State of the Practice of Abiotic and In Situ Biogeochemical Transformation Processes

Eleventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds

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BATTELLE
It can be done

AIR FORCE CIVIL ENGINEER CENTER

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Abiotic Processes

- CoC transformation occurs without direct microbial activity
- Can occur naturally, fortuitously, or under engineered conditions
  - Natural attenuation via naturally occurring reactive minerals (eg. magnetite)
  - Fortuitously from approaches that condition the aquifer for another reason or by “accident” (eg, ERD, landfills)
  - Engineered where reagents are added to intentionally promote abiotic degradation (eg. ISBGT)

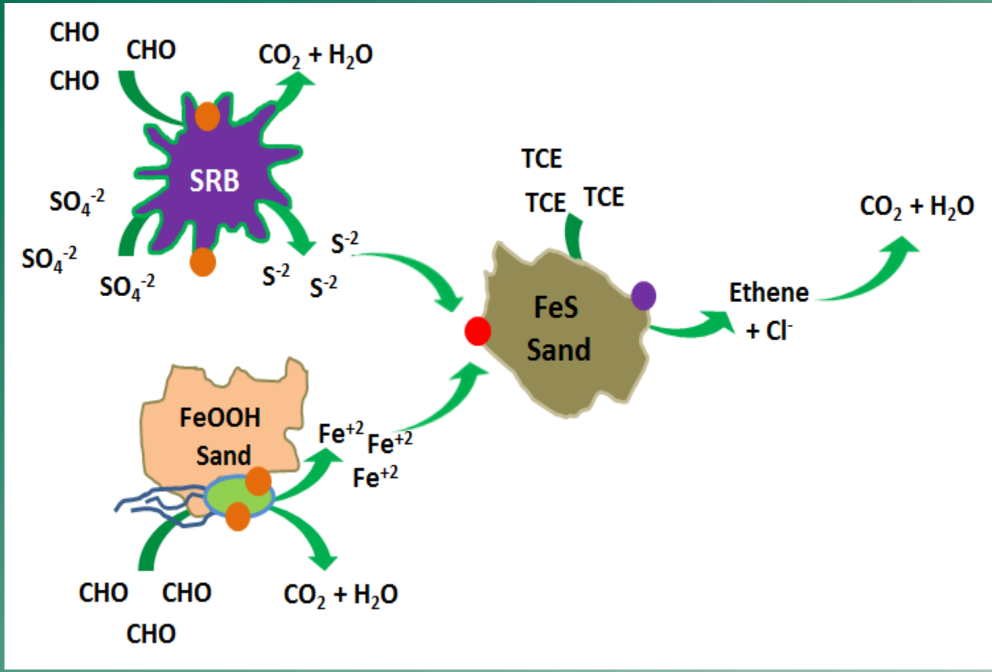
Engineered Approaches for Abiotic Transformation

- In Situ Chemical Oxidation (ISCO)
  - Chemical oxidants injected/mixed into the contaminated soil/groundwater to effect degradation (eg. permanganate, persulfate)
- In Situ Chemical Reduction (ISCR)
  - Similar to ISCO but with reductants (eg. ZVI, sodium dithionite)
- Numerous vendor products available for these approaches
- ISCO and ISCR are the subjects of other sessions

- Monitored Natural Attenuation (MNA)
  - Rely on naturally occurring processes including reactions with reactive minerals
- In Situ Biogeochemical Transformation (ISBGT)

Review: Fundamental ISBGT Principles

- ISBGT is a 3-step process
  1. Under anaerobic conditions microbial activity reduces iron and sulfate
  2. Reduced iron and sulfide form reactive minerals
  3. Reactive minerals catalyze abiotic contaminant degradation
- ISBGT can occur naturally when conditions are conducive to reactive mineral formation
- Engineered ISBGT provides the necessary substrates to drive the process to completion



Mineral	Formula
Iron sulfide	FeS
Pyrite	FeS_2
Green rusts	$Fe^{II}_4\ Fe^{III}_2\ (OH)_{12}\ SO_4 \cdot yH_2O$
Magnetite	$Fe_3\ O_4$

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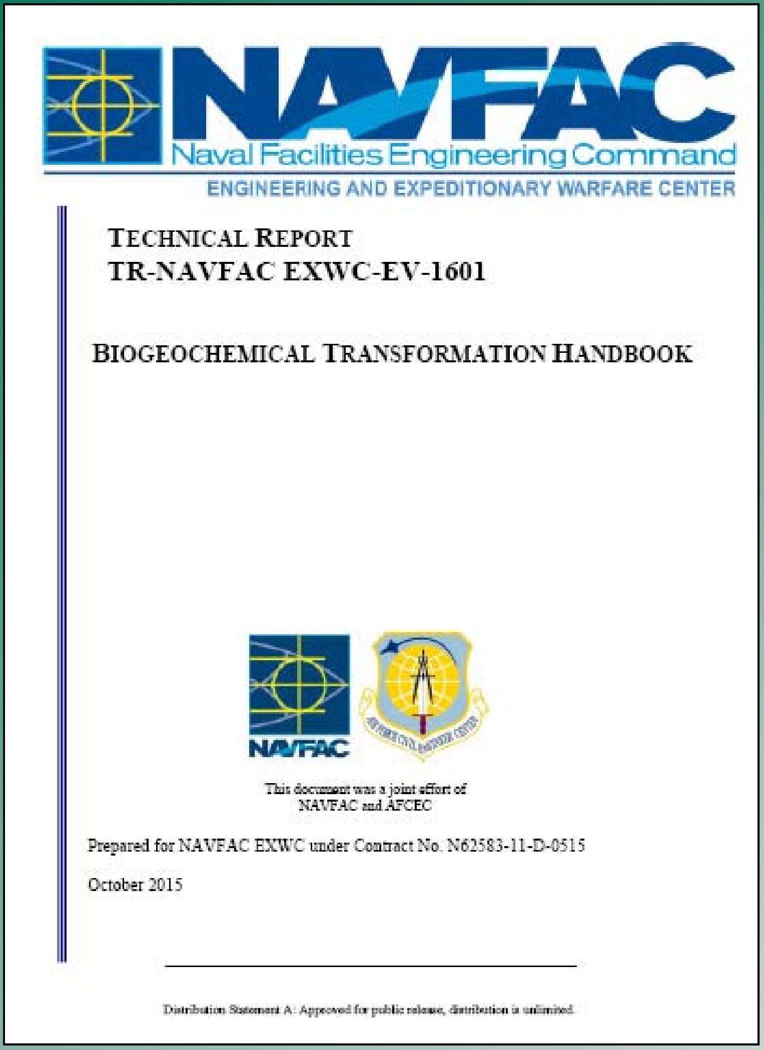
Biogeochemical Transformation Handbook - 2015

- Navy and AFCEC joint project
- Q&A format
- Provides guidance on biogeochemical transformation
  - Applicable contaminants
  - Implementability
  - Performance monitoring


NAVFAC
Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

TECHNICAL REPORT
TR-NAVFAC EXWC-EV-1601

BIOGEOCHEMICAL TRANSFORMATION HANDBOOK

This document was a joint effort of
NAVFAC and AFCEC

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October 2015

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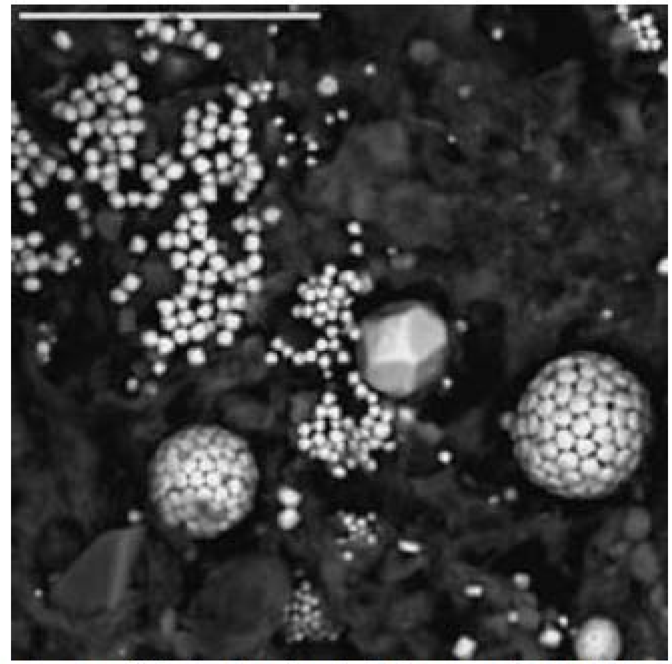
Evaluating Site Potential for Abiotic Degradation

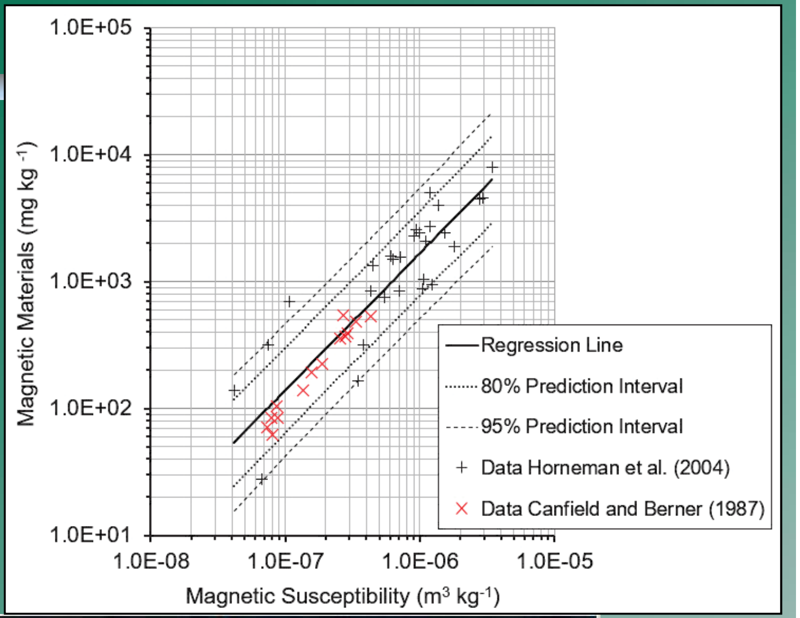
- Magnetic susceptibility (MS) for magnetite and other magnetic minerals
- SEM-EDS for visualization and elemental analysis
- X-ray Diffraction (XRD) for mackinawite, pyrite, magnetite and green rust
- Dissolved ferrous iron
- Acid volatile sulfides
- Percent clay – phyllosilicate clays (vermiculite and biotite)

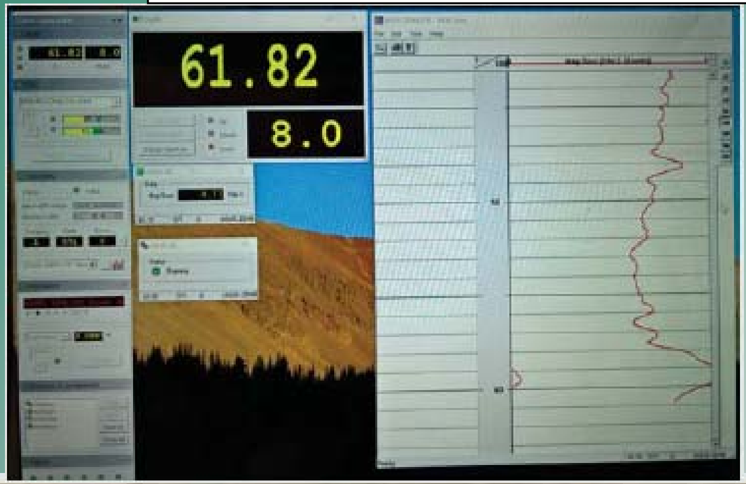


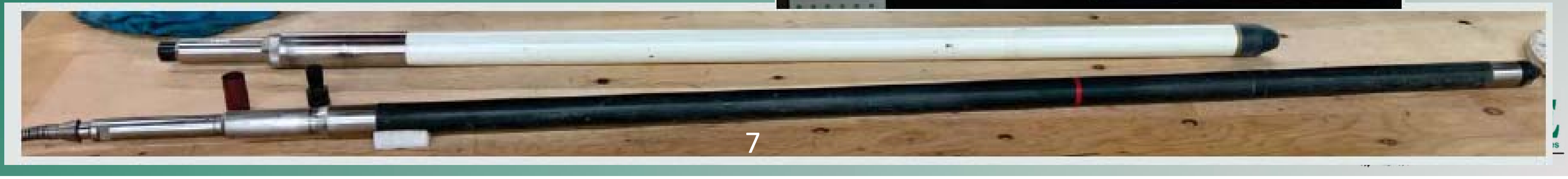
(Courtesy of U.S. Geological Survey [USGS], 2013)

High-Resolution Magnetic Susceptibility (MS)

- Magnetite may contribute to natural attenuation
- MS is an indirect measure of the magnetite content of soils
- Magnetite is a naturally magnetic material – linear relationship between MS and magnetic materials
- Use in-well sonde to provide near continuous readings over depth

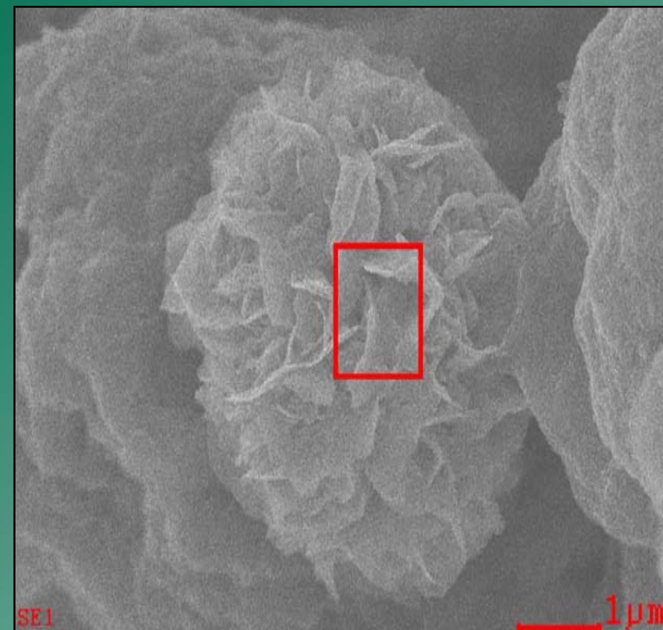


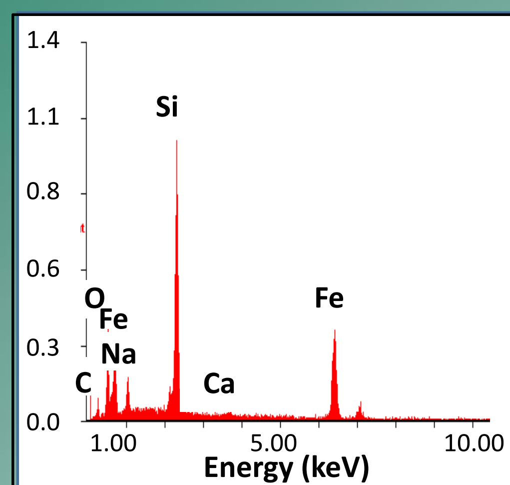




Scanning Electron Microscopy-Energy Dispersive Spectroscopy

- Scanning electron microscopy (SEM) can provide detailed images of mineral structures and locations on surfaces for EDS targeting
- Energy dispersive spectroscopy (EDS) provides surface analysis of the elemental composition of targeted areas within the images
    - Provides weight and atomic percent of elements on surface of mineral





Element	*Wt%*	*At%*
C	09.17	21.72
O	13.40	23.83
Na	05.91	07.31
Si	27.91	**24.76**
Ca	00.86	00.61
Fe	42.75	**21.78**

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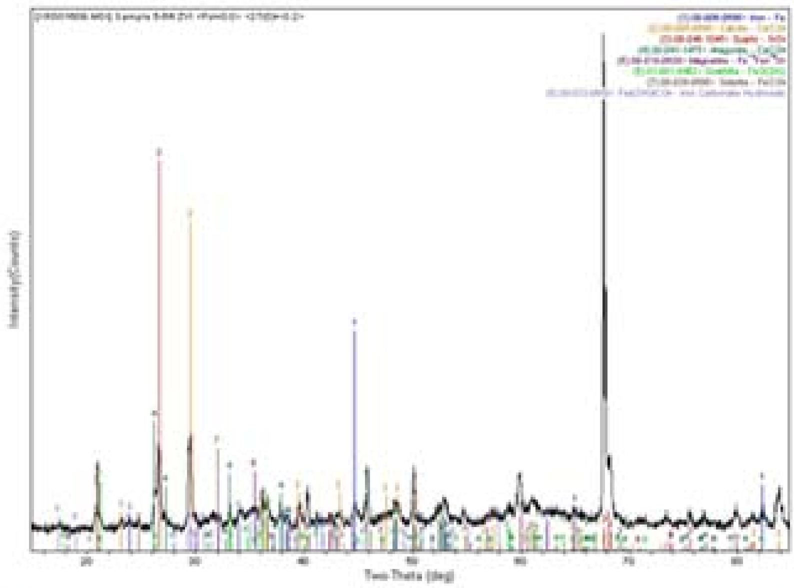
X-ray Diffraction

- X-ray Diffraction (XRD) can identify reactive minerals in soil core samples.
- Mackinawite, pyrite, magnetite and green rusts are reactive minerals of interest



Mineral Name	Formula
Aragonite	$CaCO_3$
Calcite	$CaCO_3$
Goethite	FeOOH
Iron	Fe
Iron (II) Carbonate Hydroxide	$Fe_2(OH)_2CO_3$
Magnetite	Fe_3O_4
Siderite	$FeCO_3$
Quartz	SiO_2

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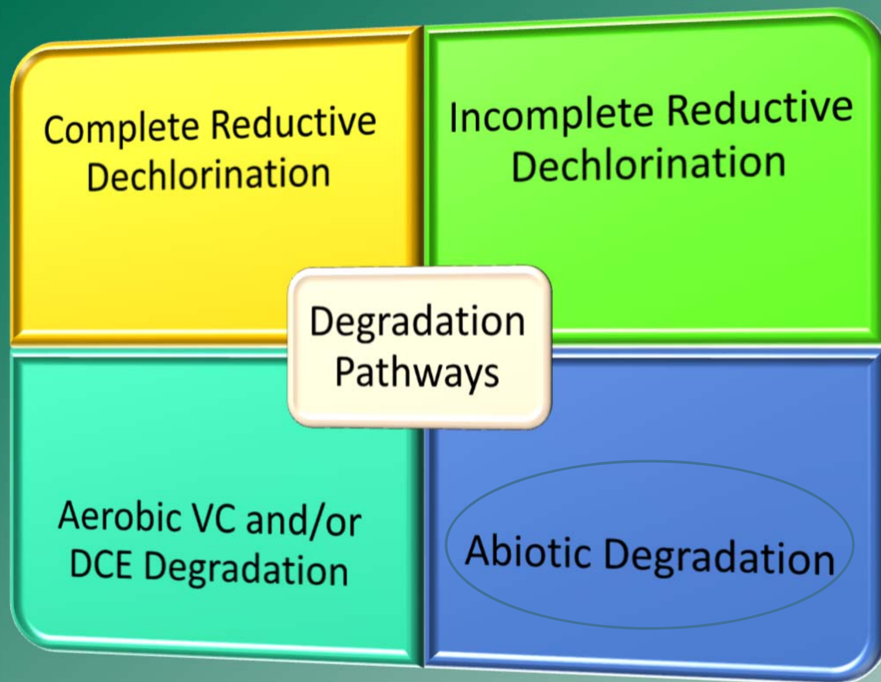
BioPIC Tool evaluates Abiotic Degradation

- **Bio**remediation **P**athway **I**dentification **C**riteria
- Based on the protocol for evaluating natural attenuation of chlorinated ethenes
- Considers biotic AND abiotic processes
- Leverages relationships between biogeochemical parameters and degradation rates to deduce major degradation pathways

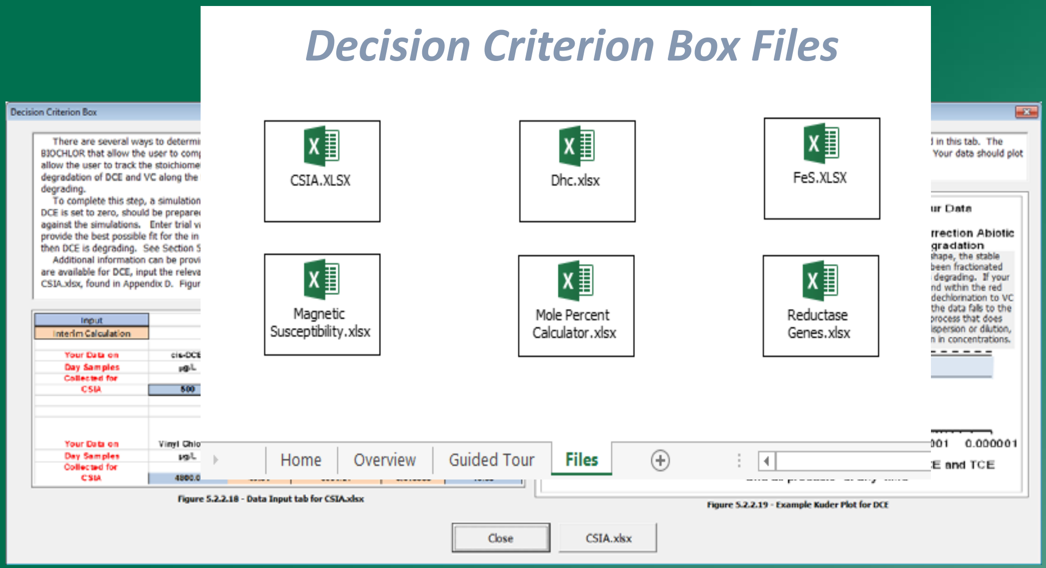


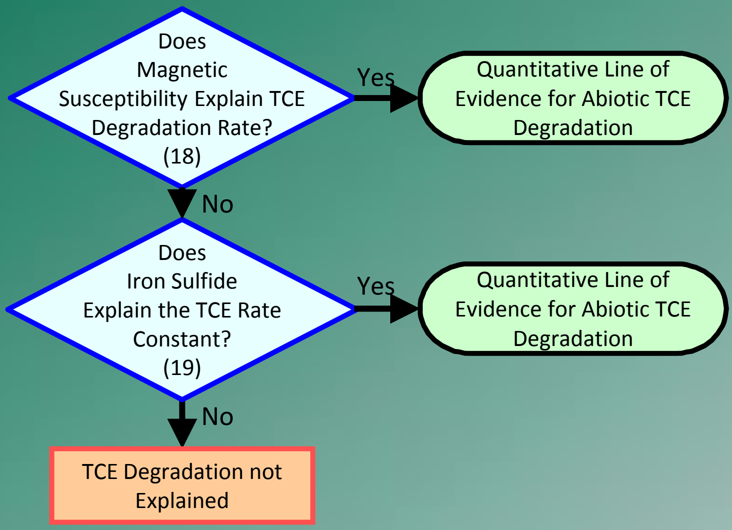
To Obtain BioPIC

https://serdp-estcp.org/content/search?cqp=Standard&SearchText=ER201129&x=0&y=0

Or search under ER-201129 Report

Excerpts from BioPIC Tool

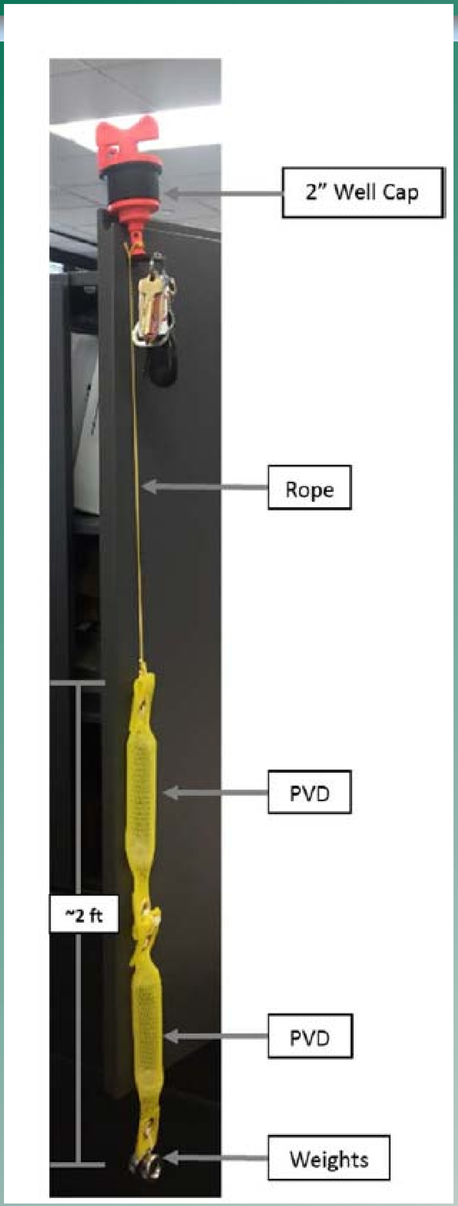




BioPIC parameters: VOC concentrations; alternate electron acceptors (e.g., oxygen, sulfate); reduced products (e.g., ferrous iron {Fe[II]}, methane [CH4]); *Dehalococcoides*(Dhc) 16S rRNA gene and reductive dehalogenase (RDase) gene abundances; CSIA and MS

Passive Sampler for Detection of Acetylene

- In-situ passive vapor diffusion (PVD) samplers
- Developed and tested by GSI under SERDP Project ER-1601 for VOCs
- Clemson is testing ability to sample acetylene under SERDP Project ER-2622
- Preliminary results – passive sampler better at detecting lower concentrations than traditional dissolved gases method



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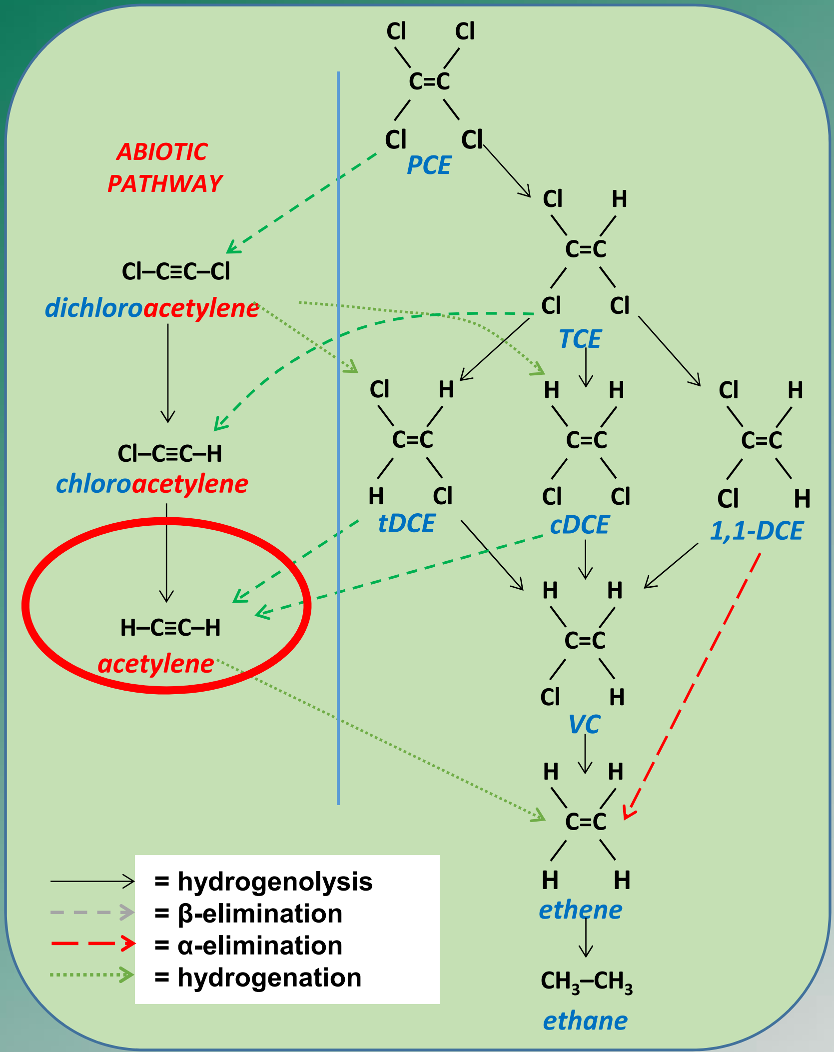
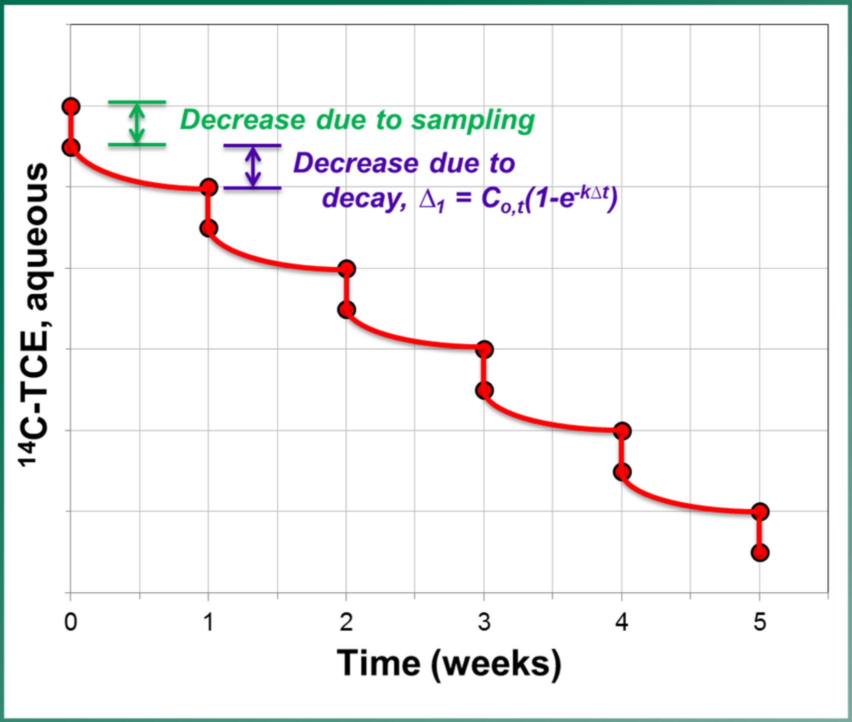
qPCR Assay for Detecting an Anaerobic Acetylene Degrader - Battelle

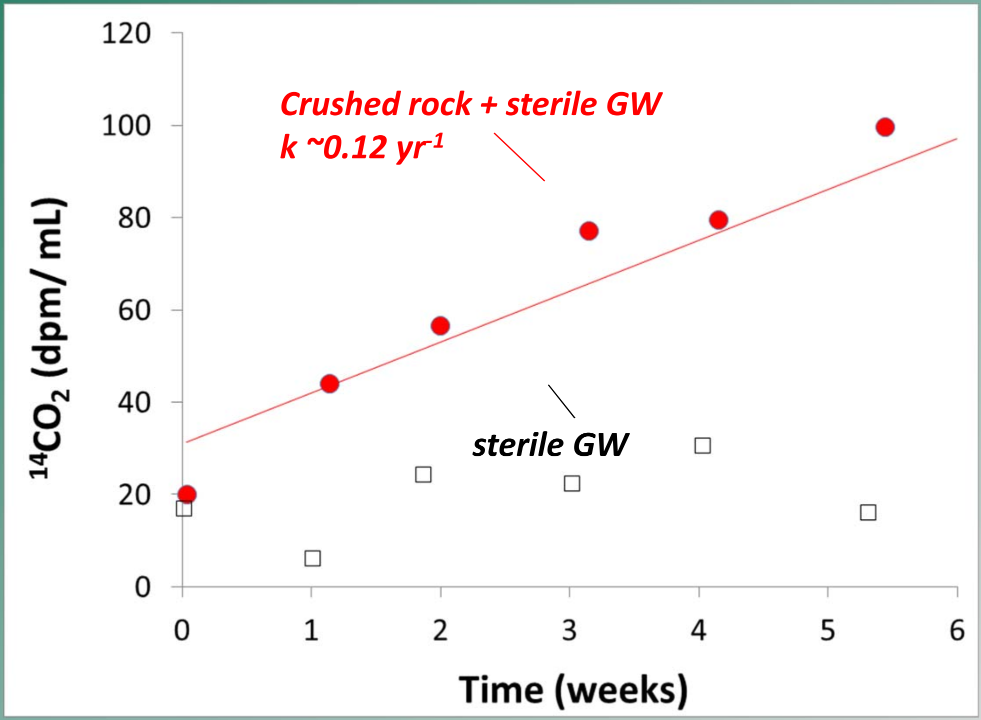
- Degradation product of chlorinated solvent abiotic remediation is acetylene
- Acetylene is labile therefore difficult to detect in the field
- Detecting an anaerobic acetylene degrader would provide evidence of the presence of acetylene.
- Detecting *Pelobacter acetylenicus* anaerobic degrader with limited substrate use at sites provide additional evidence of abiotic degradation



Evaluating Site Potential for Abiotic Degradation – Clemson University

- ^{14}C assay available
- Typically have results in 6 weeks
- Measures decrease in ^{14}C-TCE activity based on increases in $^{14}CO_2$





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SERDP/ESTCP Projects: 2016 SON Measurement and Enhancement of Abiotic Attenuation Processes in Groundwater

Project Number	Title	PI	Affiliation
ER-2617	Measuring and Predicting the Natural and Enhanced Rate and Capacity of Abiotic Reduction of Munition Constituents	Dr. Pei Chiu	University of Delaware
ER-2618	Compound Specific Isotope Analysis of Mineral-Mediated Abiotic Reduction of Nitro Compounds	Dr. William Arnold	University of Minnesota
ER-2619	Characterization of Enhanced Subsurface Abiotic Reactivity with Electrical Resistivity Tomography/Induced Polarization	Dr. Jim Szecsody	Pacific Northwest National Laboratory
ER-2621	Field Assessment of Abiotic Attenuation Rates using Chemical Reactivity Probes and Cryogenic Core Collection	Dr. Richard Johnson	Oregon Health & Science University
ER-2622	Abiotic Transformation of Chloroethenes in Low Permeability Formations	Dr. David Freedman	Clemson University
ER-2623	Identification of Abiotic Degradation Pathways of Chlorinated Ethenes by Compound-Specific Stable Isotope Analysis: A Proof-of-Concept Study	Dr. Tomasz Kuder	University of Oklahoma

Presentations in this Session

- Prospects that Abiotic Degradation of TCE by Naturally Occurring Magnetite Can Be Important for Monitored Natural Attenuation
- Assessment of Biogeochemical Processes to Manage Back Diffusion at a Fractured Sandstone Site
- Practical Applications of Chemical Reactivity Probes (CRPs) to Estimate Abiotic Reduction Rates
- Addition of Divalent Iron to Electron Donor Mixtures for Remediation of Chlorinated Ethenes: A Study of over 100 Wells
- Sulfidation of ZVI for Degradation of Chlorinated Ethenes: A New Approach to In Situ Biogeochemical Transformation

- Posters (Group 1, Session B4, Page 26)
  - 20 posters were presented on Monday evening
  - Topics ranged from new analytical tools, additional contaminants, engineered approaches, and lessons learned

Questions