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# Welcome to ITRC's Internet Training – "Systematic Approach to *In Situ* Bioremediation"

Thank you for joining us. Today's training focuses on the ITRC Technical and Regulatory Guidance Document entitled:

" Systematic Approach to *In Situ* Bioremediation in Groundwater: including Decision Trees on Nitrate, Carbon Tetrachloride and Perchlorate"

The training is sponsored by: ITRC & EPA-TIO

***Creating Tools & Strategies to Reduce Technical & Regulatory Barriers for the Deployment of Innovative Environmental Technologies***

Presentation Overview:

This course presents a decision tree for reviewing, planning, evaluating, and approving *in situ* bioremediation (ISB) systems in the saturated subsurface. It defines site parameters and appropriate ranges of criteria necessary for characterization, testing, design and monitoring of ISB technologies. Contaminants and breakdown products differ, however, many characteristics of a site used to determine the efficacy of ISB, are similar. Once a site has been characterized for ISB efficacy and the contaminants of concern and degradation products have been defined, engineered approaches can be designed, pilot tested and possibly deployed. Similarly, several aspects of ISB are characteristic of all sites, no matter what contaminant is being scrutinized. This training is based on the ITRC document entitled: "Systematic Approach to In Situ Bioremediation: Nitrates, Carbon Tetrachloride & Perchlorate." The document: (1) describes what information is needed for any ISB evaluation; (2) provides a flow diagram that defines the primary decision points; (3) provides characteristics used to evaluate monitored natural attenuation or enhanced ISB application as remediation options. Examples of how to apply this document, including respective decision trees, for nitrate, carbon tetrachloride, and perchlorate are included.

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

EPA-TIO – Environmental Protection Agency – Technology Innovation Office (www.clu-in.org)

ITRC Course Moderator:

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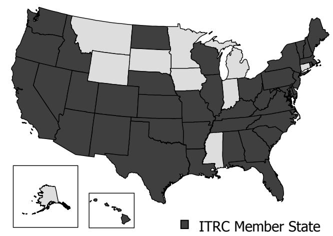
# ITRC – Shaping the Future of Regulatory Acceptance

- Natural Attenuation
- EISB (Enhanced In Situ Bioremediation)
- Permeable Reactive Barriers (basic and advanced)
- Diffusion Samplers
- Phytotechnologies
- ISCO (In Situ Chemical Oxidation)
- Systematic Approach to In Situ Bioremediation

## ITRC Membership

States




Federal Partners: DOE, DOD, EPA

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Industry, Academia, Consultants, Citizen Stakeholders

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

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## Systematic Approach to *In Situ* Bioremediation in Groundwater: Including Decision Trees on Nitrate, Carbon Tetrachloride & Perchlorate

**What You Will Learn..........**

- Essentials for understanding In Situ Bioremediation
- Systematic evaluation for ISB for treatment of particular Contaminants of Concern
- Important elements of site characterization
- Contaminant characteristics & degradation pathways
- Application of ISB for treating carbon tet., nitrate and perchlorate
- Feasibility
- Advantages & Limitations
- Decision Tree Approach to Bioremediation
- Regulatory Issues

**Logistical Reminders**

- 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
- Course Time = 2 ¼ hours
- 2 Question & Answer Periods
- Links to Additional Resources
- Your Feedback

No Associated Notes

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## Meet the ITRC Instructors

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**Bart Faris**, is a hydrogeologist with the New Mexico Environment Department's (NMED) Ground Water Quality Bureau. He is the project manager/regulator for multiple contamination sites throughout New Mexico dealing with numerous contaminants. He serves as NMED's water representative for Border Issues with Mexico. Bart is the Interstate Technology Regulatory Council (ITRC) team leader for the In Situ Bioremediation team and was the team leader for the Enhanced In Situ Biodenitrification team. He is also a member of the Technical Advisory Group for the Innovative Treatment and Remediation Demonstration (ITRD) program at Oakridge National Laboratory Y-12 carbon tetrachloride (CT) project. Bart received his B.S in Soil and Water Science from the University of Arizona in 1983, and has published papers on in situ biodenitrification and monitored natural attenuation of CT. Bart has spent over 15 years in Latin America working with community's water resources and agricultural production.

**Ronald J. Buchanan, Jr., Ph.D.**, is a Principal Consultant with DuPont Corp. Remediation Group in Wilmington, Delaware. Ron is a member of DuPont's Bioremediation Technology Network which is developing microbial anaerobic reductive dehalogenation and intrinsic bioremediation of chlorinated solvents. He is also a member of the EPA/RTDF Project Team developing and applying natural attenuation of chlorinated solvents at Dover Air Force Base in Delaware. Ron received his Ph.D. in Environmental Engineering and Science from Drexel University in 1977, and has published over two dozen papers in the field of hazardous waste management and environmental technology. He is a member of the Governor's Science Advisory Board in Pennsylvania and the Pa DEP Solid Waste Advisory Committee.

**Dimitri Vlassopoulos** has been a geochemist with S.S. Papadopulos and Associates in Bethesda, Maryland for 10 years, where he conducts and supervises applied research in contaminant hydrology and in-situ groundwater remediation technologies. His areas of expertise include analysis of the environmental fate and transport of contaminants under natural and engineered conditions, development and application of computer simulation models, and environmental forensic techniques. He received a Ph.D. in environmental geochemistry from the University of Virginia (2000), an MS in Geochemistry from the California Institute of Technology (1993), and an MS in Geological Sciences (1989) from McGill University.

**H. Eric Nuttall, Ph.D.**, is a professor of Chemical/Nuclear Engineering at the University of New Mexico. Dr. Nuttall has over 200 publications/presentations and directs graduate student research on in situ bioremediaiton as well as teaches an annual course on bioremediation. Dr. Nuttall has developed and manages a very successful field site for in situ treatment of nitrate-contaminated groundwater. Dr. Nuttall is a member of the national Interstate Technology and Regulatory Council (ITRC) for in situ bioremedation, technology verification, and chemical oxidation. This group had produced several technical guidance documents on bioremedation. He also has developed an in situ process to immobilized uranium and heavy metals which is being tested both by DOE at an UMTRA site and in Germany through WISMUT.

## What is In Situ Bioremediation?

- Bioremediation is the application of biological treatment to the cleanup of CoCs (Contaminants of Concern)
  - Microorganism
  - Hydrogeology
  - Chemistry
  - Engineering
- Create subsurface environmental conditions conducive to the degradation of chemicals via microbial catalyzed biochemical reactions

CoCs = Contaminants of Concern

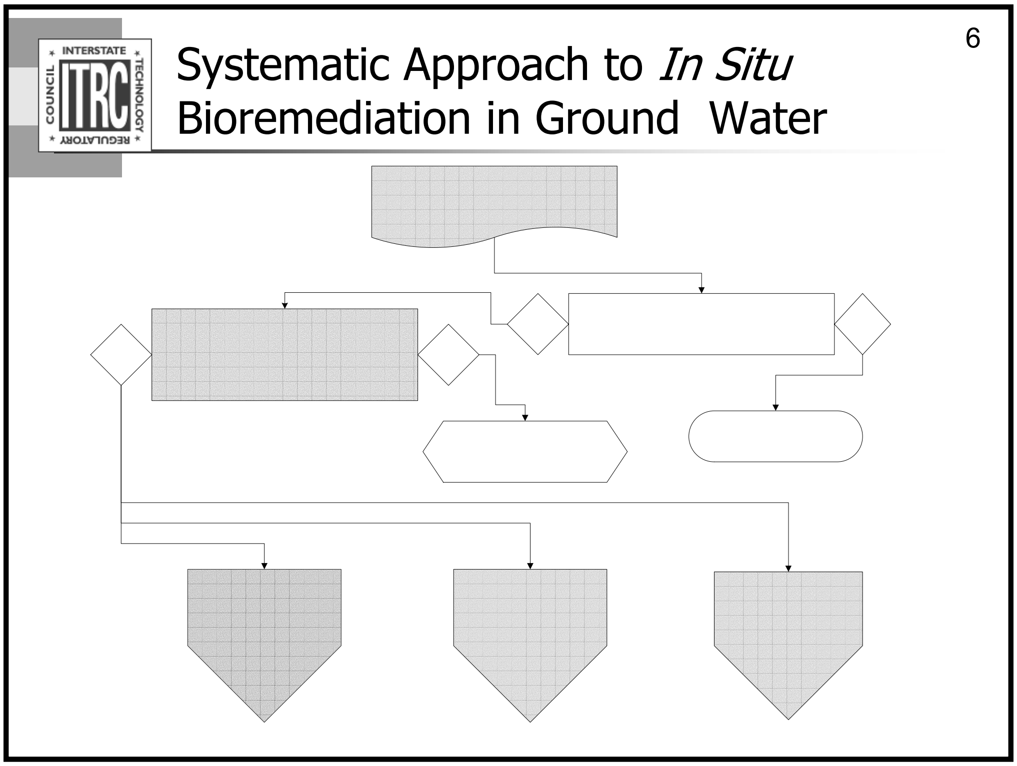
Engineered technique for optimizing subsurface conditions (hydrogeological, geochemical, microbial) to biodegrade contaminants in situ

Includes injecting substrate and nutrients (i.e., amendments)

Creates in situ conditions conducive to microbes

May include extracting and recirculating amended groundwater

Establishes/accelerates contaminant biodegradation in situ

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## Overview

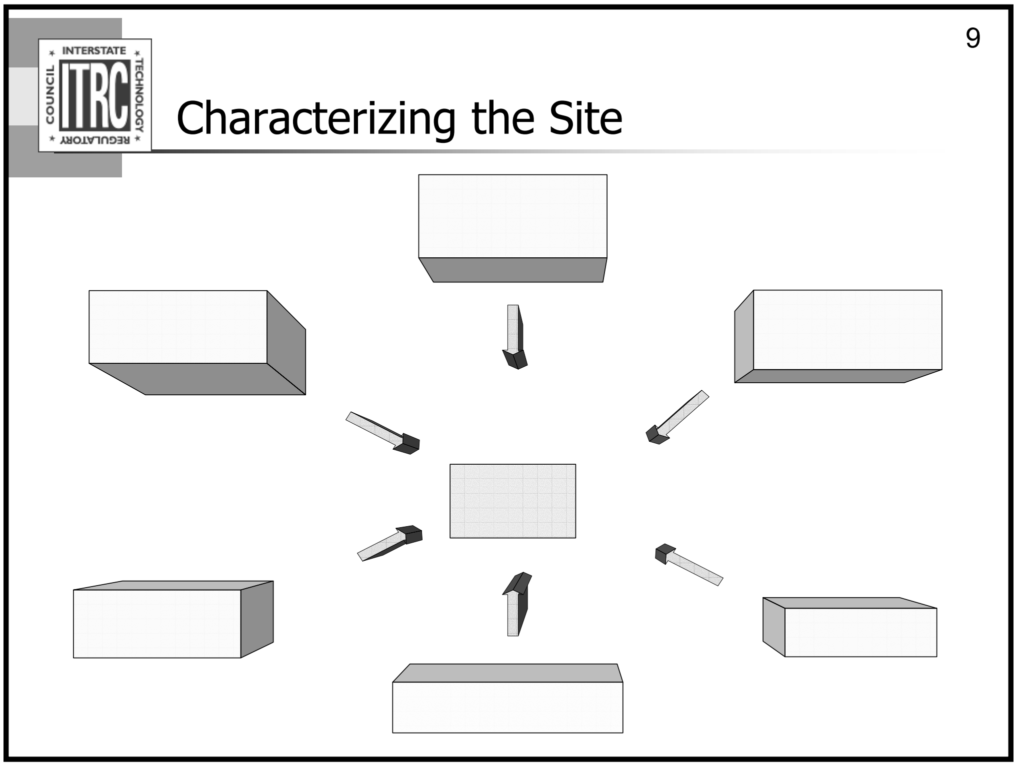
- First, Generic ISB Considerations
- Second, Specifics
- Third, Contaminants of Concern
  - Nitrate – $NO_3$ (Mature)
  - Carbon Tetrachloride $CCl_4$ (used but testing pathways is still underway)
  - Perchlorate – $ClO_4^-$ (Immature)
- Finally, Bottom Line for ISB

No associated notes

# Key Issues

- Guidance document for State & Federal regulators, RPs and consultant use of decision trees on ISB and contaminant chapters
- Injection of amendments
- Contaminant standards
- State regulations equivalent to RCRA 3020(b)
- State UIC rules for injection of contaminated ground water
- Technical challenges

No Associated Notes




Refer to Figure 2-1 in the document

***Geochemistr***

## Site Background

- Site operational history
- Contaminant source & pervasiveness
- Contaminant properties
- Contaminant relationships

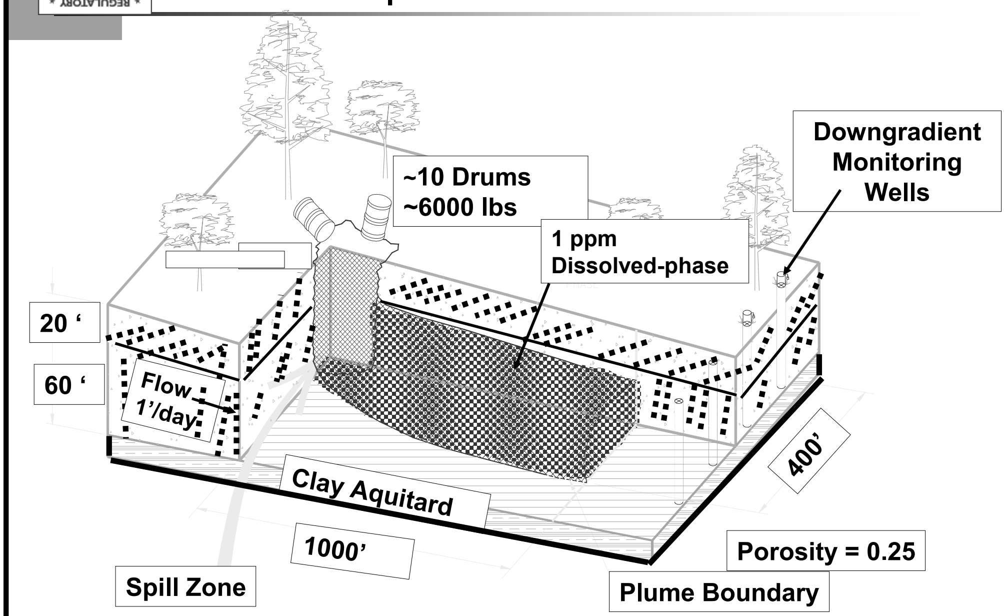
No associated notes

# Microorganisms

- Microscopic organisms that have a natural capability to degrade, destroy or immobilize a wide range of organic and inorganic compounds
- Accelerate microbial activity using nutrients
  - e.g. Phosphorus, Nitrogen
- Food
  - e.g. molasses, vegetable oil, lactates, ethanol
- Not a new science!

No associated notes

## Site Conceptual Model




No associated notes

# Hydrogeology & Transport

- Define important parameters
  - Stratigraphy
  - Hydraulic Conductivity
  - Storativity
  - Groundwater Flow & Transport
- Contaminant distribution
  - Type/mix
  - Advection & Dispersion
  - Retardation/$K_{oc}$
- Amendment delivery- including mixing
  - Type of System (passive, injection, recirculation)
  - Amendment Type
  - Amendment Delivery Rates

No associated notes

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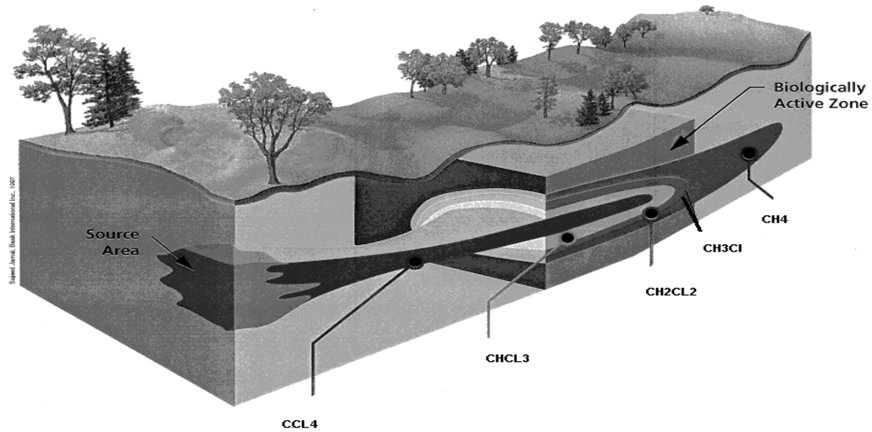
# Hydrogeology & Transport (Cont.)




No associated notes

## Chemistry

- Kinetics
- Stoichiometry

No associated notes

# Kinetics

- Monod kinetics
  - Assumes cells growing on the substrate are being degraded
- First order
  - Rate is dependent solely on the reactant under consideration
  - $dC/dT = - kC$
- Second order
  - Rate is simultaneously dependent on two parameters (e.g., added substrate and contaminant)
- Zero order
  - Rate is independent of the reactant(s) under consideration

No associated notes

# Stoichiometry

- Methanol

$NO_3^- + 5/6\ CH_3OH \rightarrow 1/2\ N_2 + 5/6\ CO_2 + 7/6\ H_2O + OH^-$

- Ethanol

$NO_3^- + 5/12\ CH_3CH_2OH \rightarrow 1/2\ N_2 + 5/6\ CO_2 + 3/4\ H_2O + OH^-$

- Acetate

$NO_3^- + 5/8\ CH_3COO^- \rightarrow 1/2\ N_2 + 5/4\ CO_2 + 1/8\ H_2O + 13/8\ OH^-$

No associated notes

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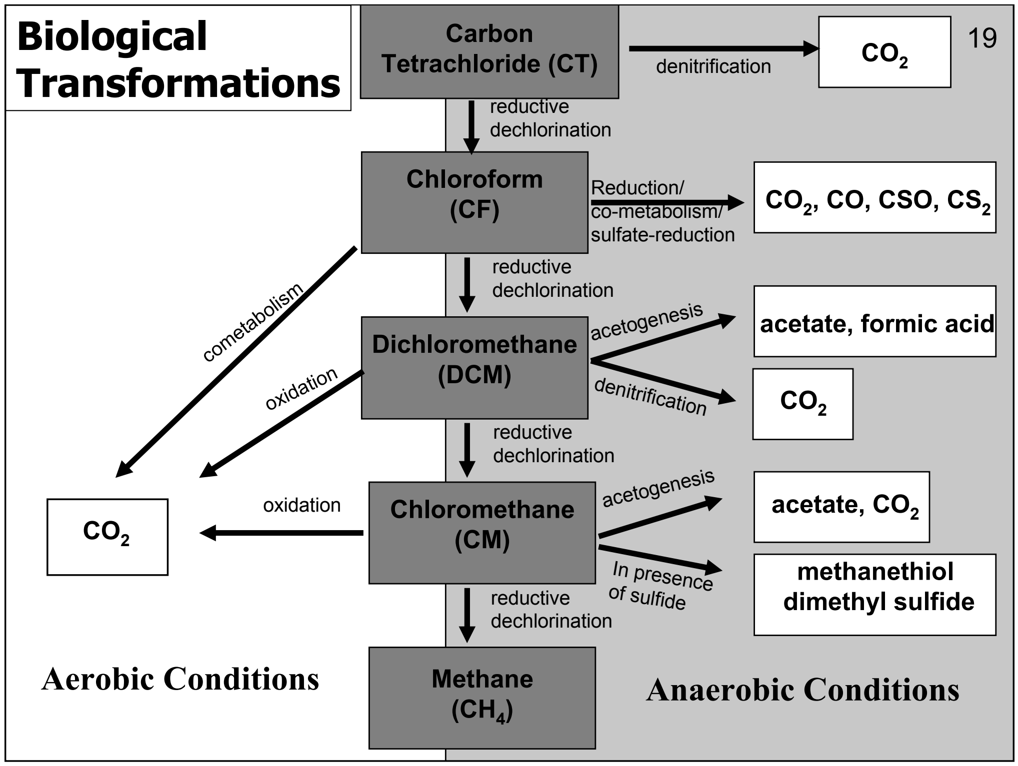
## Transformation

Abiotic
- Oxidation & Reduction reactions
- Hydrolysis
- Elimination
- Volatilization

Biotic
- Oxidation & Reduction reactions
- Cometabolism
- Assimilation
- Sequential transformation

No associated notes




No associated notes

# Geochemical Elements Important to ISB

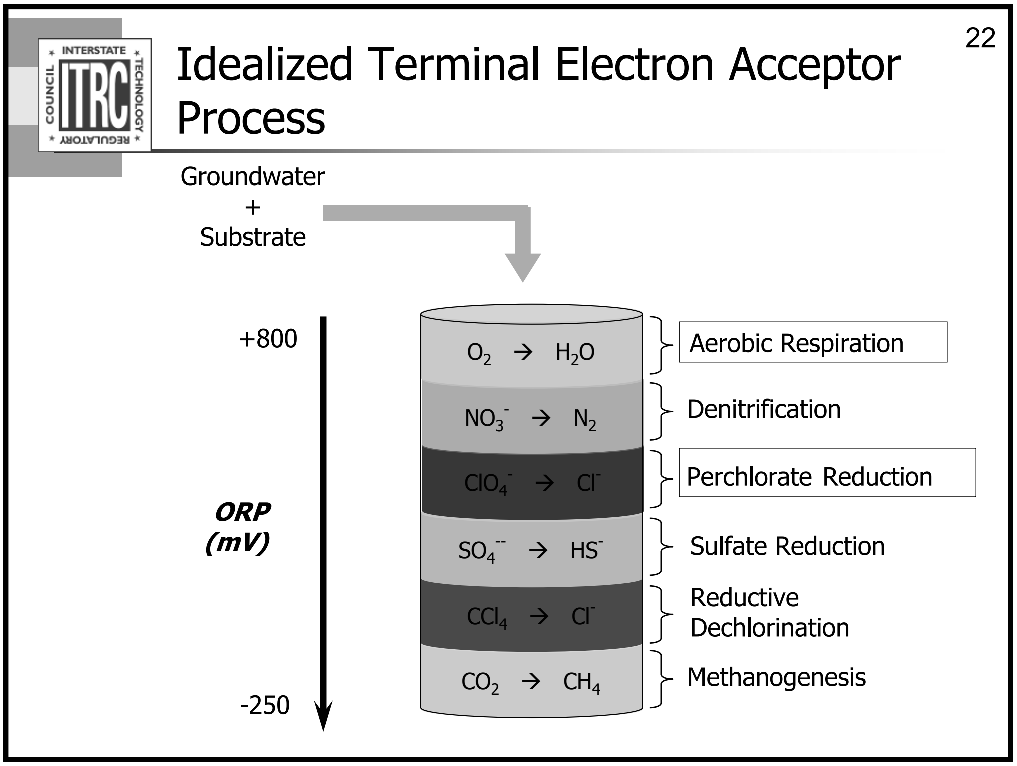
| Primary Analytes for Groundwater | Reason for Analysis |
|---|---|
| **Alkalinity** | $CO_2$ and $CO_3/HCO_3$ are produced by microbial respiration, and an increase in alkalinity may indicate microbial growth from $CO_2$ or organic acid production that lowers the pH and solubilizes carbonate. |
| **Chloride** | Used as a conservative tracer; for R-CL an increase in Cl may indicate reductive dechlorination. |
| **Dissolved Oxygen** | $O_2$ is a microbial electron acceptor and a redox indicator. High oxygen (>2 mg/l) shows aerobic conditions and $O_2$ will be the preferred electron acceptor until depleted. |
| **Manganese (dissolved)** | An increase in dissolve manganese, relative to background, (Mn[II]) may indicate that Mn(IV) is serving as an electron acceptor in anaerobic biodegradation. |
| **Iron (dissolved)** | An increase in dissolve Fe, relative to background, may indicate that Fe (III) is serving as an electron acceptor in anaerobic biodegradation. |
| **Nitrate/nitrite (total)** | A decrease in nitrate, relative to background, may indicate that nitrate is serving as an electron acceptor under slightly reducing conditions. |

No associated notes

# Geochemical Elements Important to ISB

| PRIMARY ANALYTES FOR GROUNDWATER | REASON FOR ANALYSIS |
|---|---|
| **pH** | Optimum range 5 to 9 for ISB |
| **Phosphate as P (soluble)** | Nutrient needed for microbial growth.<br>Phosphate may need to be added to promote biodegradation. |
| **Oxidation Reduction Potential (ORP) (mv)** | Measurement of reducing or oxidizing environment may be indicative of potential biological activity |
| **Sulfate** | A decrease in sulfate, relative to background, may indicate that sulfate is serving as an electron acceptor under anaerobic conditions.<br>• If this is the case, should be able to measure an increase in sulfides. |
| **Methane** | An increase in methane, relative to background, may be an indicator of reducing conditions or microbial by-product using carbon dioxide as an electron acceptor.<br>• It is generally not present at most sites. |
| **Total organic carbon** | TOC may serve as electron donors and help to determine the amount of electron donor amendment required for Biodegradation<br><br>TOC may increase retardation of the COC due to sorption. |

No associated notes




- Microbiology
- chemistry
- hydrogeology
- engineering

## Receptors

- Determine type and location
- Determine exposure/impact
- Mitigate exposure/impact (including use of ISB)

No associated notes

## Advantages & Limitations

| ADVANTAGES | LIMITATIONS |
|---|---|
| Capability to degrade chlorinated aliphatic hydrocarbons to relatively less toxic products | A perceived lack of knowledge about biodegradation mechanisms |
| Generation of relatively small amounts of remediation wastes, compared to ex situ technologies | Specific contaminants or contaminant mixture at a site may not be amenable to ISB |
| Reduced potential for cross-media transfer of contaminants commonly associated with ex situ treatment | Enhanced technologies, when needed, may be costly or their implementation may be technologically challenging |
| Reduced risk of human exposure to contaminated media, compared to ex situ technologies | Biofouling of amendment injection wells or points may be a challenge |
| Relatively lower cost of treatment compared to excavation and disposal, ex situ treatment or conventional pump-and-treat systems | |
| Potential to remediate a site faster than with conventional technologies | |

No associated notes

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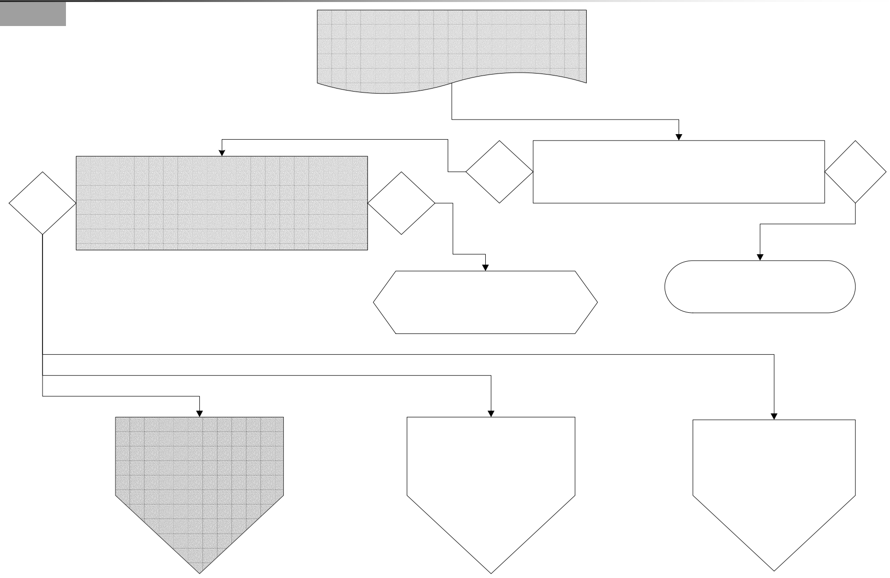
## Systematic Approach to *In Situ* Bioremediation for Nitrates in Ground Water



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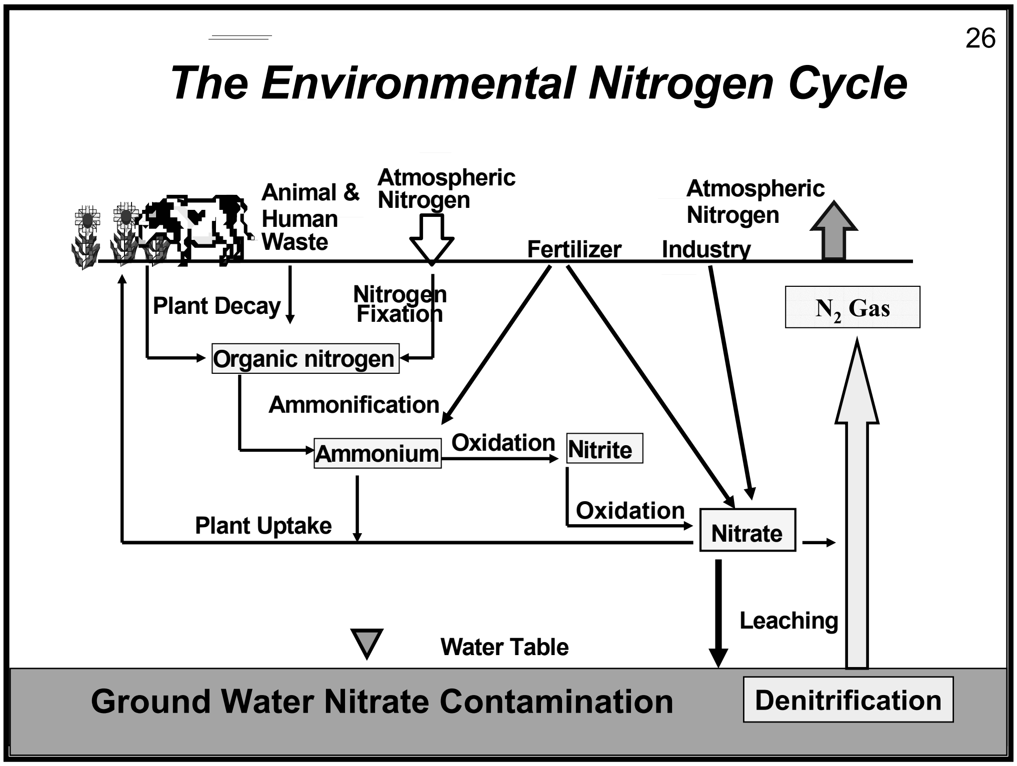


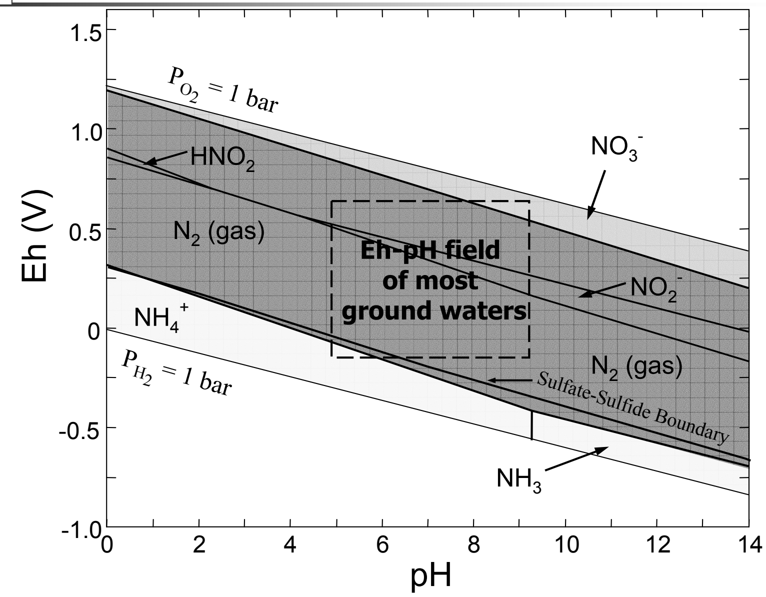

- •Nitrate is a worldwide problem as a groundwater contaminant
- •Biological denitrification of groundwater is under development as a technology to address this problem
- •Maximum Contaminant Level (MCL) is 10 mg/L nitrate-N
- •U.S. EPA estimates MCL is exceeded in 2.4% of domestic wells in U.S.
- •Two major sources: over-fertilization and human & animal waste

## Nitrate Compound Properties

- **Solubility** 70g/100g water @21ºC
- **Vapor Pressure (mmHg)** Negligible
- Will **not** adsorb to rock matrix/conservative species
- Very **stable** in groundwater
- Requires **bacteria to catalyze** the conversion to nitrogen gas
- **Nitrate** is most **oxidized** state of nitrogen

No associated notes

# Eh-pH




No associated notes

# Essential Parameters

| PRIMARY ANALYTE | REASON FOR ANALYSIS |
|---|---|
| **Nitrate/nitrite** | • You can expect a decrease in concentration if bioremediation is occurring |
| **Alkalinity** | • Due to microbial respiration production of $CO_2$, can expect an increase in alkalinity from background. |
| **Dissolved Oxygen** | • For Enhanced In Situ Biodenitrification to occur, DO concentrations must be suppressed (<2 mg/l). |
| **pH** | • For EISBD to occur effectively, pH ranges can vary considerably (6.0 – 8.5) |
| **Redox** | • Redox will indicate which parameter serves as an electron acceptor<br>• Nitrate will be $e^-$ acceptor near ORP of 750 mv |
| **Dissolved Manganese and Iron** | • If dissolved manganese is present, indicates Redox is too low and matrix Mn/Fe is serving as $e^-$ acceptor. |
| **Phosphorous (P)** | • For EISBD (Enhanced In Situ Biodenitrification) to occur effectively, P needs to be available for microbial metabolism |
| **Total Organic Carbon** | • TOC analysis will indicate availability of naturally occurring carbon sources ($e^-$ donor). |

EISBD = Enhanced In Situ Biodenitrification

## Nitrogen Transformation Reactions

**Nitrate Generating Reactions**

$RNH_2 + H_2 \longrightarrow NH_4^+ +$ energy (ammonification)

$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H +$ energy

$2NO_2^- + O_2 \longrightarrow 2NO_3^- +$ energy (nitrification)

*R signifies an organic compound

**Denitrification Reaction**

$5C + 4NO_3^- + 2H_2O \longrightarrow 2N_2 + 4HCO_3^- + CO_2$

**Nitrate Degradation sequence**

$NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$

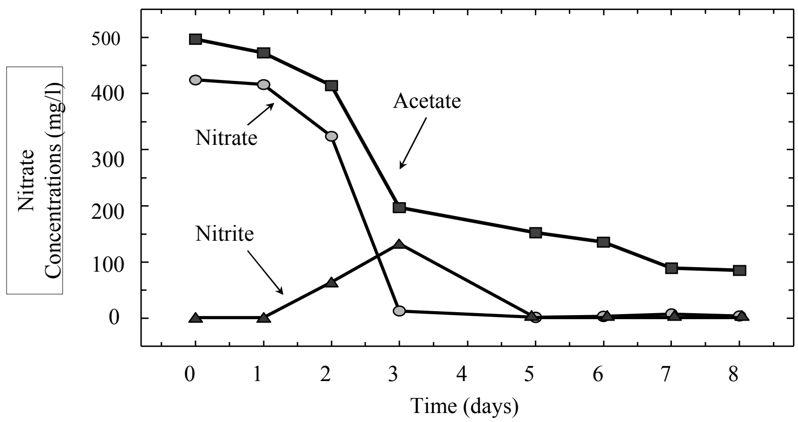
No associated notes

# Stoichiometric Ratios

| Chemical | Consumed C Amendment in denitrifying 1 mg $NO_3$-N |
|---|---|
| **methanol** | 1.91 mg of methanol |
| **acetate** | 2.64 mg of acetate |
| **ethanol** | 1.37 mg of ethanol |
| **sucrose** | 2.55 mg of sucrose |

No associated notes

# Biologically Accelerated Denitrification




To convert the numbers above to Nitrate Nitrogen values divide the number by 4.4

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## Enhanced *In Situ* Biodenitrification at field scale

- Demonstration - Technical effectiveness of in situ denitrification for an active amendment delivery system
- Location -Albuquerque’s.
  - 40-year old nitrate plume covers 550 acres with a volume of 1.69 billion gallons (6.4 billion liters)
- Cause - Over fertilization on a vegetable farm in the 1950s
- Information - Water table is 72 ft (22 m) below ground surface, top 32 ft (10 m) of the saturated zone are contaminated with 90-500 mg/L of nitrates
- Health - Near this site in 1980, a Blue Baby Syndrome incident was due to this plume
  - Demonstration by the NM Environment Dept & University of NM

**Abstract.** The purpose of this demonstration is to evaluate the technical effectiveness of in situ denitrification for an active amendment delivery system (inverted 5-spot recirculating well pattern).

The University of New Mexico teaming, with the New Mexico Environmental Department designed, constructed, and tested an inverted 5-spot recirculating well pattern denitrification system at the Mt. View site located in Albuquerque’s So. Valley. In this treatment pattern, water is pumped from each of the four corner wells and then re-injected following metered addition of a carbon source amendment into a center well. In this rather stagnate plume (nitrate contamination has been present for over 40 years) it is necessary to deploy an active pumping system to mix the carbon source with the contaminated groundwater.

## Steps in Biodenitrification

- Injection of sodium acetate (NaAc) Amendment into the contaminated ground water
- Consumption of NaAc by indigenous bacteria as an energy source
- Reduction of nitrate into nitrogen gas by bacteria
- Oxidize acetate to $CO_2$

No associated notes

# Denitrification Reactions

- Metabolic reaction:

  $0.625\ Ac + NO_3 \rightarrow 1.25\ HCO_3 + 0.5\ N_2$

- Cell synthesis reaction:

  $3.5\ Ac + NO_3 \rightarrow C_5H_7O_2N + 2\ HCO_3$

- Combined reaction:

  97% metabolic + 3% cell synthesis

  $0.712\ Ac + NO_3 \rightarrow 0.485\ N_2 + 0.03\ C_5H_7O_2N + 1.273\ HCO_3$

  - $C_5 H_7 O_2 N$ represents the chemical composition of cellular material

No associated notes

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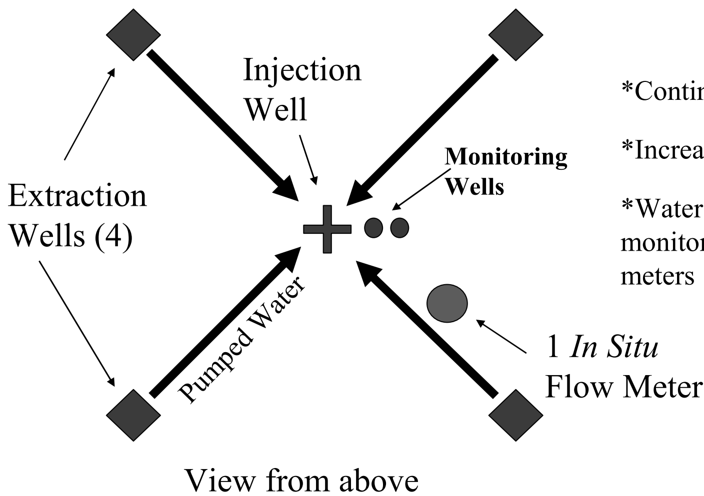
## Design/Operating Parameters

- Active amendment delivery system and mixing of nutrients with ground water
- Recirculating injection of nutrient-amended water into aquifer
- Four extraction wells at corners of square grid pattern (100 ft.x 100 ft.) (30.5 x 30.5 m), one center re-injection well, all screened from 42-65 ft (12.8 – 19.8 m).
- Two *in situ* flow meters
  - **Within 5 spot near injection well, depth at ~50 ft. (15.2 m)**
  - **Downgradient of system, depth at ~50 ft (15.2 m).**
- Total of 80,000 gallons of amended water from 4 wells re-injected into aquifer at a flow rate of 5 gal/min
- Amendment tank volume 200 gal, flow rate of 250 ml/min, injected and mixed directly in underground piping system
- Sodium acetate - 99.5 g/l, trimetaphosphate - 1.45 g/l

No associated notes

# Inverted 5-Spot Amendment Delivery System




*Continuous Denitrification

*Increases Water Movement

*Water movement can be monitored by *in situ* flow meters

No associated notes

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# Inverted 5 Spot Pattern Demonstration at South Valley, New Mexico

No associated notes

# Monitoring and Analytical Methods for Inverted 5 Spot Pattern

- Monitoring wells
  - shallow (~50 ft.) (15.2 m)
  - deep (~65 ft.), (19.8 m)
  - analyzed at 8, 23, 29 and 64 days post-treatment
- Bromide Tracer injected and measured with Ion Selective Electrode
- Nitrate and nitrite measured with Ion Chromatograph

No associated notes

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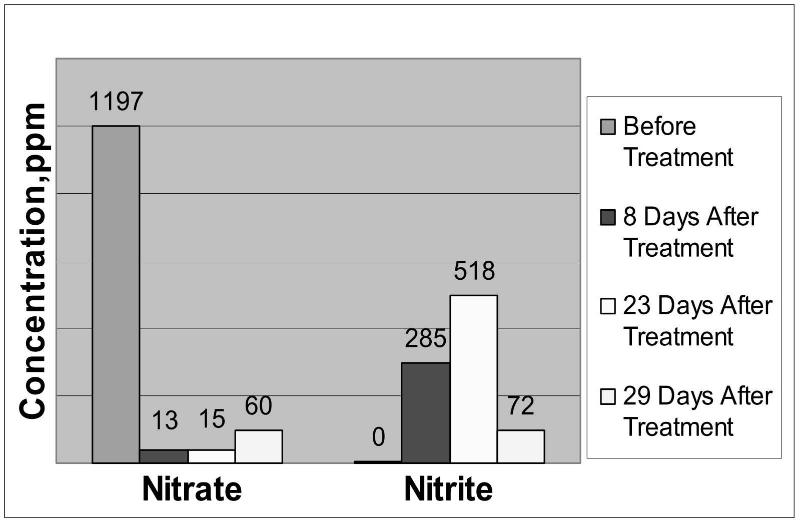
## *In Situ* Flow Meter (3-D)

- Warmer temperatures recorded on down stream side of flow sensor
- Measured velocities from .01 to 2 ft/day
- Before pumping (0.1ft/day)
- After pumping (1.2 ft/day)



No associated notes

## Nitrate and Nitrite concentrations, as $NO_3$, before and after treatment (Shallow Well)




No associated notes

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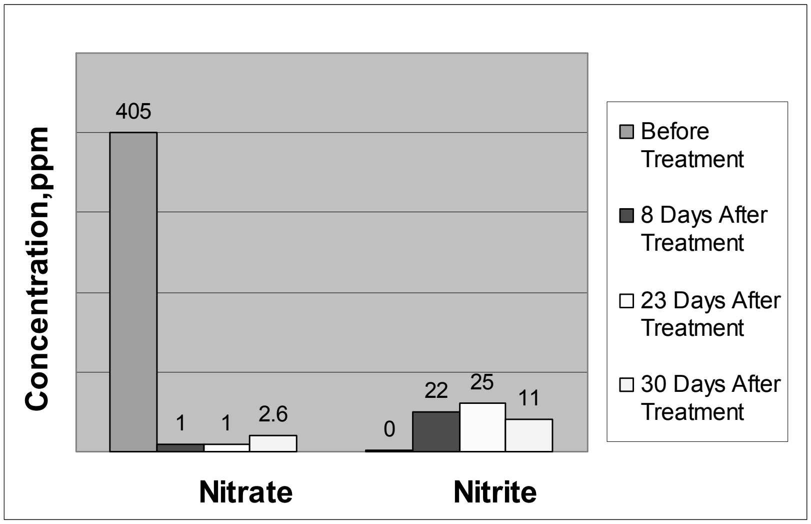
## Nitrate and Nitrite concentrations, as $NO_3$, before and after treatment (Deep Well)




No associated notes

# Conclusions

Successes

- Large-scale *in situ* bioremediation system for nitrate-contaminated ground water plume was successful
  - Reduced nitrate concentration below 10 mg/l
  - Approximately 450 Kg (1000 lbs) of nitrate were converted to nitrogen gas
  - Inverted 5-spot pattern provided good mixing, wide aerial sweep & easy operation.

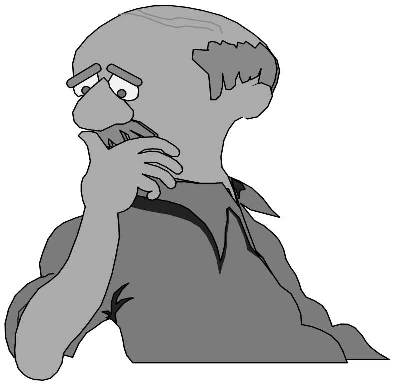
Challenges

- Biofouling of the injection well
  - Common to most ISB systems
  - Control measure should be incorporated
  - Will increases project costs
- Assure nitrite reduction goes to completion
- In the future, biofouling control measures will be incorporated into active system

No associated notes

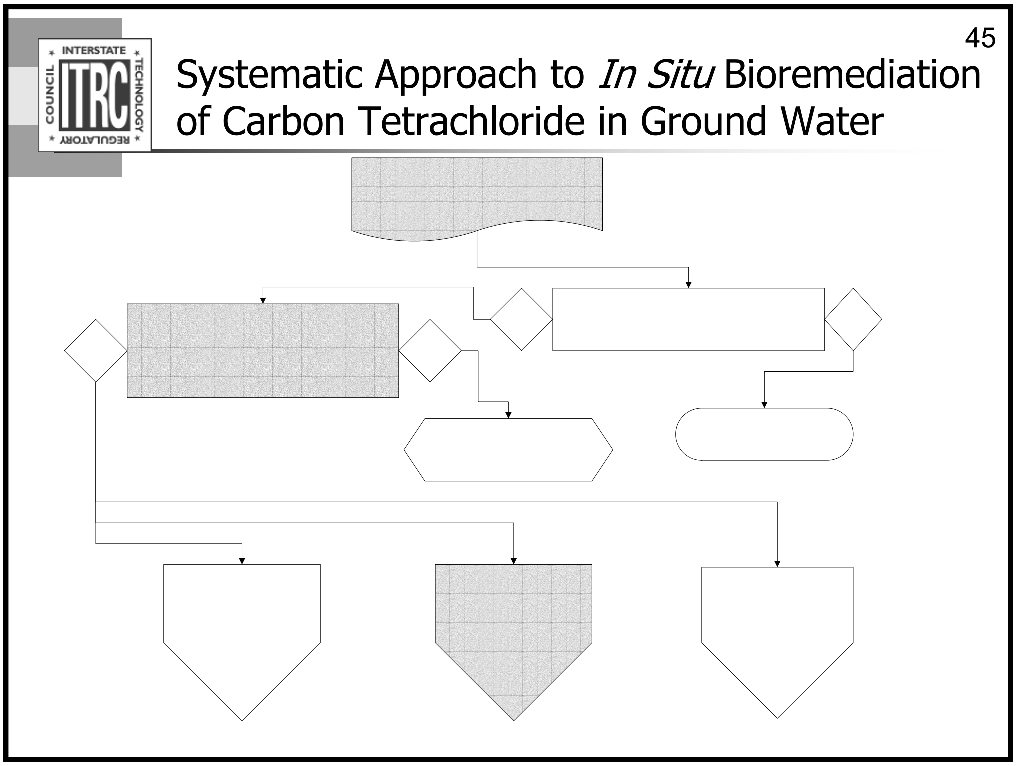
## Questions & Answers

**???**



The ITRC Document:
"Systematic Approach to *In Situ* Bioremediation in Groundwater: including Decision Trees on Nitrate, Carbon Tetrachloride and Perchlorate" is downloadable in the links page at the end of today's presentation.

No Associated Notes

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## Carbon Tetrachloride Pervasiveness

- Found at 22% of Superfund sites
- Historic grain silo sites
- Found at chlorinated solvent releases
- Found at DOE facilities

Please refer to Sections 9.2.1, 9.2.2, and 9.2.5 of the Guidance document

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## Carbon Tetrachloride Sources of Contamination

These previous uses of Carbon Tetrachloride resulted in contamination:

- Past use to make refrigerants
- Propellants in aerosol cans
- Used in fire extinguishers
- Past use as a grain storage fumigant
- Cleaning fluid
- Cold War use to recover plutonium

Please refer to Sections 9.2.1, 9.2.2, and 9.2.5 of the Guidance document

# Degradation Products and Properties

| Property | CT ($CCl_4$) | CF ($CHCl_3$ ) | DCM ($CH_2Cl_2$) | CM ($CH_3CL$) |
|---|---|---|---|---|
| **Molecular weight** | 153.82 | 119.38 | 84.93 | 50.49 |
| **Density/Specific Gravity @ 20 ºC** | 1.5940 | 1.4835 | 1.3255 | 0.92 |
| **Partition Coefficient ($K_{OC}$)** | 110 | 31 | 21 | 6 |
| **Water Solubility mg/L @ 25 ºC** | 793 | 7,710 C | 13,000 | 6,500 |
| **Henry's Law Constant atm-cu meter/mole @ 25 ºC** | $2.76 \times 10^{-2}$ | $3.67 \times 10^{-3}$ | $3.25 \times 10^{-3}$ | $1.27 \times 10^{-2}$ |
| **Boiling Point** | 76.8 ºC | 61.2 ºC | 39.75 ºC | -24.2 ºC |
| **Melting Point** | -23 ºC | -63.2 ºC | -95 ºC | -97.6 ºC |
| **Vapor Density (Air=1)** | 5.32 | 4.12 | 2.93 | 1.8 |
| **Vapor Pressure (mmHg)** | 115 | 197 | 435 | 2,103 |

Please refer to Table 9-1 of the Guidance document for a more complete table

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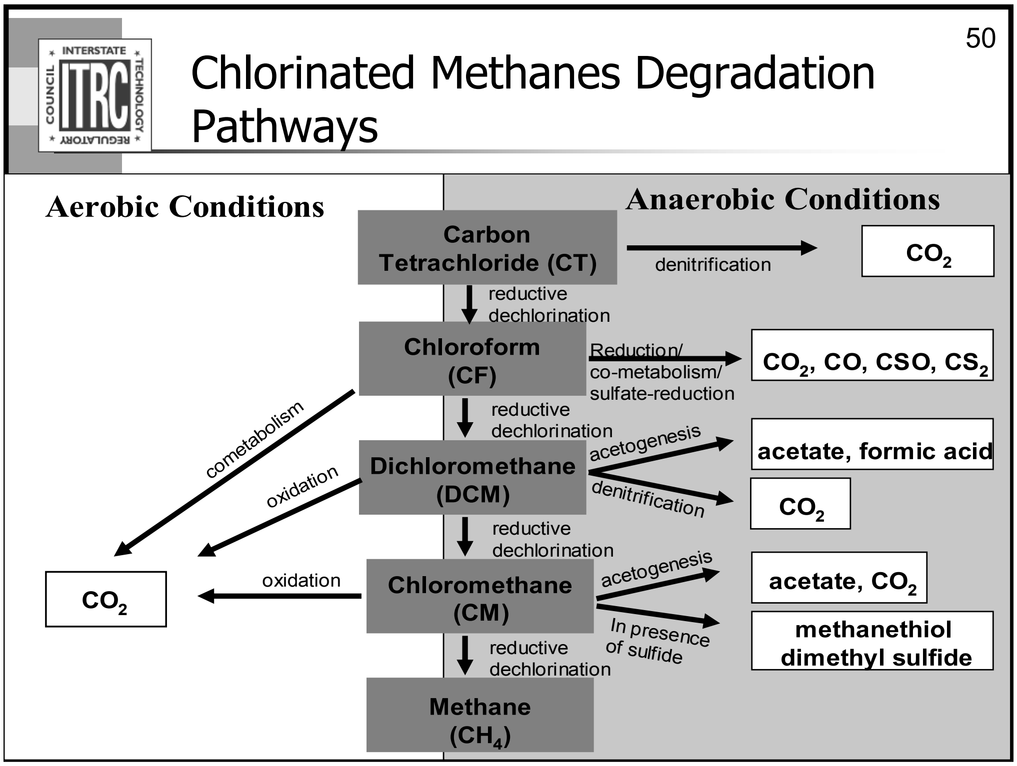
## Contaminant Relationships

- Degradation products
  - CF, DCM, CM
- Petroleum hydrocarbons
- Nitrate
- Grain fumigant
  - "80-20" (CT and carbon disulfide)
  - "70-30" (DCA and CT)
  - Organophosphate pesticides
  - Chloropicrin ($Cl_3CNO_2$)
  - EDB

Please refer to Sections 9.2.1, 9.2.2, and 9.2.5 of the Guidance document



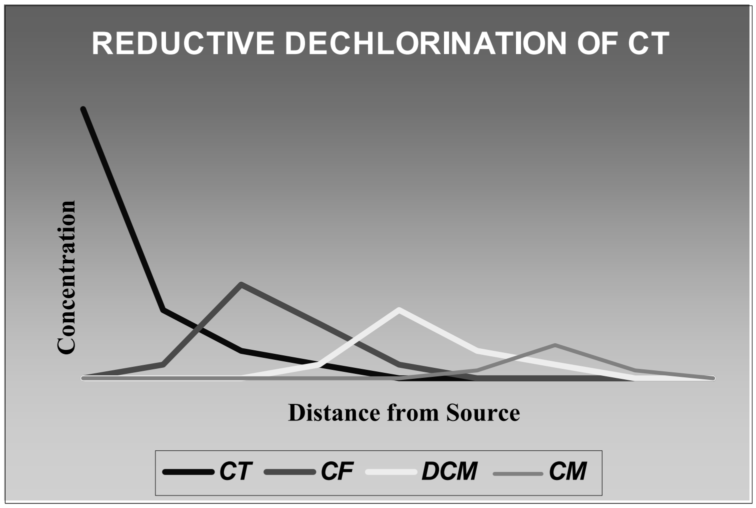

Please refer to Figure 9-4 of the Guidance Document

# Direct Reductive Dechlorination of CT

- Bacteria Halorespire CT that serves as an electron acceptor
- Two electrons are transferred at each step (source of energy for bacteria)
- CT sequentially reduces and looses a Cl ion during each step
- CT $\longrightarrow$ CF $\longrightarrow$ DCM $\longrightarrow$ CM $\longrightarrow$ $CH_4$

Please refer to section 9.3.3.1 and Figure 9-1 (Reductive Dechlorination Decision Tree) of the guidance document.

# Idealized Sequence of Direct Reduction of Chlorinated Methanes




No associated notes

## Anaerobic Cometabolism

- Cometabolic Reductive Dechlorination
  - CT is fortuitously degraded by enzymes or cofactors and degradation products appear
- Cometabolic Denitrification
  - Occurs under denitrifying conditions
  - Results in little to no production of CF
  - Requires a greater management of an enhanced ISB system

Please refer to sections 9.3.3.2 through 9.3.3.4 and Figure 9-2 (Cometabolic Denitrification Decision Tree) of the guidance document.

## Case Study – Cometabolic Denitrification

- Schoolcraft, Michigan CT plume
- Full scale ISB project implemented to treat plume at leading edge
- Bioaugmentation of *Pseudomonas stutzeri KC*
- Row of extraction and injection wells to create a biocurtain for contaminant interception and destruction
- Successfully removed CT and $NO_3$

http://www.egr.msu.edu/schoolcraft/story/html

## Case Study – Cometabolic Denitrification

- 200 Area at Hanford DOE (Central Plateau)
- Possibly 600,000 Kg of CT entered soil column
- ISB demonstration between 1995-1996
- CT ~ 2 mg/l, $NO_3$ ~ 250 mg/l
- GW extracted, nutrients added, re-injected
- Approximately 2 Kg of CT destroyed with little CF production

http://apps.em.doe.gov/ost/pubs/itsrs/itsr1742.pdf

# Case Study –Cometabolic Reductive Dechlorination

- Grain silo in Tucumcari, NM
- Discovered while conducting a LUST investigation, plumes comingled
- $NO_3$ background of 20 mg/l $NO_3$-N
- Gasoline served as electron donor
- Observed degradation products of CT
- Observed cometabolic denitrification

http://www.nmenv.state.nm.us/gwb/intricom/html

## Fate and Transport

- Since there are many competing pathways catalyzed by different bacteria, there is no simple stoichiometric equation.
- Reductive Dechlorination Pathway is straightforward.

$$2(CCl_4) + 3(C_3H_5NaO_3) + 13\ (OH^-) \longrightarrow 3Na^+ + 8\ Cl^- + 11CO_2 + 28\ H^+$$

Please refer to section 9.4 of the guidance document.

# Essential Parameters

| PRIMARY ANALYTE | REASON FOR ANALYSIS |
|---|---|
| **CT** | Decreases in concentration if ISB is occurring |
| **CF** | This CoC is a degradation product of reductive dechlorination of carbon tetrachloride |
| **DCM** | This CoC is a degradation product of reductive dechlorination of carbon tetrachloride |
| **CM** | This CoC is a degradation product of reductive dechlorination of carbon tetrachloride |
| **Chloride** | An increase in chloride concentration from background may indicate a reductive dechlorination of carbon tetrachloride. |
| **Nitrate/nitrite** | This CoC is expected to decrease in concentration if bioremediation is occurring. Also, if this electron acceptor becomes depleted, carbon tetrachloride may reductively dechlorinate creating degradation products. |

No associated notes

# Essential Parameters Cont'd

| PRIMARY ANALYTE | REASON FOR ANALYSIS |
|---|---|
| **Dissolved Mn and Iron** | If dissolved manganese or iron is present, indicates ORP is too low and matrix Mn/Fe is serving as $e^-$ acceptor. |
| **Sulfate** | If sulfate concentrations are less than background and ORP is low, sulfate may be serving as an electron acceptor and reduction may be occurring. |
| **Sulfide** | If sulfide ($H_2S$) concentrations are greater than background, sulfate may be serving as an electron acceptor producing sulfides. |
| **Phosphorous (P)** | For ISB of carbon tetrachloride to occur effectively, sufficient P needs to be available for microbial metabolism. (P may need to be added as an amendment) |
| **Total Organic Carbon** | TOC analysis will indicate availability of naturally occurring carbon sources ($e^-$ donor). |
| **Methane** | This constituent may be present as the final degradation product of carbon tetrachloride dechlorination or may be present if ORP conditions are so low that methanogenesis is occurring. |

No associated notes

# Essential Field Parameters

| PRIMARY ANALYTE | REASON FOR ANALYSIS |
|---|---|
| **Alkalinity** | Due to microbial respiration production of $CO_2$, you can expect an increase in alkalinity from background. |
| **Dissolved Oxygen (DO)** | For ISB of carbon tetrachloride to occur, DO concentrations must be depleted (<2 mg/l). |
| **pH** | ISB of carbon tetrachloride occurs effectively in wide pH ranges (5.5-9.5). |
| **ORP** | The ORP may be used in conjunction with electron acceptor concentrations as a qualitative indicator of ORP conditions and in identifying which electron acceptor(s) may be active. |

No associated notes

# Regulatory Standards

| *State* | Numeric Standards (µg/L) | State Regulation |
|---|---|---|
| **New Mexico** | CT – 10<br>CF – 100<br>DCM – 100<br>CM – no numeric standard | New Mexico Water Quality Control Commission Regulation 20.6.2.3103 NMAC |
| **New Hampshire** | CT – 5<br>CF – 6<br>DCM – 5<br>CM – 3 | New Hampshire<br>Groundwater Management and Groundwater Release Detection Permits<br>Env-Wm 1403 |
| **Arizona** | CT– 5<br>CF – no numeric standard<br>DCM – 5<br>CM – no numeric standard | |
| **Virginia** | | Uses Safe Drinking Water Act, part 141, title 40 CFR. |
| **Colorado** | CT– 0.27<br>CF – 6<br>DCM – 4.7<br>CM – no numeric standard | Water Quality Control Commission (5 CCR 1002-41) |

No associated notes

# Regulatory Standards (cont'd)

| State | Numeric Standards (µg/L) | | | | State Regulation |
|---|---|---|---|---|---|
| Missouri | | Scenario A | Scenario B | Scenario C | RSMo §260.565 -260.575 and administrative rule 10 CFR 25-15.010 |
| | CT | 2 | 3 | 5 | |
| | CF | 0.8 | 1 | 1 | |
| | DCM | 51 | 71 | 150 | |
| | CM | No numeric standard | | | |
| Oklahoma | CT– 4<br>CF – 10<br>DCM – no numeric standard<br>CM – 2.7 | | | | Oklahoma Standard for Groundwater Protection and Corrective Action Subchapter 7, §785:45-7-2 |
| North Dakota | CT- 5<br>CF - 100 MCL or HAL<br>DCM- 5<br>CM- 3 | | | | Standards of Quality for Waters of the state Chapter 33-16-02, ND Adm Code |
| Pennsylvania | Used Aquifers | | | Used Aquifers | Pennsylvania Land Recycling Program Regulations Subchapter C, §250.304 and §250.305 |
| | TDS ≤ 2,500 | | | TDS > 2,500 | |
| | CT | 5 | | 500 | |
| | CF | 100 | | 10,000 | |
| | DCM | 3 | | 300 | |
| | CM | 3 | | 300 | |

No associated notes

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## Challenges of CT ISB Systems

- Determining the reductive pathway most suitable for your site
  - Characterization
  - Lab scale treatability tests
  - Pilot scale field demonstrations
- Biofouling and amendment mixing
- Regulatory concerns

Please refer to sections 9.4.3, 9.5, and 9.6 of the guidance document for the above bullets, respectively.

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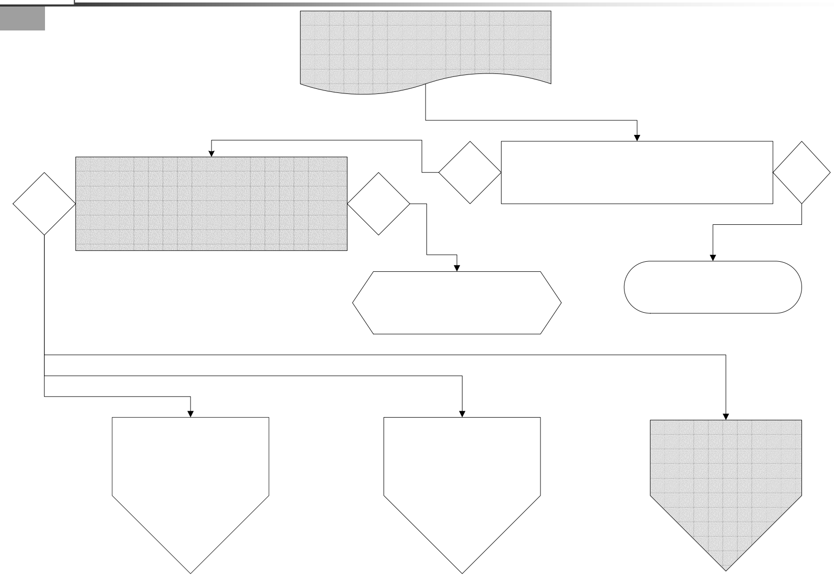
## Systematic Approach to *In Situ* Bioremediation of Perchlorate in Ground Water



Not a new Science

**Will E**

**Yes** **Biore**

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## Perchlorate

- Realization of widespread contamination in the US since 1997, following development of low level analytical method (ppb).
- Human health concerns centered on thyroid gland effects
- EPA derived RfD of 1 μg/L, but toxicological studies are ongoing.
- Ecological studies also ongoing but exposure pathways still not well known.

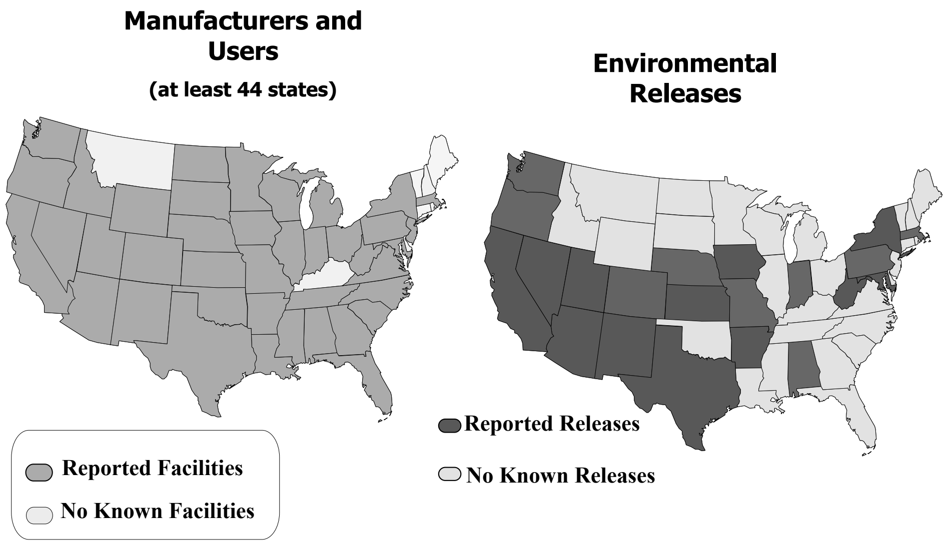
No associated notes

## Perchlorate Sources

- Contamination originates when perchlorate salts (ammonium, potassium, magnesium, sodium) dissolve in ground and surface waters
- Ammonium salt used as solid propellant for rockets, missiles, and fireworks
- Used in munitions, explosives
- Numerous industrial uses (airbag inflators, nuclear reactors, electroplating, paint manufacture, etc.)
- Rare natural occurrences

Please refer to sections 10.2 and 10.3

# Perchlorate Pervasiveness




Please refer to Sections 10.2 and 10.3

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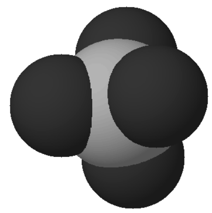
## Properties of Perchlorate Ion



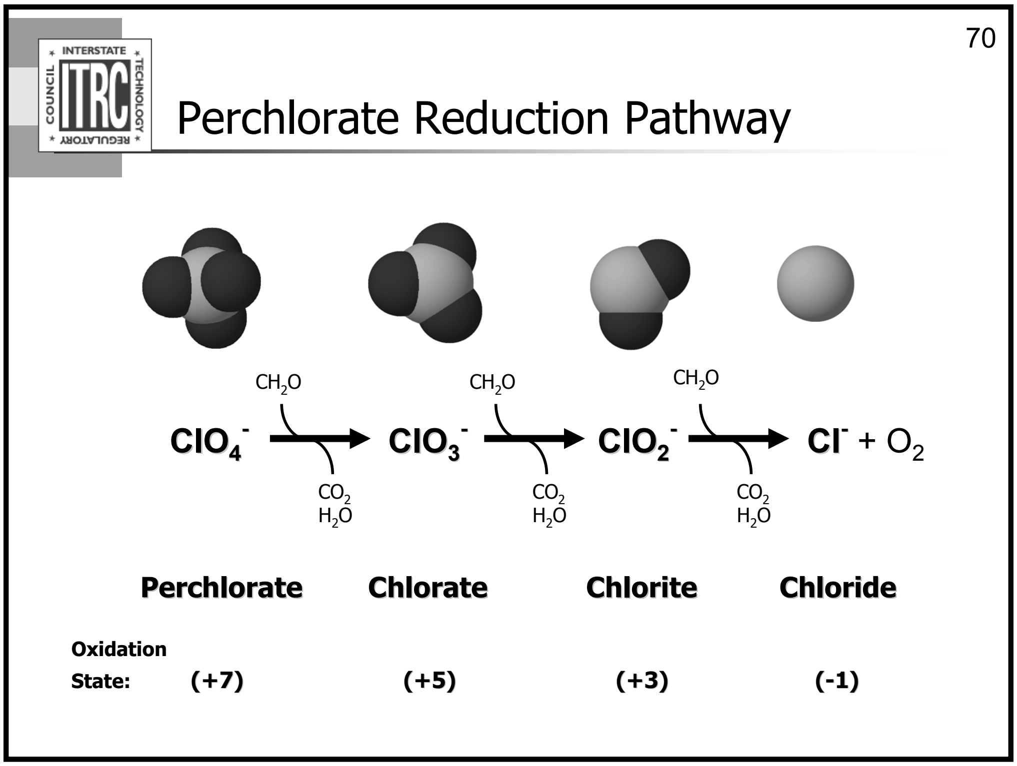
- Not volatile
- Highly soluble
- Does not adsorb strongly to surfaces (negatively charged ion)
- Stable in ground water environments
- Not readily reduced due to kinetic barriers

Please refer to section 10.3.2 and table 10-1

## Contaminant Relationships

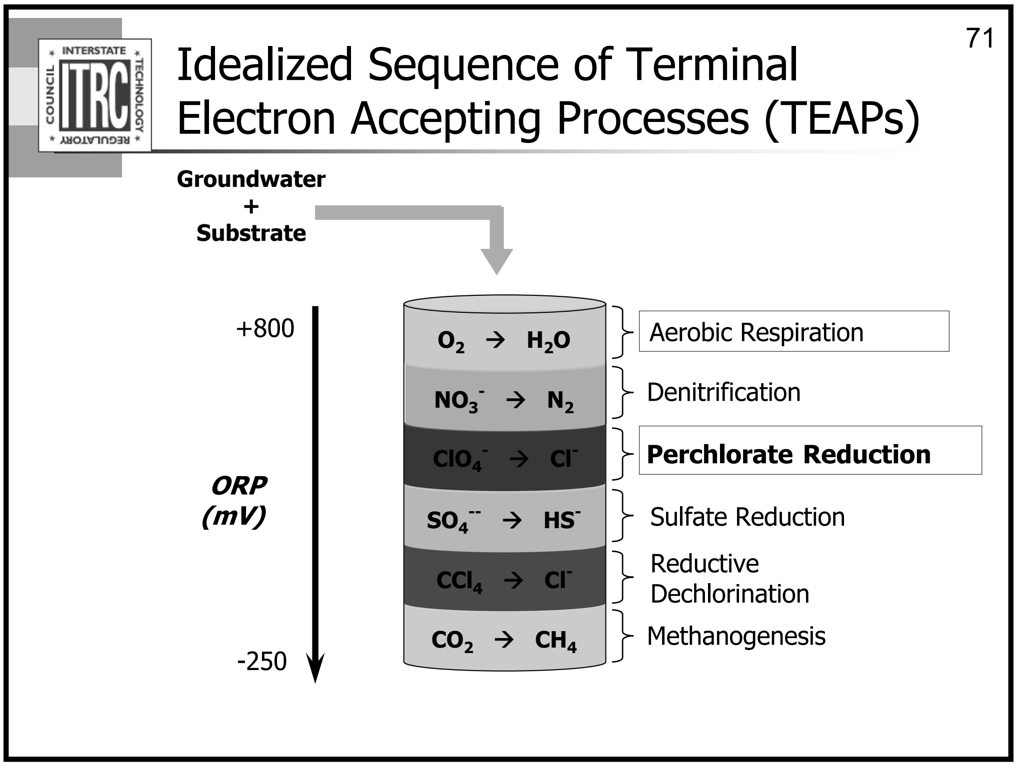
- Degradation Products:
  - Chlorate ($ClO_3^-$)
  - Chlorite ($ClO_2^-$)
  - Chloride ($Cl^-$)
- Co-contaminants include:
  - Nitrate
  - Sulfate
  - VOCs
  - Nitroaromatic explosives (TNT, HMX, RDX)

Please refer to section 10.3.3




Progressive reduction in oxidation state of chlorine atom through loss of oxygen atoms

Please refer to section 10.5.3




- Microbiology
- chemistry
- hydrogeology
- engineering

# Essential Parameters

| | |
|---|---|
| **Dissolved Oxygen** | Low or absent for anaerobic conditions |
| **pH** | Optimal range is 6.5 – 7.5 |
| **ORP** | Optimal range is 0 to 100 mV.<br>If too low, sulfate reduction may be the dominant TEAP.<br>If too high, Mn oxide or nitrate reduction may be dominant TEAPs. |
| **Total Organic Carbon** | An adequate organic carbon source (electron donor) is needed for reductive degradation to occur. |
| **Nitrate + Nitrite** | Nitrate and nitrite may compete with perchlorate as electron acceptor |
| **Chlorate** | Intermediate degradation product, may be indicative of perchlorate reduction |
| **Chlorite** | Intermediate degradation product, may be indicative of perchlorate reduction, but may not be detected due to rapid reduction to chloride. |
| **Chloride** | Final degradation product of the reductive process.<br>May be difficult to distinguish from background values. |

Please refer to section 10.5 and table 10-4

# Current Perchlorate Regulatory Guidance

| | Drinking Water (μg/L) | Remediation (μg/L) |
|---|---|---|
| Arizona | | 14 (health based guide) |
| California | | 4 |
| Massachusetts | 1.5 | |
| New Mexico | | 1 |
| New York | 5 | |
| Nevada | 18 | 18 |
| Texas | | 4 |
| US EPA Guidance | 4 to 18 | |
| EPA Region 1 | | 1.5 |
| EPA Region 9 | 4 | 14 |

Please refer to section 10.4 and table 10-3 for additional information and references.

# Ex-Situ Bioremediation of Perchlorate

- Ex-situ Bioremediation of perchlorate is a proven technology:
  - Aerojet (N. CA)
    - 4 full-scale bioreactors operating since 1998
    - 2,500 µg/L consistently reduced to <4 µg/L
  - San Gabriel Superfund Site (CA)
  - Tyndall AFB (FL)
  - Thiokol (UT)
  - Longhorn Ammunition Plant (TX)
  - NWIRP (McGregor, TX)

Please refer to section 10.8.1

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# In-Situ Bioremediation of Perchlorate

- In-situ bioremediation of perchlorate is an emerging technology
- Laboratory-scale studies, R&D
  - Penn State University, Southern Illinois University, Envirogen, GeoSyntec
- Field Demonstrations
  - Aerojet (San Gabriel, CA)
  - Edwards AFB (CA)
- Biobarrier (immobile C source)
  - NWIRP ( McGregor, TX)
  - Baldwin Park OU, (San Gabriel, CA)

Please refer to section 10.8.1

## Technology Status/Future Needs of ISB for Perchlorate

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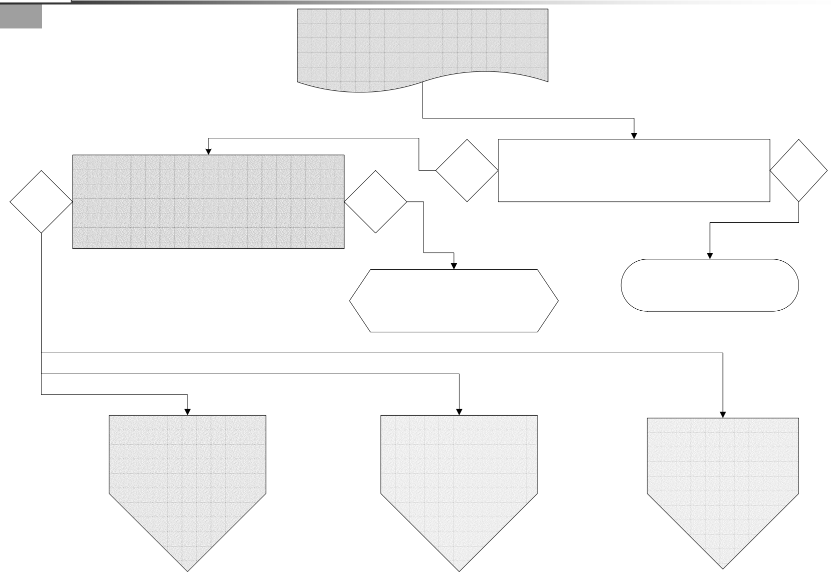
- Wide variety of potentially suitable electron donors for enhancing halorespiration (compost, mulch, vegetable oil, sugars, alcohols, lactate, acetate, etc.)
- ISB may be implemented through liquid phase injection or in biobarriers
- Few in-situ field applications have been completed, but more studies are underway
- Due to emerging nature of ISB, will require treatability testing and pilot-scale field demonstration on a site-specific basis

Please refer to sections 10.6.3 to 10.6.5

# In Summary



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## In Situ Bioremediation Issues

- Regulatory
  - RCRA 3020 (b)
  - Underground Injection Control
  - Contaminant Specific Issues

Biofouling (Section 4.4.7)

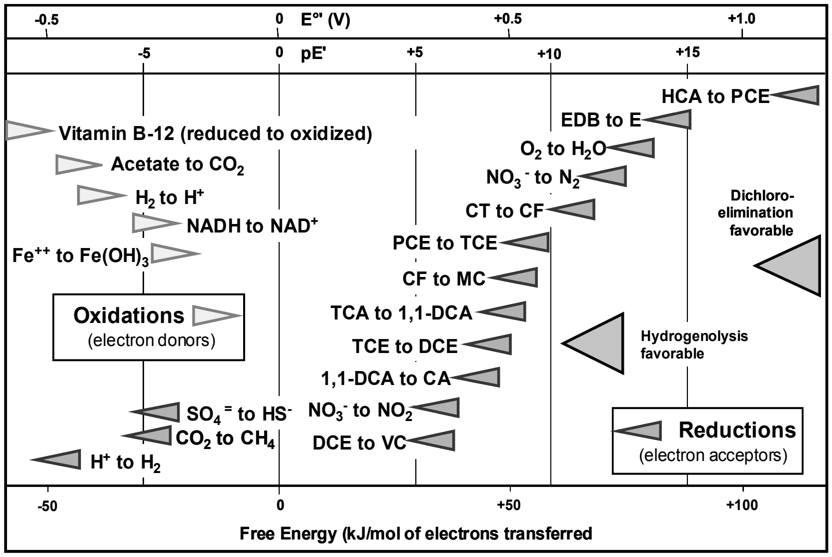
Amendment Mixing (Section 4.4.8)

# UIC Regulatory Variables

| STATE | STATUTE | REGULATION | POLICY | COMMENTS |
|---|---|---|---|---|
| New Mexico | Water Quality Act, Chapter 74, Article 6 NMSA 1978 | Water Quality Control Commission Regulations 20.6.2 NMAC | Draft MNA | Pollution Prevention Permits (Discharge Plans) are issued for injection of amendments |
| North Dakota | Underground Injection Control Program, Chapter 33-25-01 NDAC | Sections 16, 17 & 18 | | ISB wells are permitted by rule if part of a remediation project |
| Virginia | | | | Regulates ISB under each program like hazardous waste, surface water, and other remediation programs. Allows injection only For the purpose of remediation. |
| Missouri | Clean Water Act, 10 CSR206 | Class III Mineral Resources Injection Or Production Well Operating Permits | | |
| Colorado | NA | NA | NA | Colorado defers to UIC under USEPA Although ISB is regarded as std. remediation tool |

No associated notes

# Bottom line for ISB



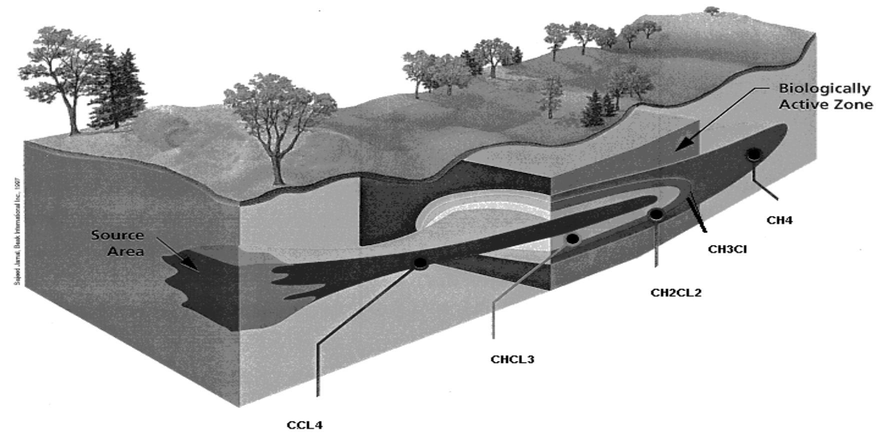

No associated notes

## Bottom line for ISB

- Understand subsurface hydro-geological regime (i.e. flow and transport)
- Understand contaminants (properties and fate)
- Create conditions conducive to biodegradation (substrates)
- Assure transforming microbes are present
- Touch ALL regulatory bases
- Implement ISB!!

No associated notes

# Questions & Answers




No associated notes

# Thank you for your participation

Links

To

Resources

Thank you for participating in ITRC Internet Training. To get more information on ITRC and to provide feedback – Go to www.itrcweb.org

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

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

**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