This training is designed to introduce state regulators, environmental consultants, site owners and community stakeholders to the document created by the ITRC's In Situ Bioremediation Technical Team and the Remediation Technologies Development Forum (RTDF) Bioremediation Consortium titled, "Natural Attenuation of Chlorinated Solvents in Ground Water: Principles and Practices". The training focuses on the basic information one needs to determine and document the conditions necessary for natural processes to be an effective part of remediating chlorinated solvents in ground water. It provides a framework, that is, how to think about natural attenuation based on science. The information contained in this manual and presentation is based on research activities of the RTDF and from experience and knowledge of the participating members.

****

ITRC – Interstate Technology and Regulatory Council (www.itrcweb.org)

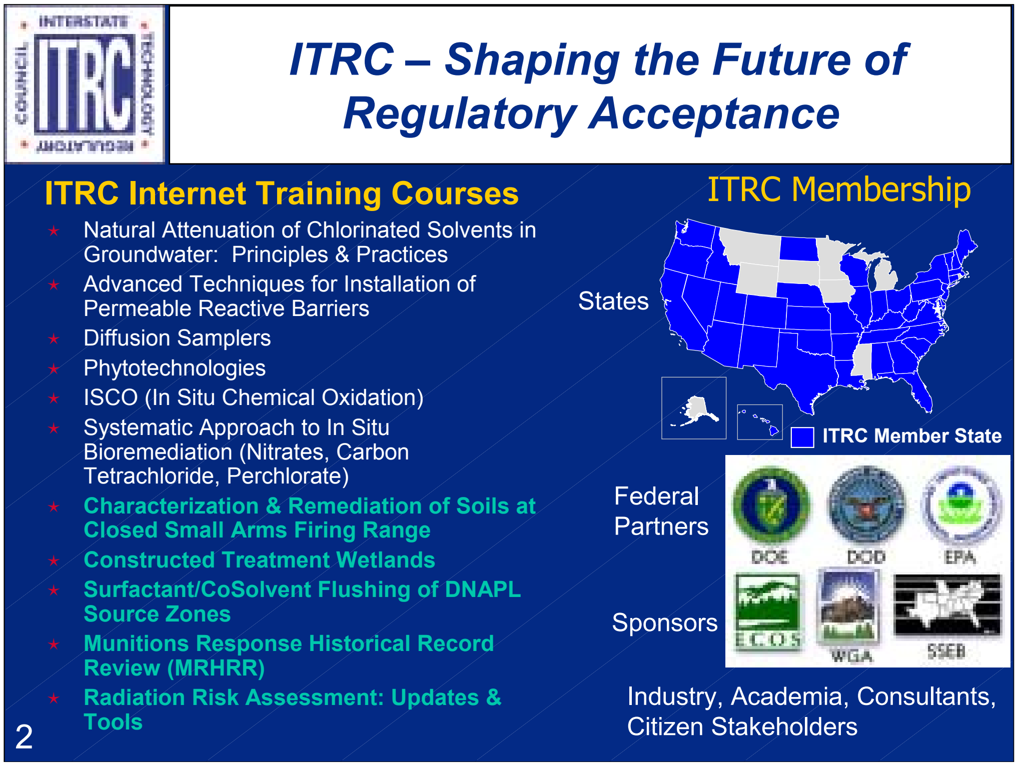
EPA-TIO – Environmental Protection Agency – Technology Innovation Office (www.clu-in.org) – hosts delivery of ITRC Internet-based training courses

RTDF = Remediation Technology Development Forum

(www.rtdf.org)

ITRC Course Moderator:

Mary Yelken – (myelken@earthlink.net)



The bulleted items are a list of ITRC Internet Training topics – go to www.itrcweb.org and click on "internet-based training" for details.

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. ITRC consists of 40 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 streamline the regulation 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 approaching 6,000 people from all aspects of the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

ITRC originated in 1995 from a previous initiative by the Western Governors' Association (WGA). In January 1999, it affiliated with the Environmental Research Institute of the States, ERIS is a 501(c)3 nonprofit educational subsidiary of the Environmental Council of States (ECOS). ITRC receives regional support from WGA and the Southern States Energy Board (SSEB) and financial support from the U.S. Department of Energy, the U.S. Department of Defense, and the U.S. Environmental Protection Agency.

To access a list of ITRC State Point of Contacts (POCs) and general ITRC information go to www.itrcweb.org.

Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices

Presentation Overview

- ✓ Overview of Natural Attenuation
- ✓ Common Issues
- ✓ Questions and answers
- ✓ Biological Attenuation Mechanisms
- ✓ Patterns of Natural Attenuation
- ✓ Questions and answers
- ✓ Links to additional resources
- ✓ Your feedback

Logistical Reminders

- ✓ Course Time = 2 hours
- ✓ Phone Audience
  - Keep phone on mute
  - * 6 to mute your phone and again to un-mute
  - Do NOT put call on hold
- ✓ Simulcast Audience
  - Use ? at top of each slide to submit questions

No Associated Notes

Today's Presenters

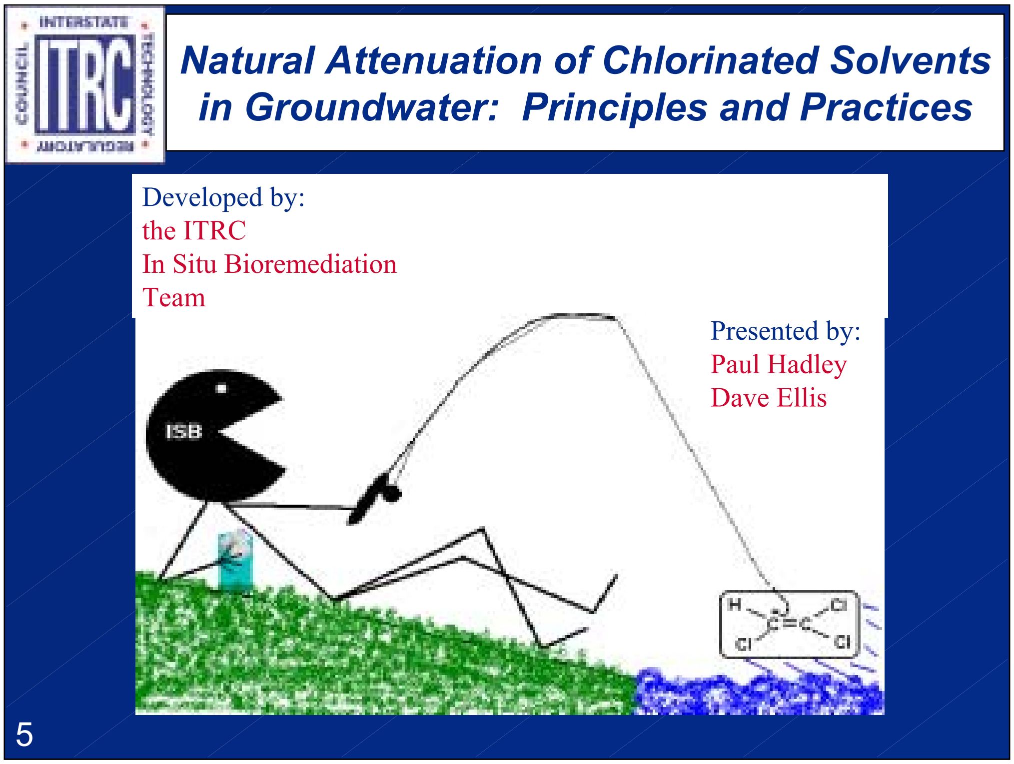
- Paul Hadley (Instructor)
  - ITRC Accelerated In Situ Bioremediation Training Course Team Leader
    - California EPA
    - phadley@dtsc.ca.gov
- Dave Ellis (Instructor)
  - Remediation Technology Development Forum (RTDF)
    - DuPont
    - david.e.ellis@usa.dupont.com

4

No Associated Notes

Paul W. Hadley is a Hazardous Substances Engineer with the California Department of Toxic Substances Control. Paul holds a bachelors degree in biochemistry and a master of science degree in civil/environmental engineering, both from the University of California at Davis. Paul is currently chairperson of the In Situ Bioremediation Task Group of the ITRC Work Group. During his fifteen years in the hazardous waste field, Paul has published more than a dozen articles on issues of risk and remediation at hazardous waste sites.

David E. Ellis Ph.D., P.G. is a Principal Consultant in DuPont's Corporate Remediation Group in Wilmington, Delaware. He leads the company's programs in remediation technology. Dave is also Chair of the EPA RTDF Consortium on Bioremediation of Chlorinated Solvents, a member of the National Research Council on Natural Attenuation, a member of the Board of Directors of the ITRC, and sits on several university committees. Dave received his Ph.D. at Yale University in 1978, and has published over 40 articles in environmental technology, geochemistry, and high temperature thermodynamics.



Instructor Notes:

• Jointly prepared by the Bioremediation of Chlorinated Solvents Consortium of the RTDF and the ITRC In Situ Bioremediation Work Team

• RTDF: Remediation Technologies Development Forum

• This training will demonstrate how the ITRC document "*Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices*" can be of value to parties interested in Natural Attenuation (NA)

Document Intent

- Provides a framework for how to approach integrating natural attenuation considerations into site projects in a "Question and Answer" format
- Guide the public, regulators, site managers, and practitioners on how to validate, interpret and validate natural attenuation

6

Instructor Notes:

•The Principles and Practices document was prepared to disseminate up to date scientific information regarding NA of chlorinated solvents

• The document also references appropriate sampling and interpretation protocols and guides readers to other relevant materials

•This training will increase the participants familiarity with the document

• Specifically, it will allow parties interested in NA to determine the following:

  - When the document should be used, and how it is useful
  - How the document should be used, and what features make it easy to use
  - How the document can add to the process of integrating NA into a long-term site management plan

What is Natural Attenuation?

"naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants ..."

7

Instructor Notes:

• This definition is taken directly from the Office of Solid Waste and Emergency Response (OSWER) of the Environmental Protection Agency (EPA)

• NA is also known as intrinsic remediation or natural restoration

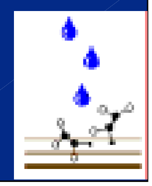
• The National Contingency Plan permits the use of NA as a remedy or portion of a remedy for Superfund sites

• In Situ Processes Include:

- Biodegradation
- Dispersion
- Dilution
- Adsorption
- Volatilization
- Chemical or Biological Stabilization or Destruction of Contaminants

Why Natural Attenuation?

- Because NA happens
- Because NA happens in situ
- Because NA is a destruction technique
- Because NA can be cost effective
- Because NA can be a good remedy
- Because NA is an important part of a treatment train
- Because NA requires virtually no energy



8

Instructor Notes:

• NA is a common sense approach to protect human health and the environment

• NA is a cost effective alternative that can be used as a stand-alone technology or in association with other remediation technologies to reduce overall remediation costs

• Important to understand NA processes before implementing any remedial measure

When is NA Considered?

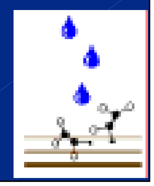
- When it is protective
- When clear proof of attenuation exists
- When a source cannot be removed and long-term treatment is needed
- When groundwater receptors are not affected
- When alternatives pose higher risks
- When the plume’s fate is understood

Instructor Notes

None

What Do You Need To Propose Natural Attenuation?

- Show treatment pathways & processes
- Show the rate of treatment
- Show a treatment mass balance
- Evaluate NRC’s three lines of evidence

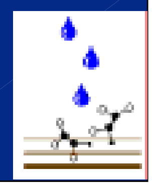


Instructor Notes:

None

The Three Lines of Evidence

1) Reduction in concentration along the flow path downgradient
2) Documented loss of contaminant mass by
   - chemical and geochemical data
   - biological decay rate data
3) Microbiological laboratory data supporting degradation and decay rates

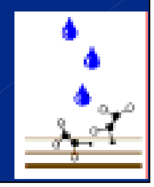


Instructor Notes:

Table 5 in the P&P document outlines the data required to support the three lines of evidence.

Natural Attenuation Costs

- Long term monitoring is significant
- Expand parts of the site assessments
- NA sometimes costs more than treatment



12

Instructor Notes:

None

How Often is NA Effective?

- Not enough experience yet to accurately predict for chlorinated solvents
- Wiedemeier and Wilson predict 20% as a stand alone NA remedy
- We suggest that in a few years NA may be part of a treatment train at another 50% of sites. This is based on existing biodegradation surveys

Instructor Notes:

None

Evaluating and Documenting NA (1)

- Step 1: Review available site data
- Step 2: Review/develop site conceptual model
- Step 3: Screen data for evidence of NA
- Step 4: Identify additional data requirements
- Step 5: Collect additional site data

Instructor Notes:

None

Evaluating and Documenting NA (2)

- Step 6: Refine site conceptual model
- Step 7: Interpret data and test fit to conceptual model
- Step 8: Conduct an exposure pathway analysis
- Step 9: If accepted, integrate NA into long term site management strategy

15

Instructor Notes:

None

Why Not Natural Attenuation?

- When a receptor is impacted
- When a plume is clearly expanding
- When the amount of attenuation is insufficient
- When the cost/benefit ratio is high

Instructor Notes

None

Common Issues Associated with Natural Attenuation

- Offsite migration
- Public/regulatory acceptance
- Plume expansion
- Time to remediate
- Intermediates and end products
- Comparability with other remedies

17

Instructor Notes:

None

Time For Questions /Answers / Comments

Q: What are some of your concerns and/or issues about implementing NA at a site?

Q: In what situations have you had success in using NA *or* in what situations have you faced opposition that has hindered the deployment of the technology?

18

Instructor Notes:

None

Common Chlorinated Solvents

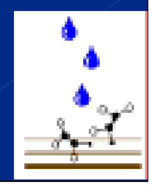
- PCE - Tetrachloroethylene C_2Cl_4
- TCE - Trichloroethylene C_2HCl_3
- DCE - Dichloroethylene $C_2H_2Cl_2$
  - (cis & trans)
- VC - Vinyl Chloride C_2H_3Cl
- CT - Carbon Tetrachloride CCl_4
- CF - Chloroform $CHCl_3$
- DCM - Dichloromethane CH_2Cl_2
  - (Methylene Chloride)
- TCA - 1,1,1 Trichloroethane $C_2H_3Cl_3$

Instructor Notes:

None

DNAPLs Are Difficult

- Physical properties make DNAPLs difficult to locate, remove and/or treat
- Other undesirable properties
- Complications when looking for DNAPL
- How does the presence of DNAPL affect site remediation strategy?



20

Instructor Notes:

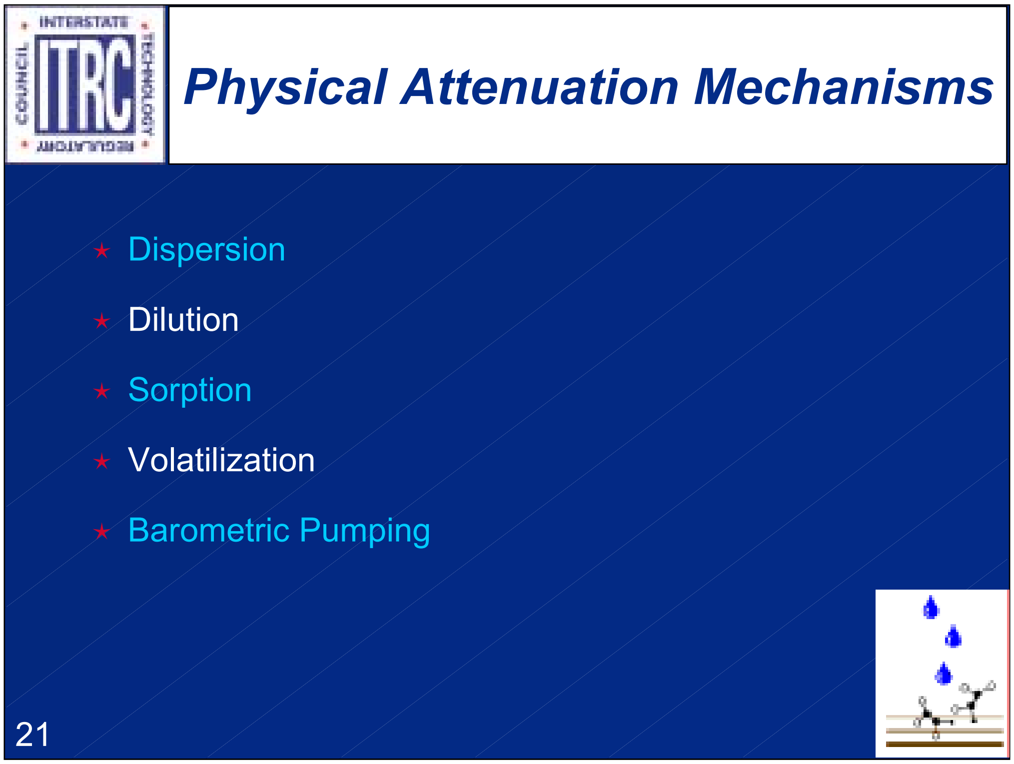
• **DNAPL:** Dense Non-Aqueous Phase Liquid

• **Bullet 1:** Denser than water; almost insoluble in water; can exist as vapor phase in vadose or dissolved phase in groundwater (GW); can also exist as residuals, droplets, coatings or pools

• **Bullet 2:** Complex distribution controlled by geology; low solubility results in very long dissolution times: P&T will be required for at least the same period of time; slow desorption/diffusion out of geological matrix: it takes longer to get out than it took to get in

• **Bullet 3:** Sometimes investigation (drilling) and treatment techniques (dewatering coupled to SVE) can enhance the penetration of DNAPLs deeper into the subsurface, example: drilling through a confining layer in a source area could allow DNAPL to drain into a deeper aquifer

• **Bullet 4:** Proven technologies that can remediate DNAPL in groundwater are not available; technologies such as pump and treat quickly reach the point of diminishing return for mass removal; a small residual mass can recontaminate a large volume of groundwater; remediation strategy should be long term, cost effective and protective of human health and the environment



Instructor Notes:

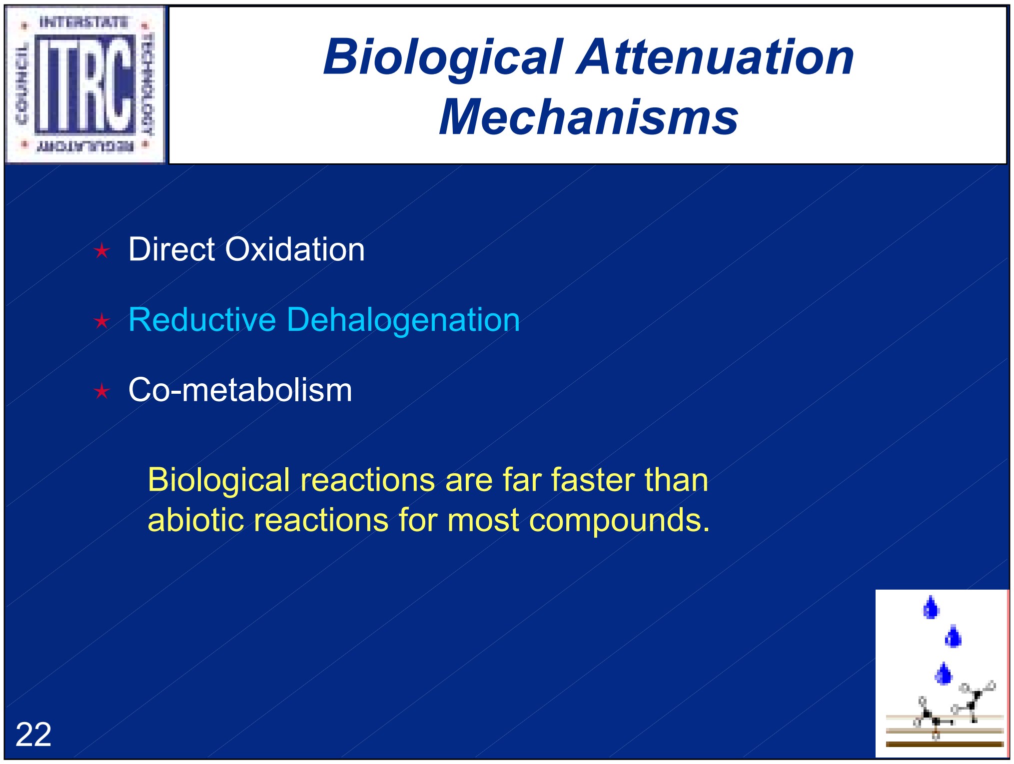
• **Dispersion:** The spreading of a solute outward from its expected advective path, primarily due to mechanical mixing. *Implications for NA:* 1.) Chemicals will transport away from the source area at a rate approximately equal to the velocity of groundwater, and 2.) Physical mixing and diffusion will cause chemicals to spread out along the flow path (i.e., plumes will get wider).

• **Dilution:** A decrease in chemical concentration in a fluid. *Underlying Process:* Fluid containing chemicals mix with fluid containing low concentrations of chemicals or no chemicals at all. *Equation:* $C_{final} = C_{initial} (Fi/[Fi + Fd])$ where C is concentration, F is flow rate and i and d are the initial and diluting solutions. *Implications for NA:* Chemical concentration decreases along the flow path in a relationship dependent on source size and concentration, and on groundwater velocity.

• **Sorption:** General term to define the process of how chemicals attach (sorb) and detach (desorb) themselves to solid particles in solution (soils). *Underlying Process:* Chemicals sorb because they dissolve into the organic matter on soil, diffuse into the soil matrix or are attracted by electrical charge. Chemicals desorb because of diffusion along a concentration gradient or displacement by a molecule with a higher affinity for the site. *Freundlich Isotherm:* $x/m = kC^{1/n}$, where x/m = solute sorbed/unit weight sorbent, k = constant, C = concentration of solute remaining in solution, 1/n = constant.

• **Volatilization:** Mass transfer of dissolved chemicals from a liquid phase to a gaseous phase. *Underlying Process:* Air flows into and out of the vadose zone as the barometric pressure increases and decreases, respectively. *Implications for NA:* Volatilization from GW into the vadose zone, and subsequent loss to the atmosphere leads to a gradual decrease in shallow GW concentration. Usually minor.

• **Barometric Pumping:** Vertical movement of soil gas in response to atmospheric pressure fluctuations. *Underlying Process:* Air flows into and out of the vadose zone as the barometric pressure increases and decreases, respectively. *Implications for NA:* Combined with normal volatilization, this process can remove chemical mass from the subsurface to the atmosphere where either dilution or a chemical reaction with light will occur. This process can significantly influence subsurface vapor transport.



Instructor Notes:

• **Direct Oxidation:** The chlorinated compound is directly used as a growth substrate (food source) and broken down to inorganic molecules such as carbon dioxide, water, and chloride.

• **Reductive Dehalogenation:** The chlorinated compound is converted to another chemical by replacing chlorine atoms with hydrogen atoms.

• Co-metabolism: The chlorinated compound is converted to another chemical by microorganisms during growth on other carbon compounds.

Cometabolic Reductive Dechlorination

- A small percentage of organism's metabolism
- Relatively slow and non-specific
- Degradation is usually first order
- Subsequent steps are often slower than the preceding ones
- Growth of the organism is not stimulated
- May be observed in aquifers with high numbers of sulfate reducers, methanogens, and acetogens

Cometabolic has many **undesirable features**

Small percentage of organisms' metabolism - **need lots of substrate**

Slow, usually first order,

Subsequent dechlorination steps often **tenfold** slower than preceding ones

Organisms **don't grow from it**, so never gets faster

Can be important in some habitats with a lot of these bugs

Dehalorespiration

- Can be large percent of an organism's metabolism- less reductant needed
- Usually fast and specific
- Usually follows Michaelis-Menten kinetics
- Subsequent steps may not be slower than previous ones
- Organism growth supported, rate of degradation increases over time

24

Advantages of dehalorespiration

Large percentage of organisms' metabolism- need less substrate

Usually pretty fast and specific -

Enzyme catalyzed means that follows MM kinetics- Low Km- can take down to low concentrations

Organism grows- can be rate acceleration

Chlorinated Solvent Degradation

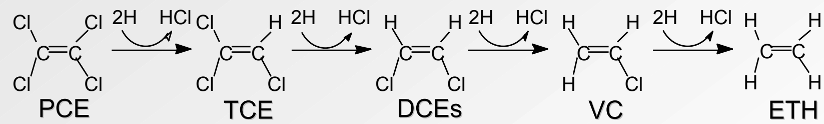
PROCESS	PCE	TCE	c-DCE	VC	TCA	DCA	CT	CF	DCM
Direct Aerobic	N	N	Y&N	Y	N	N	N	N	Y
Cometabolic w/ CH_4	N	Y	Y	Y	Y&N	N*	N	Y	NR
Cometabolic w/ toluene	N	Y	Y	Y	N	N*	N	Y&N	NR
Cometabolic w/ NH_4	N	Y	Y	Y	Y	N*	N	Y	NR
Direct Anaerobic	N	N	N	Y	N	N	N	N	Y
Anaerobic/ Denitrification	Y&N	Y&N	N*	N*	N*	N*	Y	Y&N	NR
Anaerobic/Sulfate reduction	Y	Y	Y	Y	Y	Y	Y	Y	NR
Anaerobic/ Methanogenic	Y	Y	Y	Y	Y	Y	Y	Y	NR

N: Not documented in the literature
Y: Documented in the literature many times; concensus opinion
Y&N: Documented in the literature more than once of both occurrence and absence
N*: Not documented in the literature to date, but not investigated significantly
NR: Process may occur but Not Relevant since competing process occurs more rapidly

Instructor Notes:

None

Degradation Pathway



Relative Degradation Rates:

PCE >TCE > VC > DCE

26

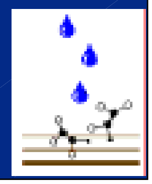
Degradation of a chlorinated compound involves the removal of a chlorine. This process occurs in a step wise fashion, where one chlorine is removed at a time. This process is often referred to as the "degradation pathway", outlined above.

In addition, the "relative degradation rates" have been provided. As a rule of thumb, the more chlorines a compound has the longer the it takes to degrade. However, this isn't always the case. As shown above, dichloroethylene degrades a faster rate than Vinyl Chloride.

Patterns of Natural Attenuation

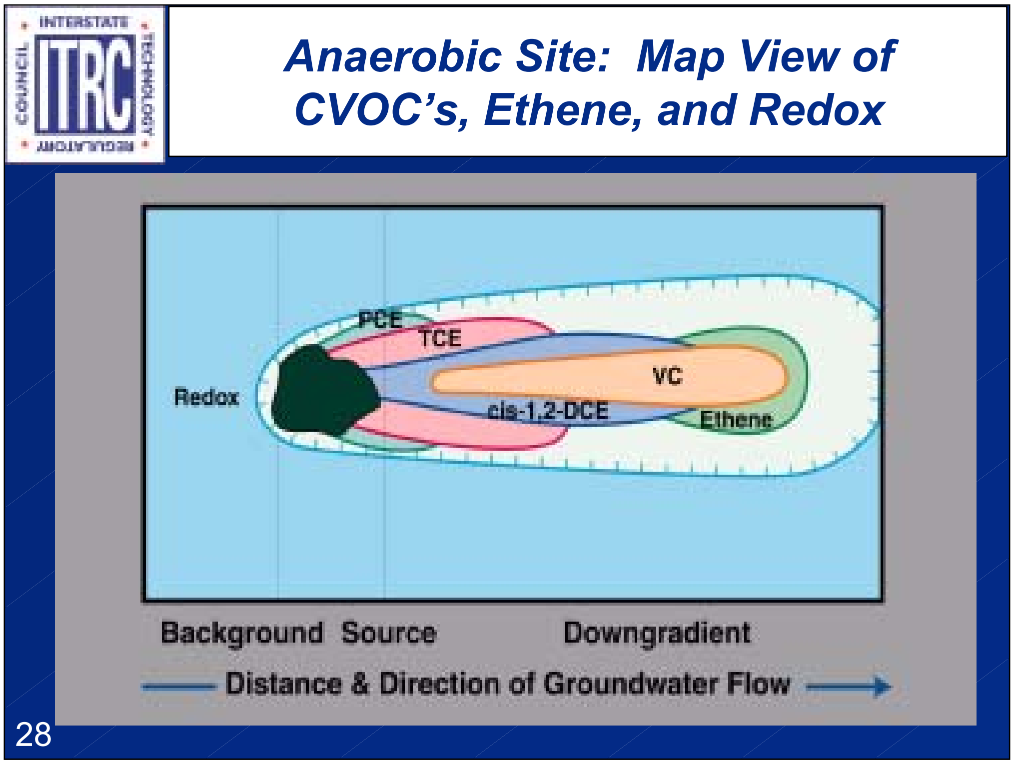
- Physical processes alone
- Anaerobic conditions
- Sequential anaerobic – aerobic conditions
- Sequential anaerobic – anaerobic conditions
- Aerobic or cometabolic conditions

27



Instructor Notes:

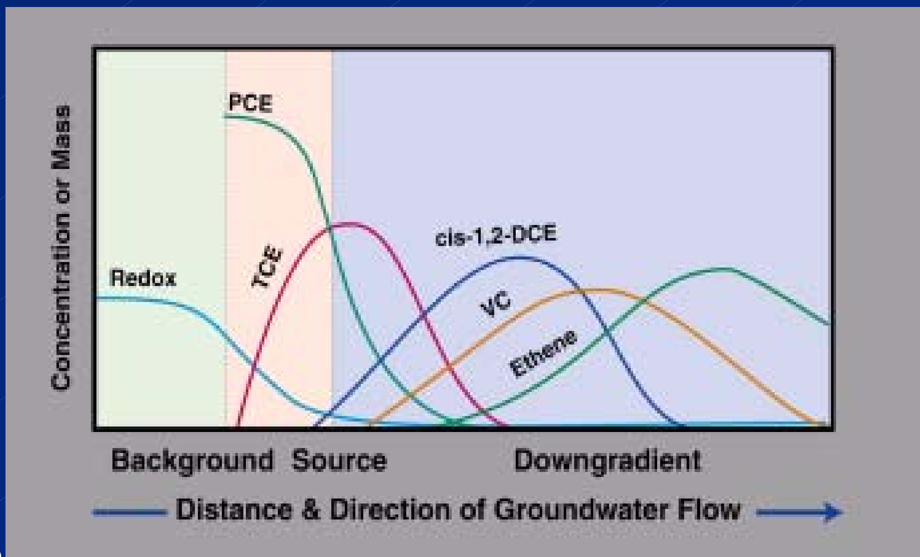
None



Instructor Notes:

None

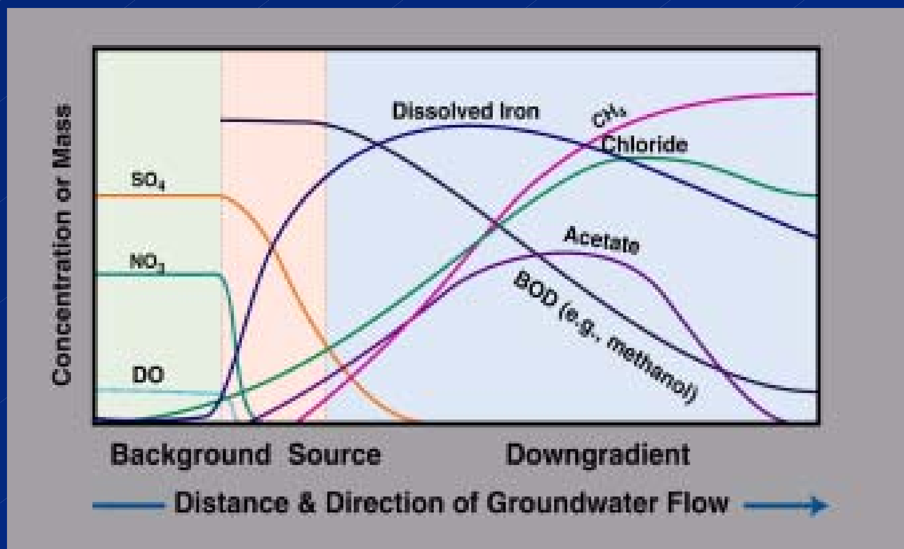
Anaerobic Site: Cross Section of CVOC's, Ethene, and Redox



Instructor Notes:

None

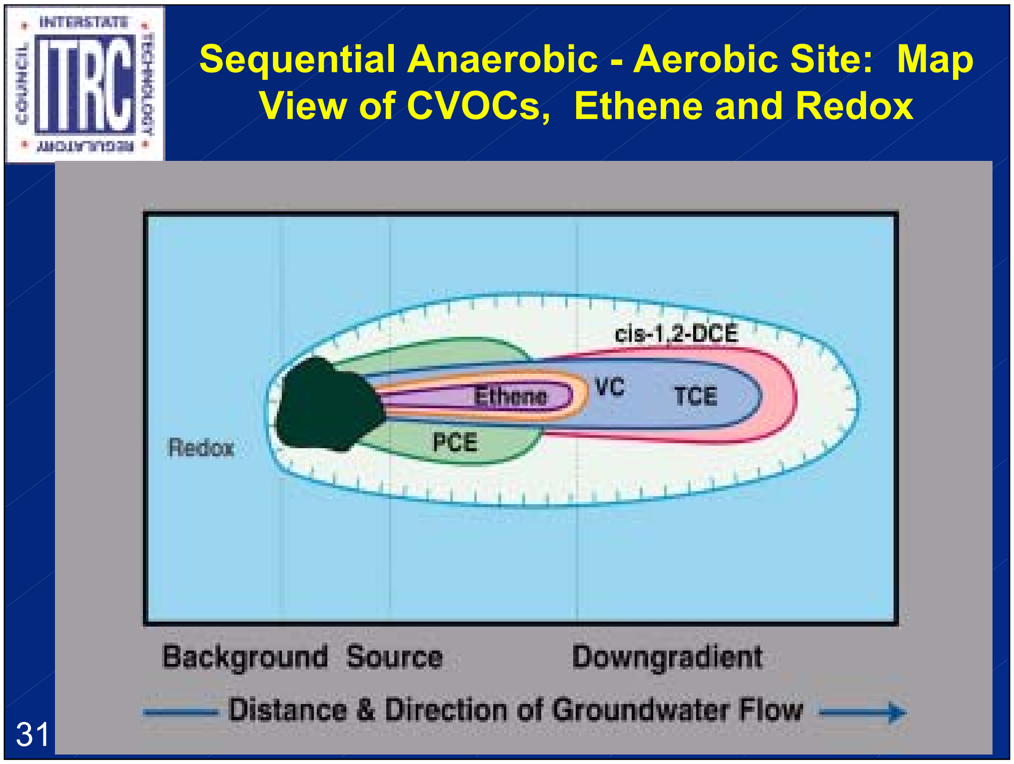
Anaerobic Site: Cross Section of Organic and Inorganic Parameters



30

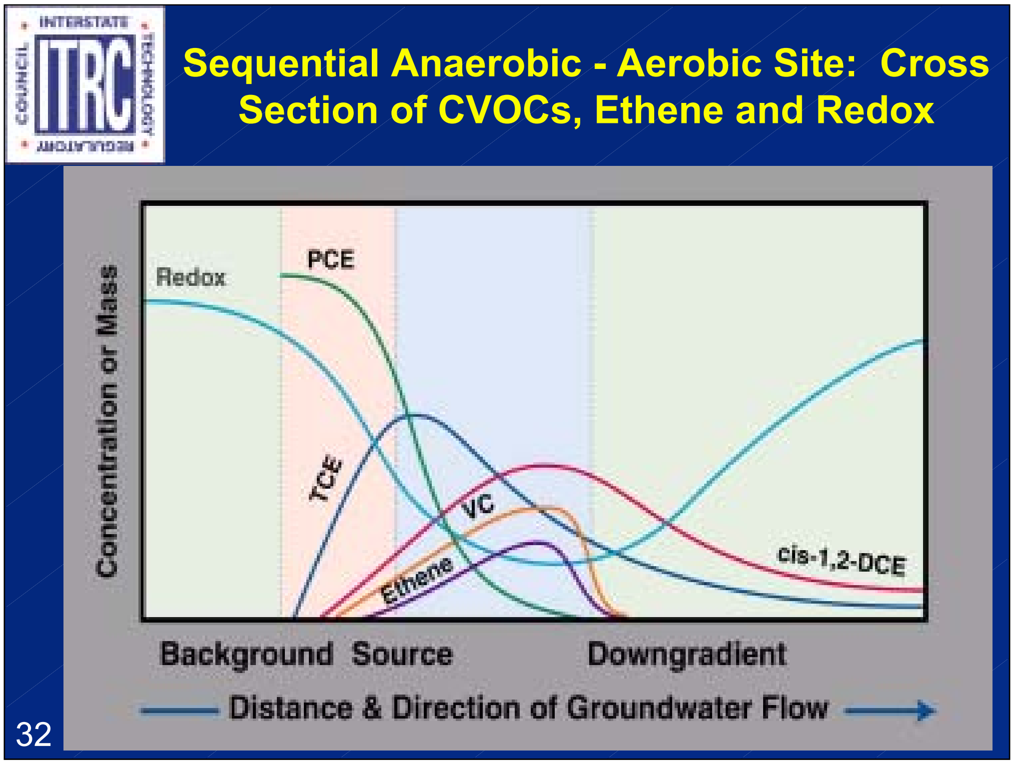
Instructor Notes:

None



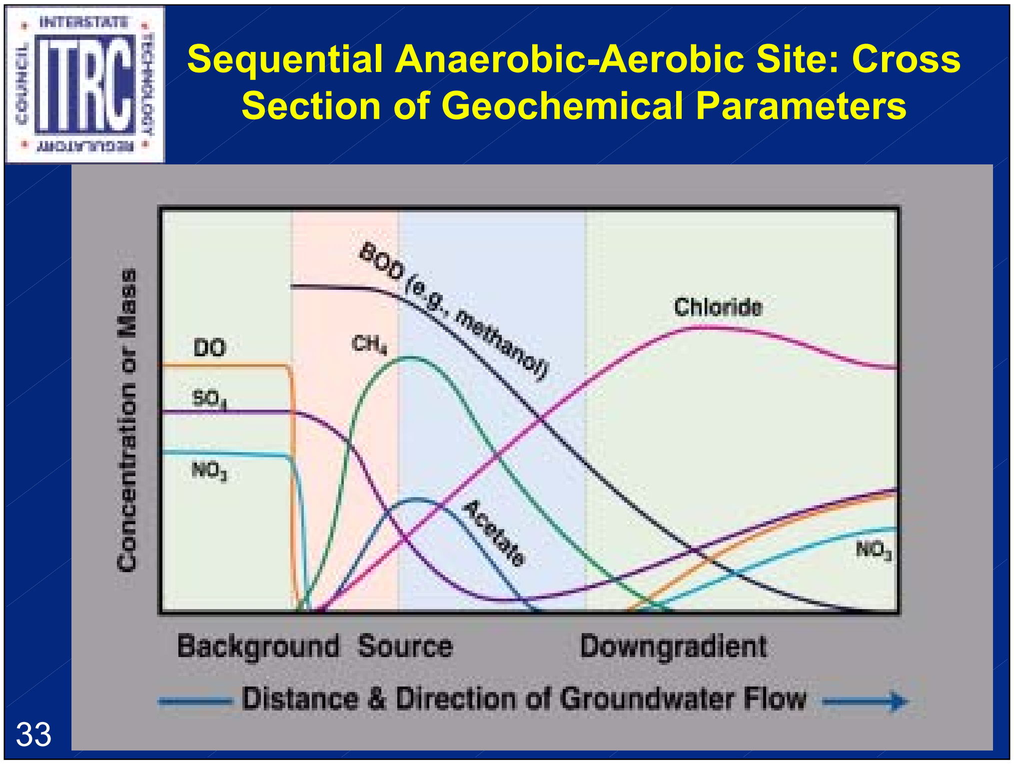
Instructor Notes:

None



Instructor Notes:

None



Instructor Notes:

None

Ubiquity of Microorganisms

- Microorganisms (bacteria) are everywhere
- There are 10^5 - 10^7 bacteria in every gram of soil
- Bacteria can form resting stages (spores) that are viable for thousands of years
- Bacteria can survive in extreme environments: from -25^{o} to 120^{o} C, from pH < 2 to pH > 12

Instructor Notes:

In general, all "types" of bacteria (e.g. aerobic, anaerobic) are present at all sites. However, all bacteria involved in all of the potential biodegradation pathways for chlorinated solvents are not necessarily present at every site. For example, it is believed that all of the bacteria needed for the reductive dechlorination of PCE or TCE to DCE are present at approximately 90% of all sites, and all of the bacteria needed for the reductive dechlorination of PCE or TCE to ethene are present at approximately 75% of all sites.

PCE, TCE → *cis*-DCE

Organisms	e^- donors	e^- acceptors	Morphology
"Dehalobacter restrictus"	H_2	none	rod
Dehalospirillum multivorans	H_2, formate, pyruvate, etc.	thiosulfate, nitrate fumarate, etc.	spiral
"*Enterobacter agglomerans*"	non-ferment-able substrates	O_2, nitrate, etc.	rod
Strain TT4B	acetate	none	rod

Many cultures can take PCE to cis-DCE

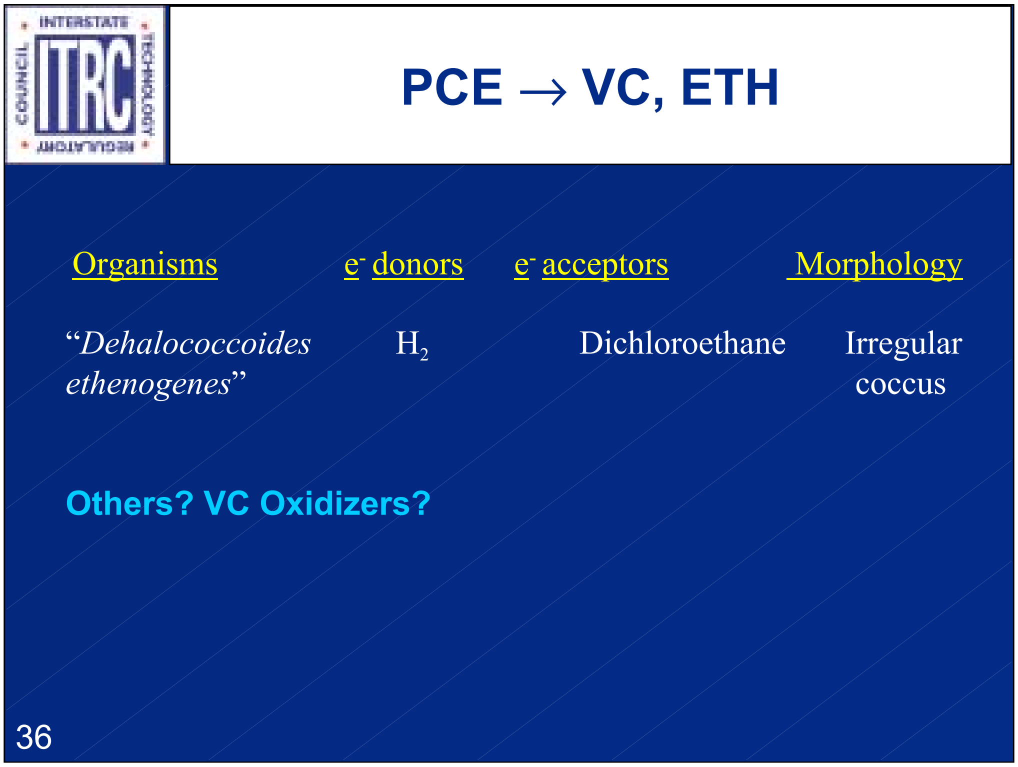
Dehalobacter restrictus - Holliger - Only uses H2 and PCE/TCE

Dehalospirillum multivorans - Diekert's group uses a variety of donors and other electron acceptors

An organism resembling **Enterobacter** agglomerans - Sharma and McCarty - facultative aerobe - uses other acceptors - repress

TT4B - uses acetate- and little else, not well described-\

Others- lots of organisms can make cis - we have another



Past cDCE- Only one culture - not yet described in lit

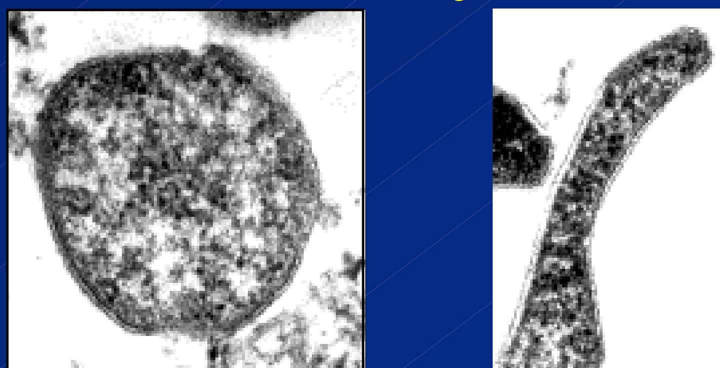
Call it **Dehalococcoides ethenogenes**, which can convert PCE to VC and ETH
Only uses H2 as electron donor

Others- are out there- not well characterized

Also, Frank will tell about exciting evidence for oxidation of VC using ferric iron - thus if you can get past DCE - good - VC can go with other electron acceptors

Dehalococcoides ethenogenes

Thin-section electron micrographs showing
coccoid and elongated cells

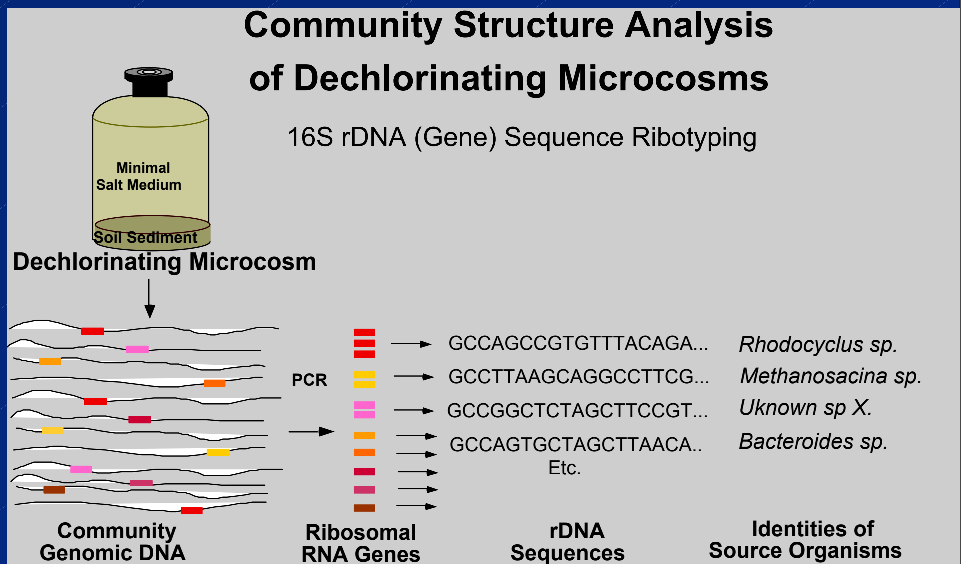


Photos courtesy of Dr. Steve Zinder, Cornell University

37

EM of organism - irregular coccus-
has unusual cell wall - looks like an archaebacterium

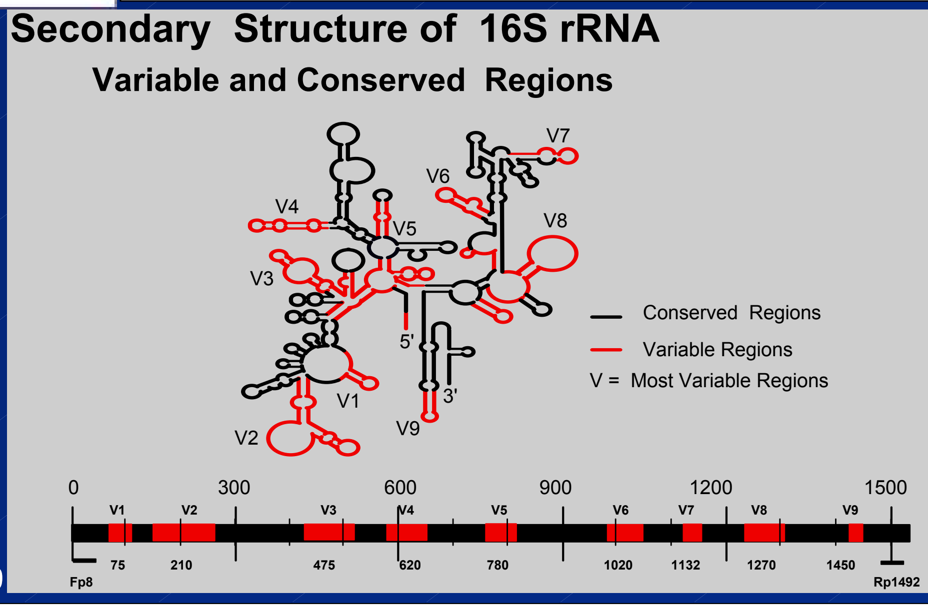
16S rDNA (gene) Sequence Ribotyping



Instructor Notes:

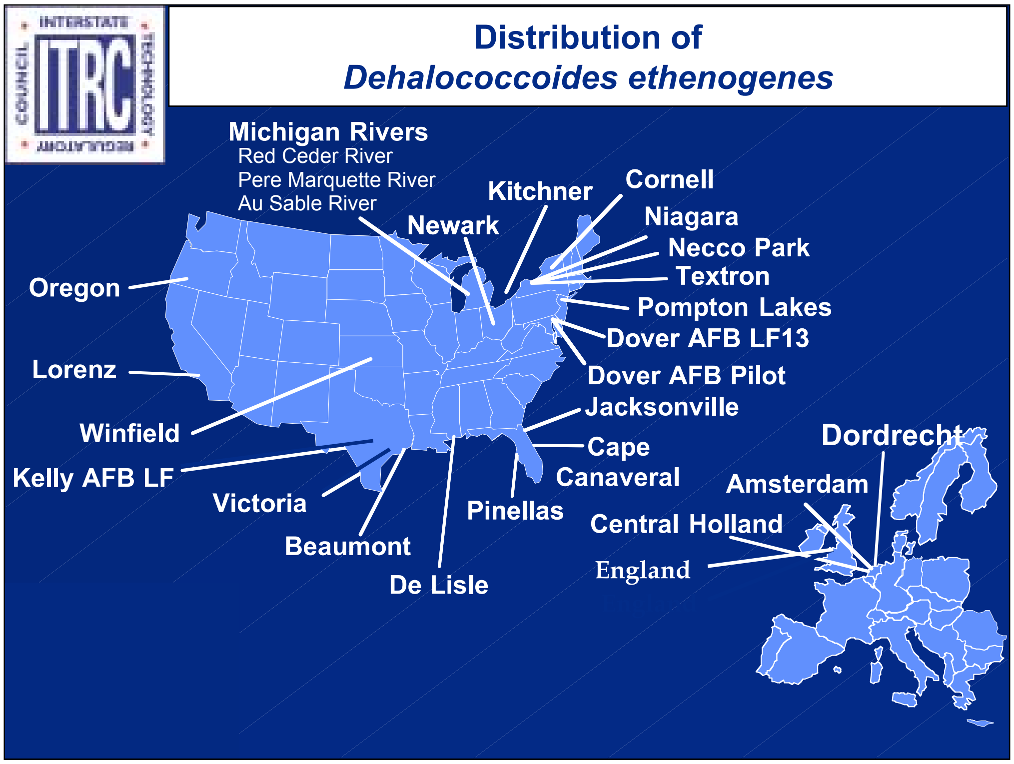
None

16S rRNA - secondary structure



Instructor Notes:

None



Instructor Notes:

None

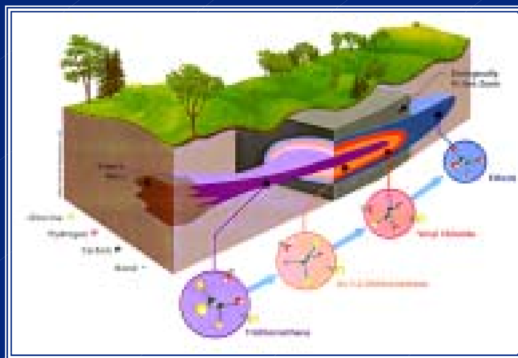
What About Natural Attenuation Has Changed?

- New geochemical and microbiological information
- Developed a new site assessment paradigm
- A new systematic approach to site evaluation
- EPA NA Policy directive issued
- NRC Report on NA issued
- Wider acceptance of NA by regulators and the public

Instructor Notes

None

Technical Presentation Wrap-up



Questions and Answers

Thank you for attending this ITRC training course.

For more information on ITRC training opportunities visit: **www.itrcweb.org**

42

Instructor Notes:

None

Links to Additional Resources

For more information on ITRC training opportunities visit:
www.itrcweb.org

43

Additional resources for this ITRC internet training event are available at:

http://clu-in.org/conf/itrc/natatt/ click on "links to additional resources"

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

•Join a team – with just 10% of your time you can have a positive impact on the regulatory process

•Sponsor ITRC's technical teams and other activities

•Be an official state member by appointing a POC (Point of Contact) to the State Engagement Team

•Use our products and attend our training courses

•Submit proposals for new technical teams and projects

•Be part of our annual conference where you can learn the most up-to-date information about regulatory issues surrounding innovative technologies