developers in the collection of performance data to satisfy the requirements of multiple states

✓Helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations

✓Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

How you can get involved with ITRC:

✓Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches

✓Sponsor ITRC's technical team and other activities

✓Use ITRC products and attend training courses

✓Submit proposals for new technical teams and projects