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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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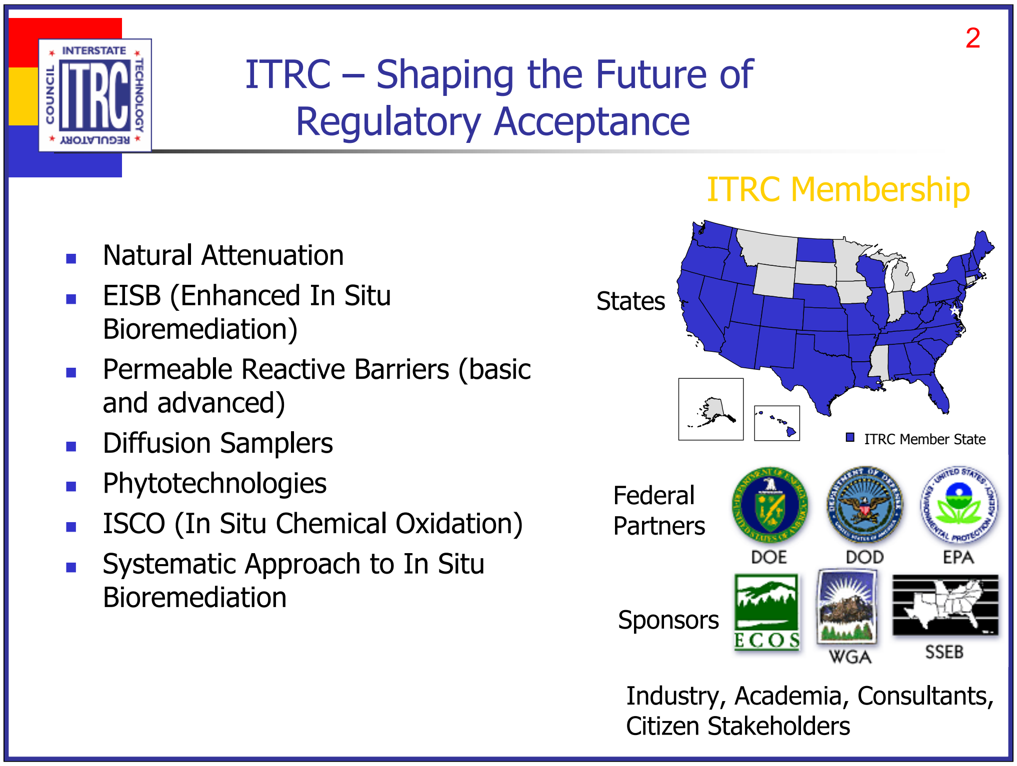

The bulleted items are a list of ITRC Internet Training topics – go to www.itrcweb.org and click on "internet training" for details.

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

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

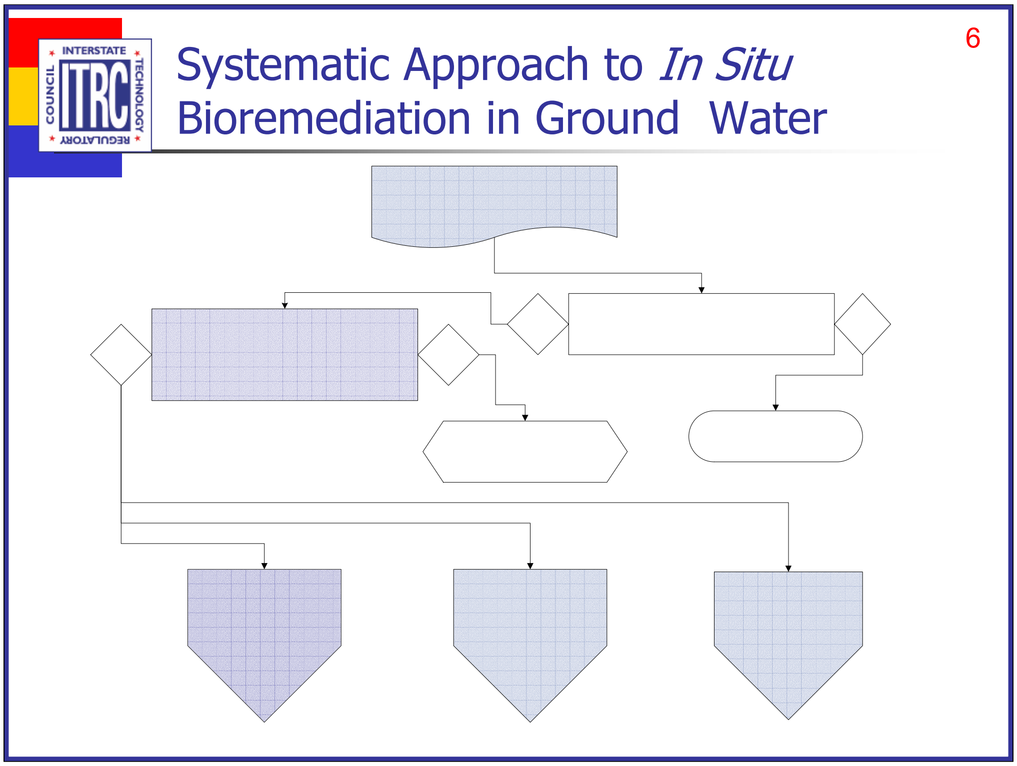
Engineered technique for optimizing subsurface conditions (hydrogeological, geochemical, microbial) to biodegrade contaminants in situ

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



Not a new Science

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Yes **Biore**

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Overview

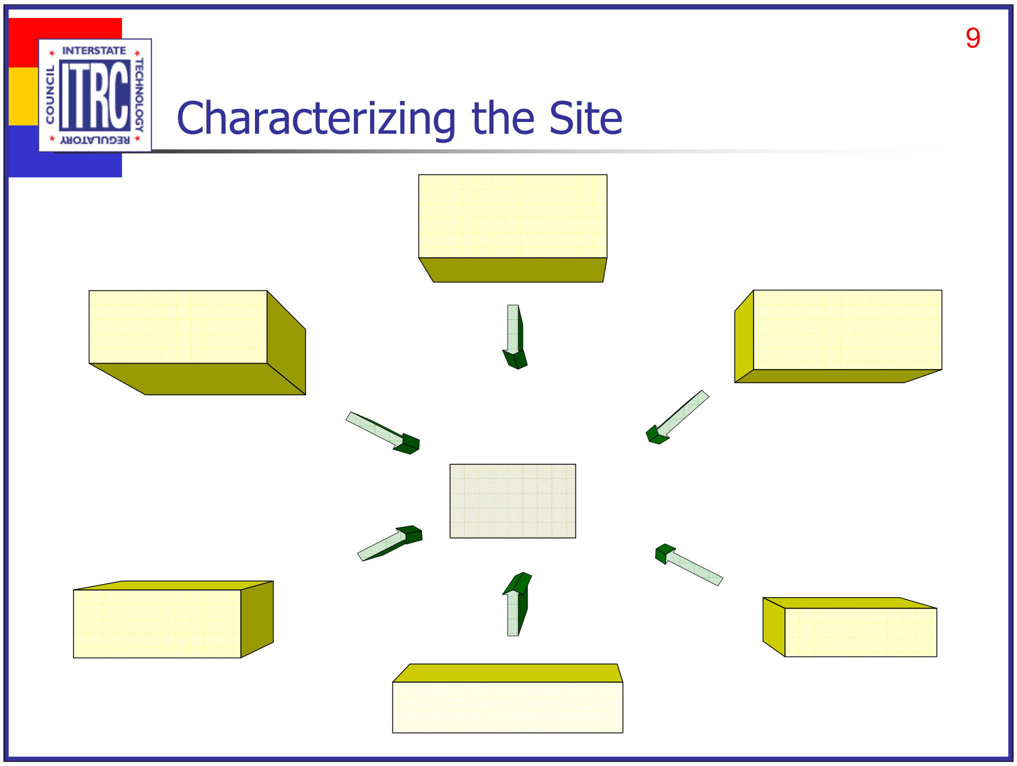
- First, Generic ISB Considerations
- Second, Specifics
- Third, Contaminants of Concern
  - Nitrate – NO_3 (Mature)
  - Carbon Tetrachloride CCl_4 (used but testing pathways is still underway)
  - Perchlorate – ClO_4^- (Immature)
- Finally, Bottom Line for ISB

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

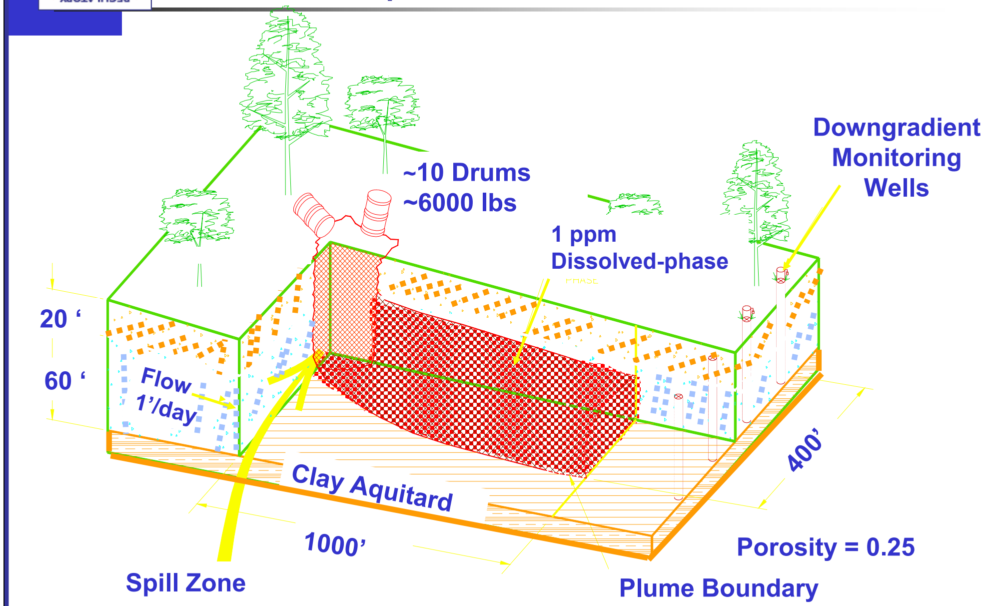
No associated notes

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



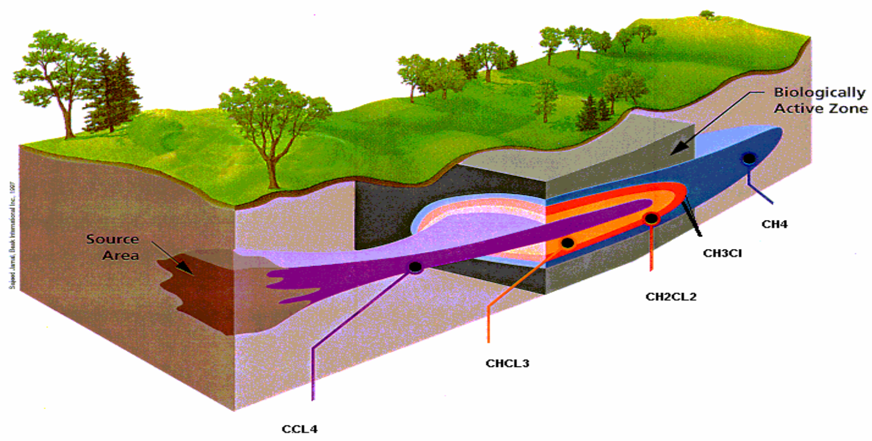
No associated notes

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

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

Transformation

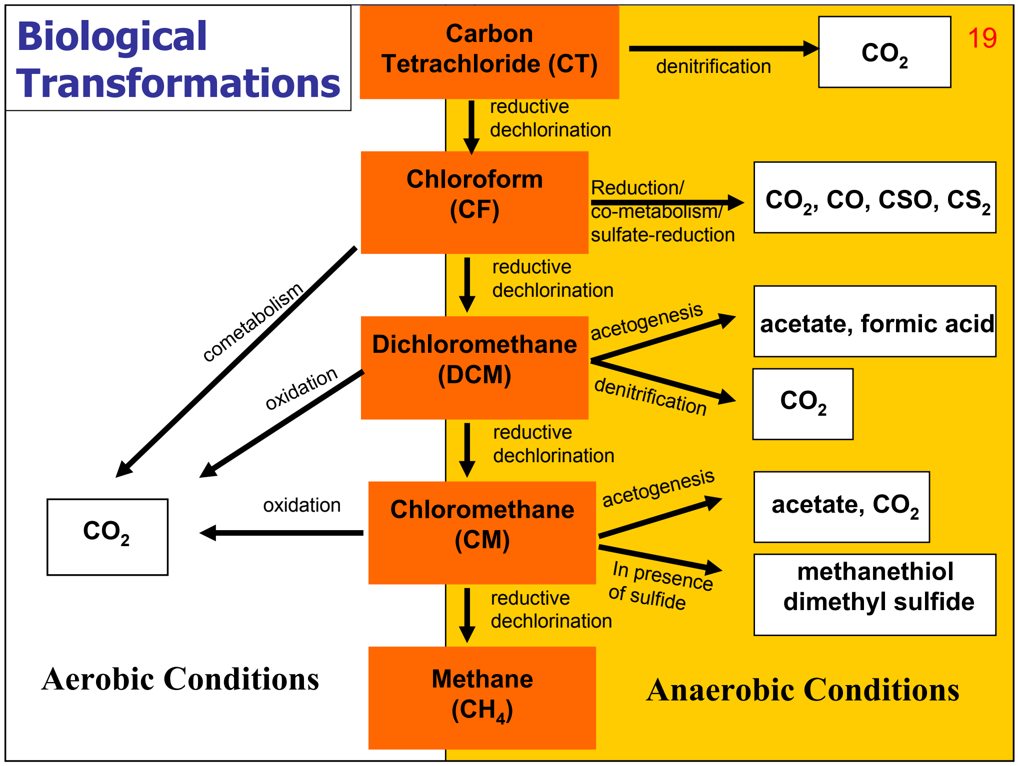
Abiotic

- 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

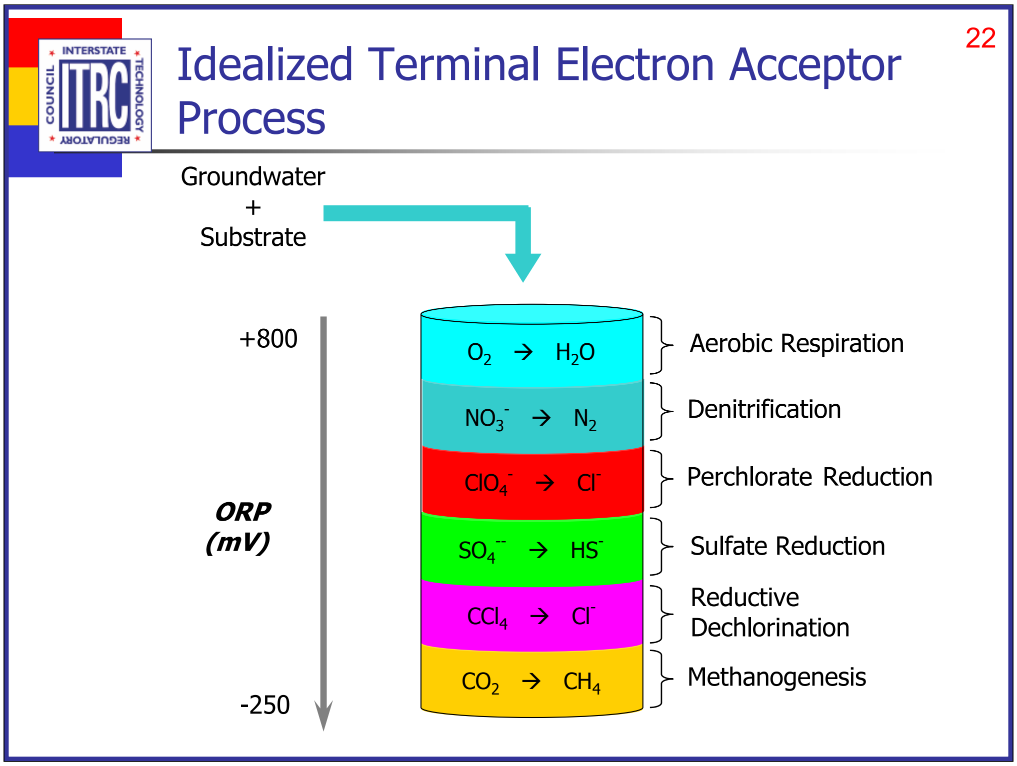
Primary Analytes for Groundwater	Reason for Analysis
Alkalinity	CO_2 and CO_3/HCO_3 are produced by microbial respiration, and an increase in alkalinity may indicate microbial growth from CO_2 or organic acid production that lowers the pH and solubilizes carbonate.
Chloride	Used as a conservative tracer; 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. 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. • 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. • 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 TOC may increase retardation of the COC due to sorption.

No associated notes



- Microbiology
- chemistry
- hydrogeology
- engineering

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Receptors

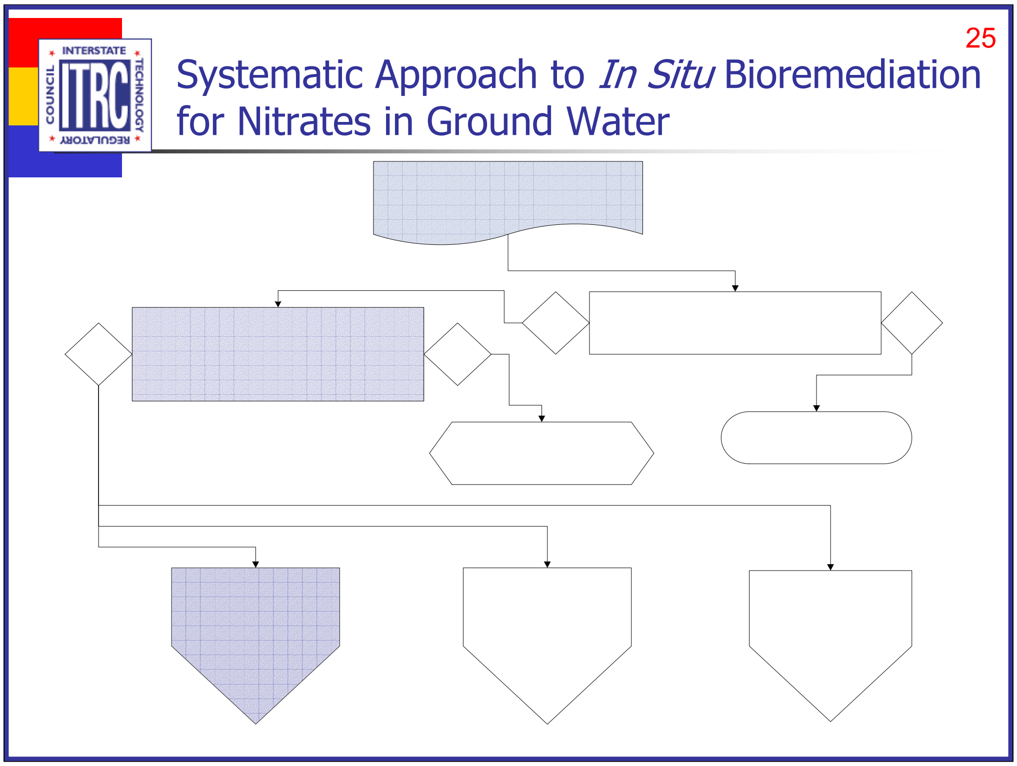
- Determine type and location
- Determine exposure/impact
- Mitigate exposure/impact (including use of ISB)

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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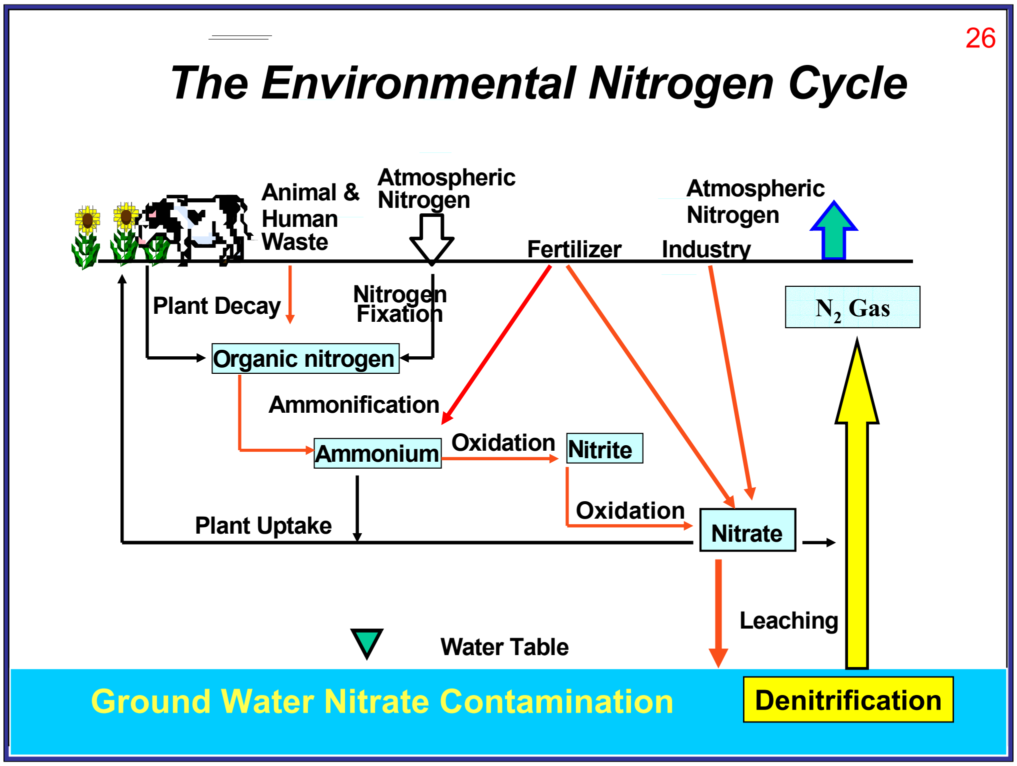

- Nitrate is a worldwide problem as a groundwater contaminant
- Biological denitrification of groundwater is under development as a technology to address this problem
- Maximum Contaminant Level (MCL) is 10 mg/L nitrate-N
- U.S. EPA estimates MCL is exceeded in 2.4% of domestic wells in U.S.
- Two major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

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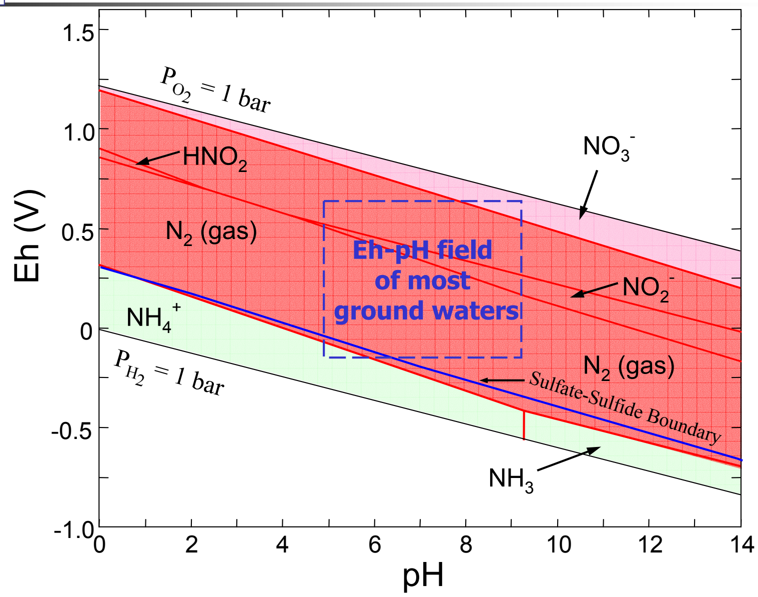
Nitrate Compound Properties

- **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 • 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

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

Nitrate Degradation sequence

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

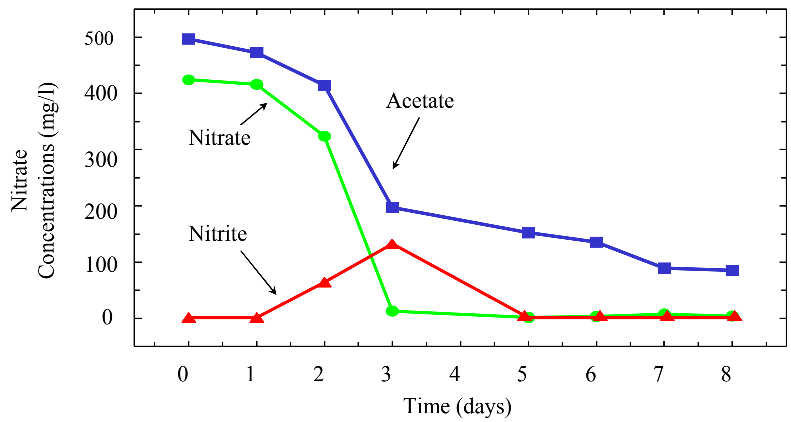
No associated notes

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

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

  - $C_5H_7O_2N$ represents the chemical composition of cellular material
  - Ac represents Acetate (CH_3COO^-)

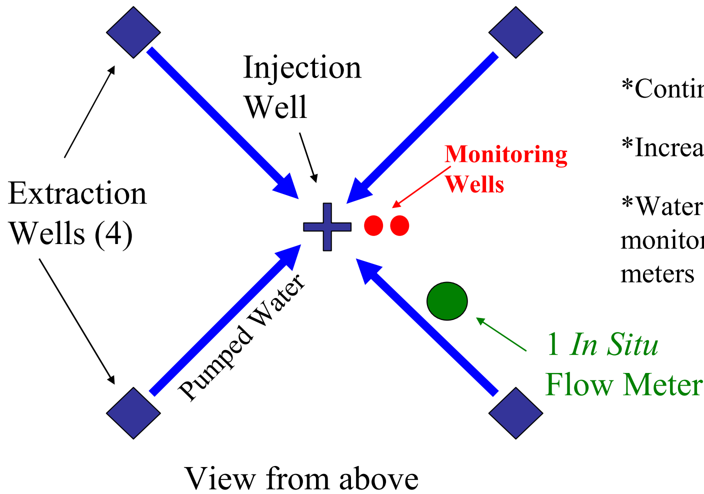
No associated notes

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

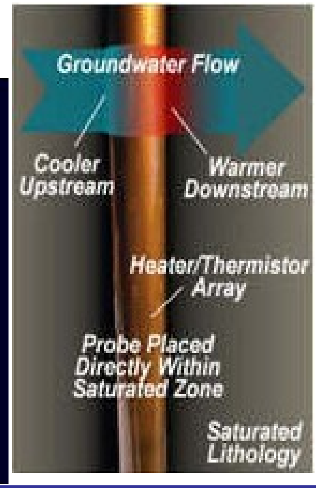
Monitoring and Analytical Methods for Inverted 5 Spot Pattern

- 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

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

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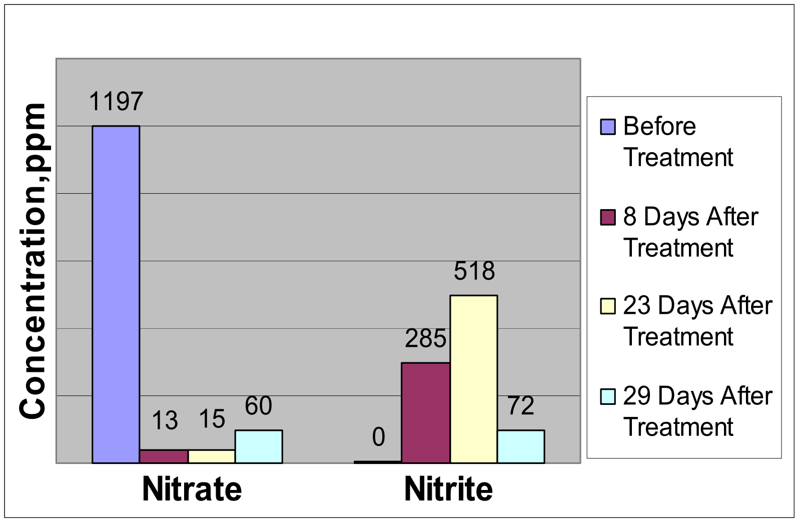
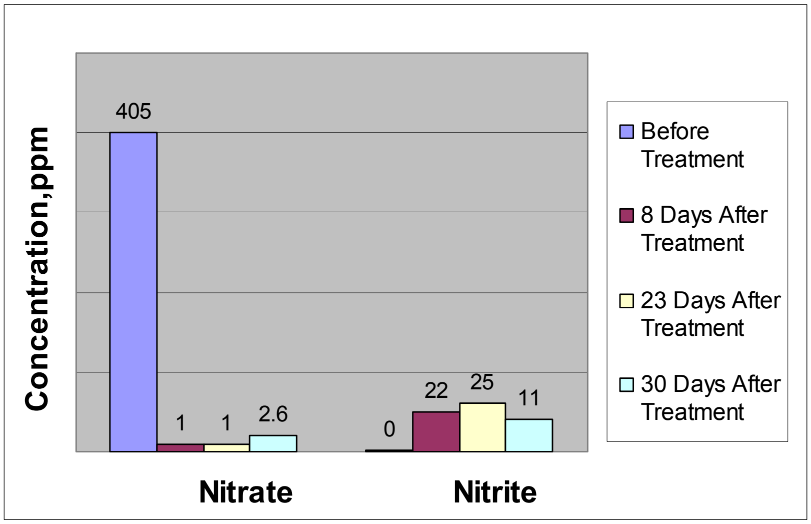
Nitrate and Nitrite concentrations, as NO_3, before and after treatment (Shallow Well)



No associated notes

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



No associated notes

Conclusions

Successes

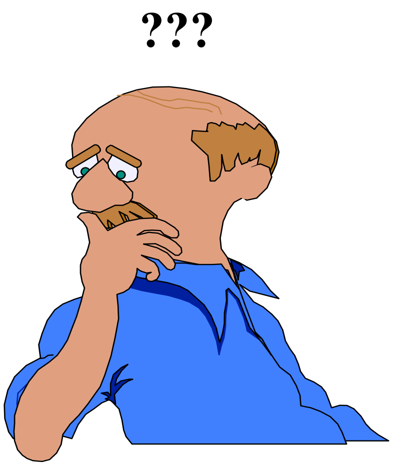
- Large-scale *in situ* bioremediation system for nitrate-contaminated ground water plume was successful
  - Reduced nitrate concentration below 10 mg/l
  - Approximately 450 Kg (1000 lbs) of nitrate were converted to nitrogen gas
  - Inverted 5-spot pattern provided good mixing, wide aerial sweep &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

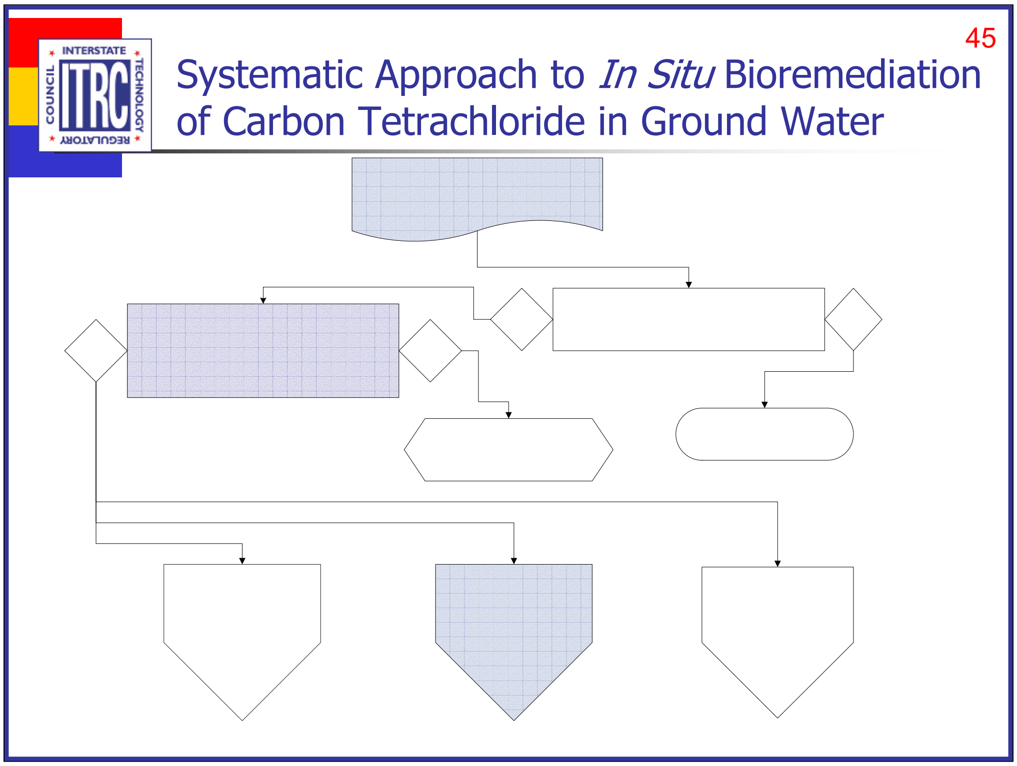
No associated notes

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

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	2.76×10^{-2}	3.67×10^{-3}	3.25×10^{-3}	1.27×10^{-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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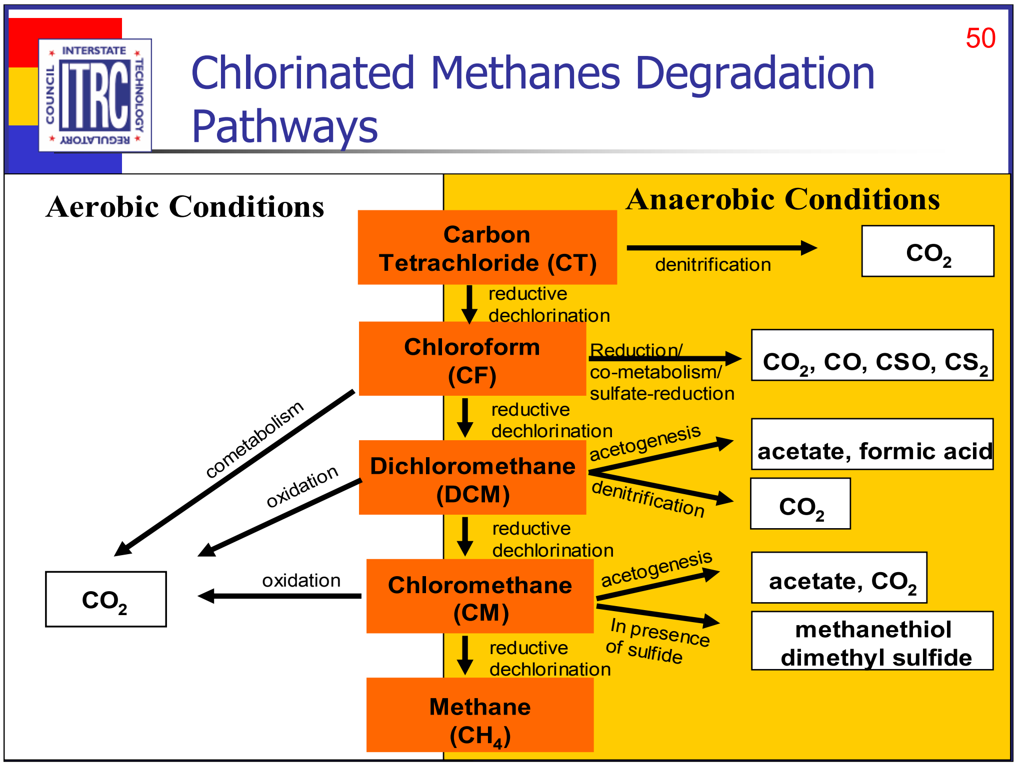
Contaminant Relationships

- 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.

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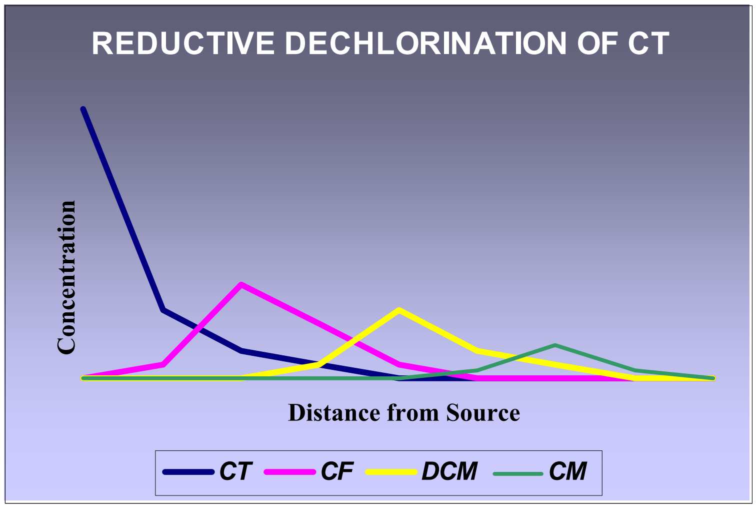
Idealized Sequence of Direct Reduction of Chlorinated Methanes



No associated notes

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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.

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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.

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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 CF – 100 DCM – 100 CM – no numeric standard	New Mexico Water Quality Control Commission Regulation 20.6.2.3103 NMAC
New Hampshire	CT – 5 CF – 6 DCM – 5 CM – 3	New Hampshire Groundwater Management and Groundwater Release Detection Permits Env-Wm 1403
Arizona	CT– 5 CF – no numeric standard DCM – 5 CM – no numeric standard	
Virginia		Uses Safe Drinking Water Act, part 141, title 40 CFR.
Colorado	CT– 0.27 CF – 6 DCM – 4.7 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
		Scenario A	Scenario B	Scenario C	
Missouri	CT	2	3	5	RSMo §260.565 -260.575 and administrative rule 10 CFR 25-15.010
	CF	0.8	1	1	
	DCM	51	71	150	
	CM	No numeric standard			
Oklahoma	CT– 4 CF – 10 DCM – no numeric standard CM – 2.7				Oklahoma Standard for Groundwater Protection and Corrective Action Subchapter 7, §785:45-7-2
North Dakota	CT- 5 CF - 100 MCL or HAL DCM- 5 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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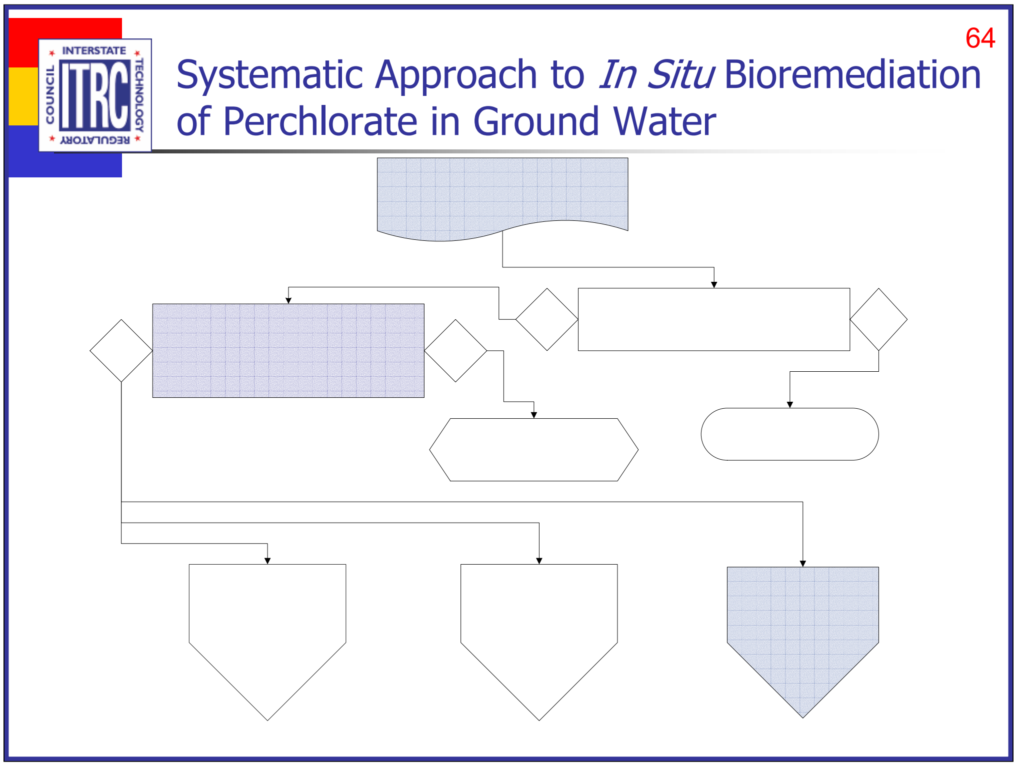
Challenges of CT ISB Systems

- 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.



Not a new Science

Yes

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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

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Perchlorate Sources

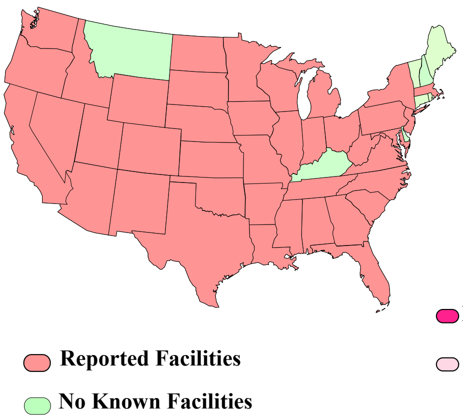
- Contamination originates when perchlorate salts (ammonium, potassium, magnesium, sodium) dissolve in ground and surface waters
- Ammonium salt used as solid propellant for rockets, missiles, and fireworks
- Used in munitions, explosives
- Numerous industrial uses (airbag inflators, nuclear reactors,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

Please refer to sections 10.2 and 10.3

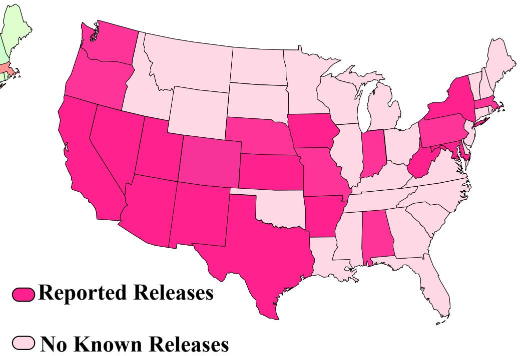
Perchlorate Pervasiveness

Manufacturers and Users

(at least 44 states)

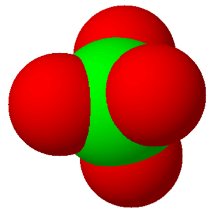


Environmental Releases



Please refer to Sections 10.2 and 10.3

Properties of Perchlorate Ion



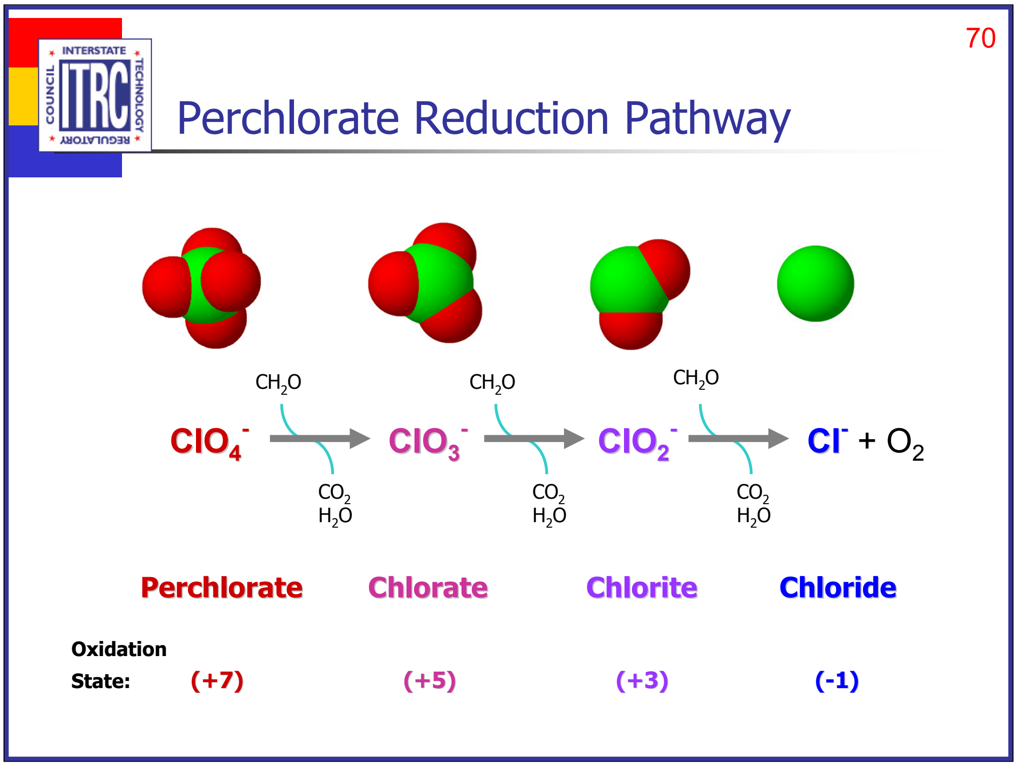
- Not volatile
- Highly soluble
- Does not adsorb strongly to surfaces (negatively charged ion)
- Stable in ground water environments
- Not readily reduced due to kinetic barriers

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

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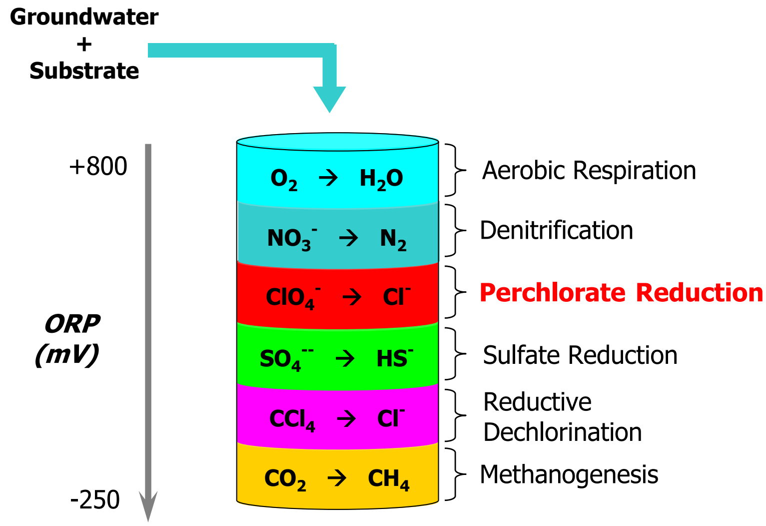
Idealized Sequence of Terminal Electron Accepting Processes (TEAPs)



- 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. If too low, sulfate reduction may be the dominant TEAP. 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. May be difficult to distinguish from background values.

Please refer to section 10.5 and table 10-4

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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

In-Situ Bioremediation of Perchlorate

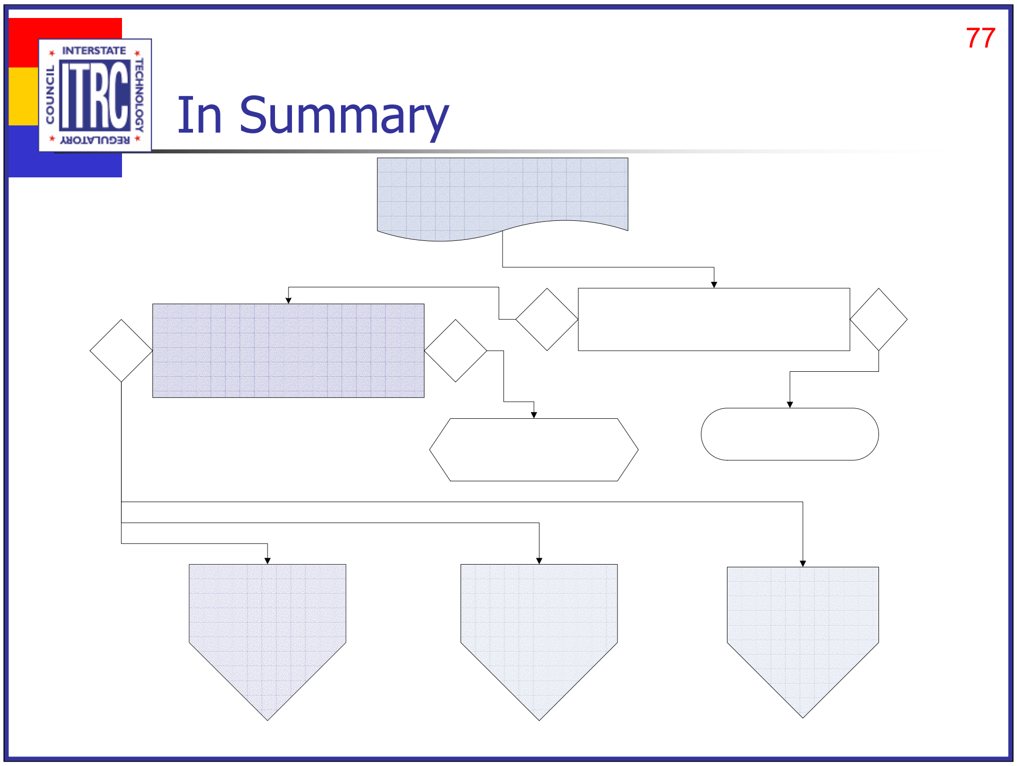
- In-situ bioremediation of perchlorate is an emerging technology
- Laboratory-scale studies, R&D
  - Penn State University, Southern Illinois University, Envirogen, GeoSyntec
- Field Demonstrations
  - Aerojet (San Gabriel, CA)
  - Edwards AFB (CA)
- Biobarrier (immobile C source)
  - NWIRP (McGregor,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

Please refer to section 10.8.1

Technology Status/Future Needs of ISB for Perchlorate

- 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



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In Situ Bioremediation Issues

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

Biofouling (Section 4.4.7)

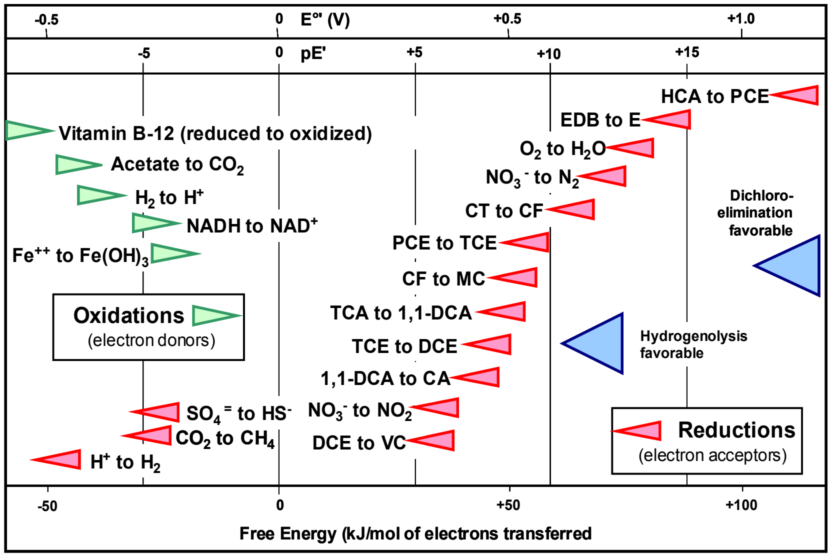
Amendment Mixing (Section 4.4.8)

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

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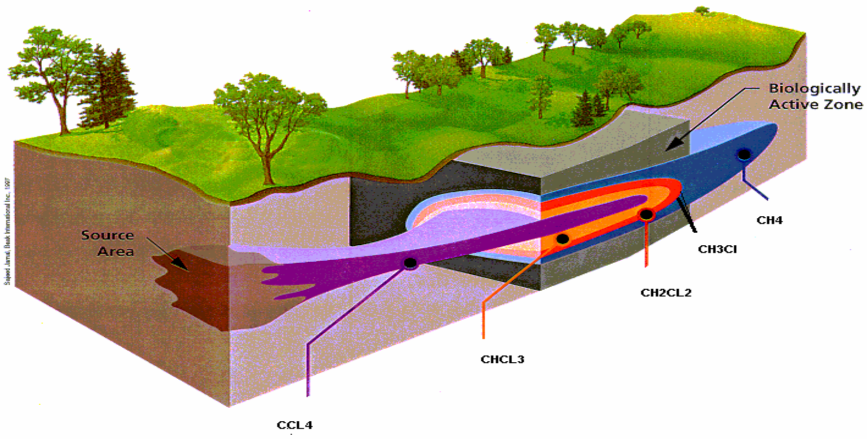
Bottom line for ISB

- 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

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To
Resources

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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