Multi-Component & Multi-Functional Amendments

WSP is one of the world's leading engineering professional services consulting firms. We engineer projects that will help societies grow for lifetimes to come. Our 5,000 multidisciplinary environmental experts are part of our 36,000 talented people in more than 500 offices across 40 countries. www.wsp.com

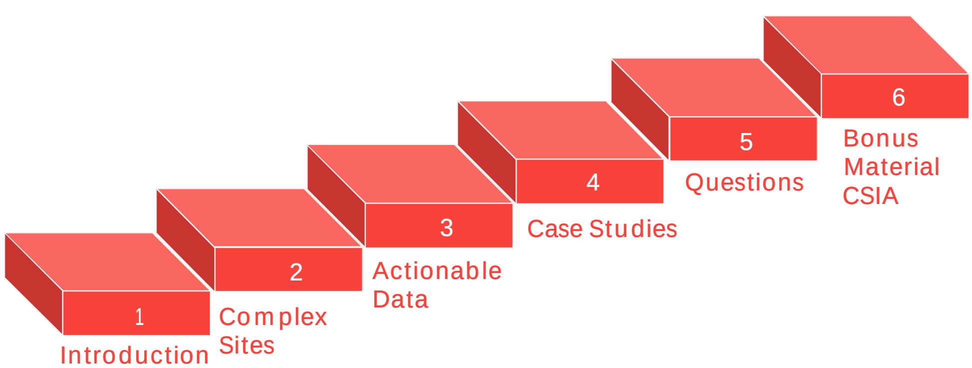
WSP is actively recruiting for strategic positions across the U.S.

Matt Burns

- 978-844-3907 (mobile)
- matt.burns@wsp.com
- linkedin.com/in/mattburnswsp

Introduction

Outline



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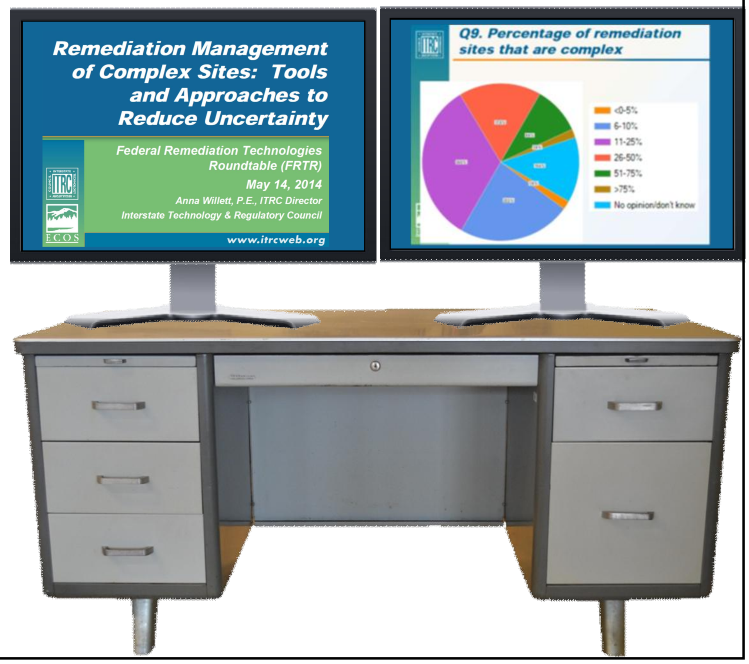
Complex Sites

Asked: What is the percentage of remediation projects that are complex?

3

Response: More than half of the respondents thought less than 25% of all sites are complex. (brown, darker blue, and purple)



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Complex Sites

Asked: Do you work on complex sites?

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Response: About half of respondents have worked on 6 or more complex sites and half have been working on complex sites for 15+ years

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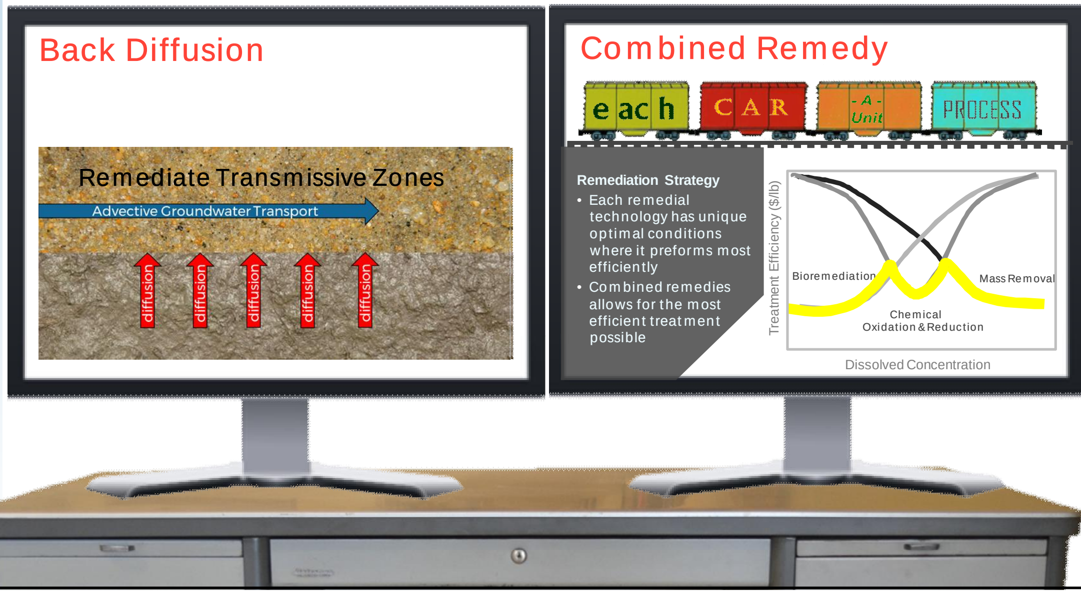
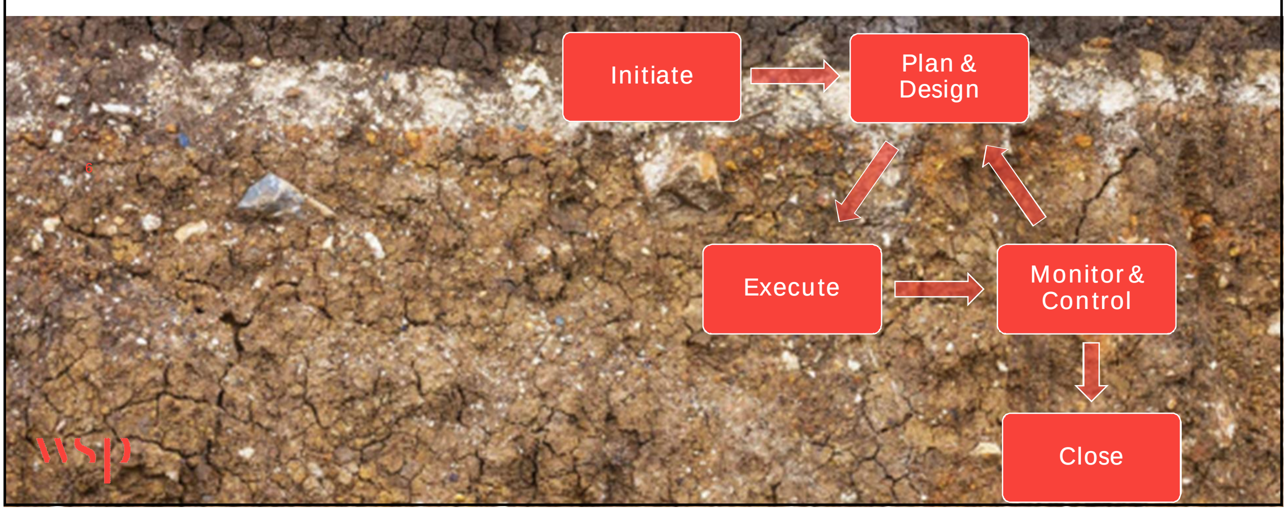
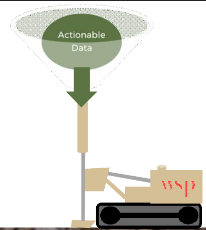
Complex Sites

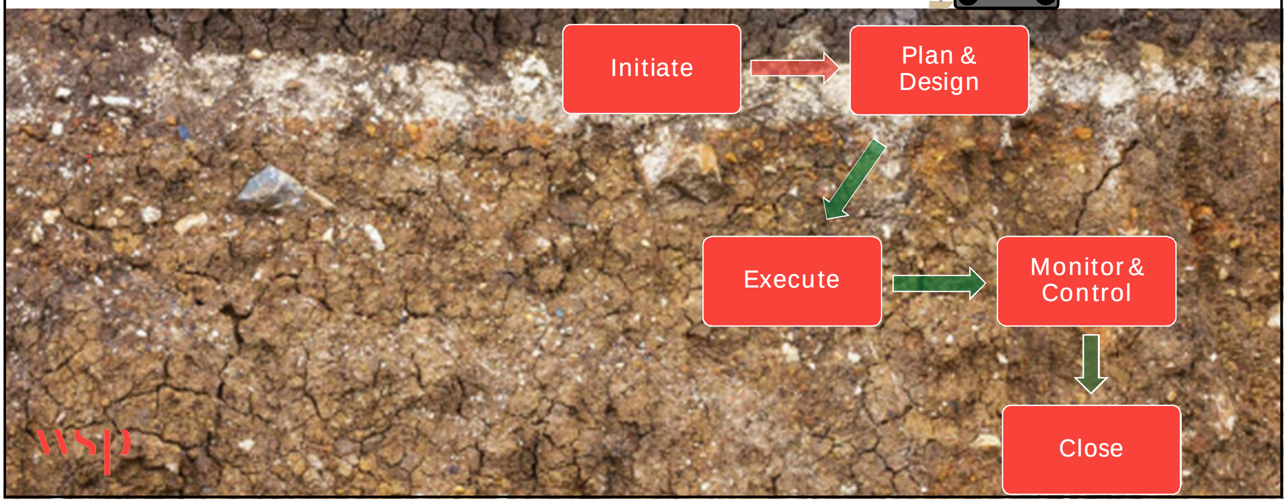


Managing Complex Sites



Managing Complex Sites





Actionable Data

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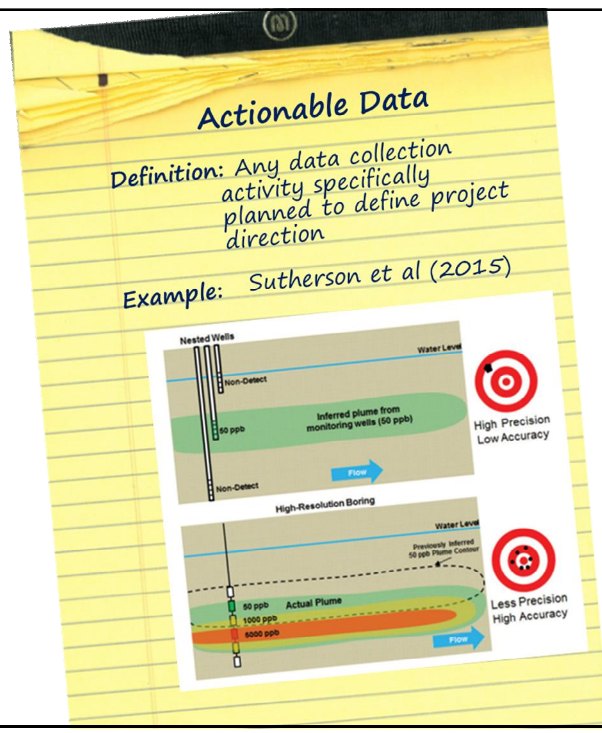
Actionable Data



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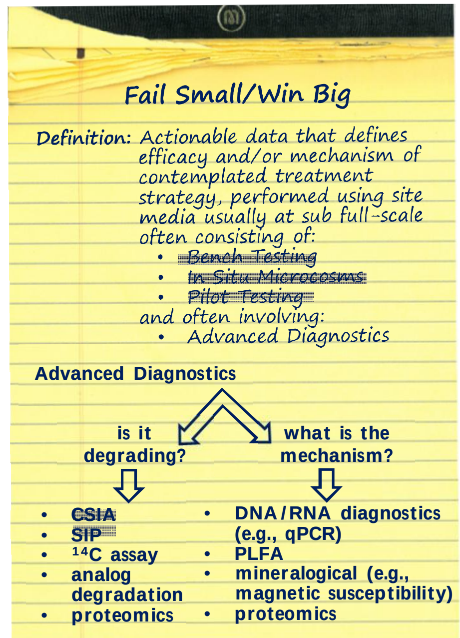

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Recorded Webinar:

On Microbial Insights Website

Successful Advanced ISCO Analytical Practices

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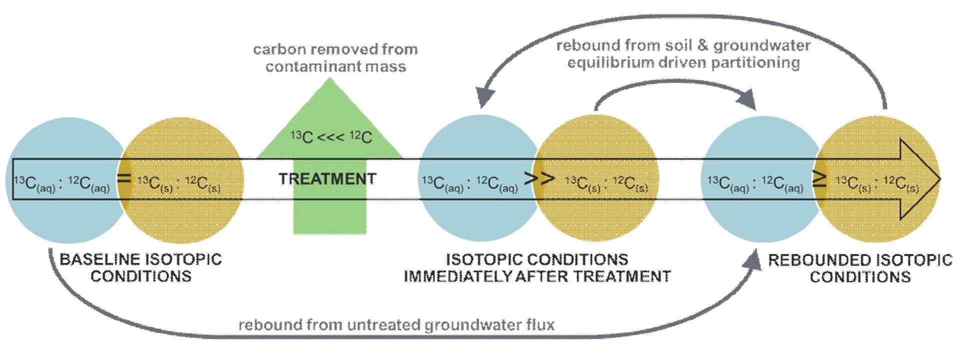

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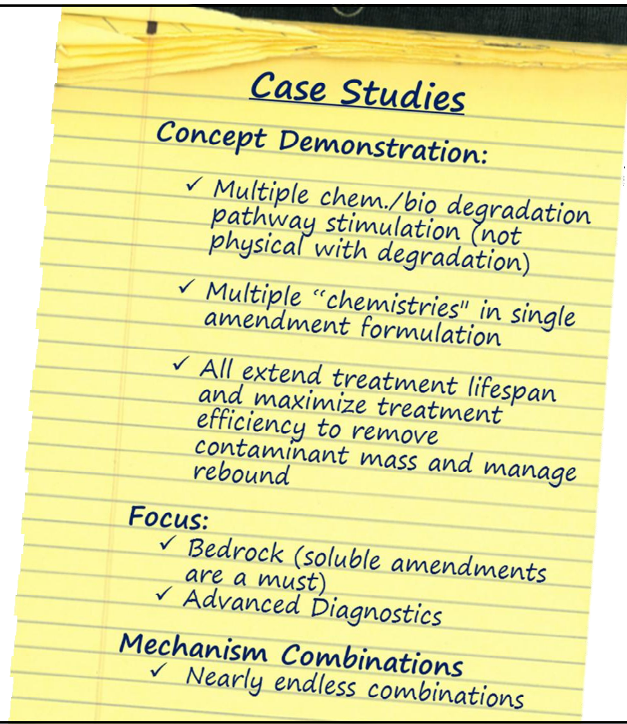
At a glance



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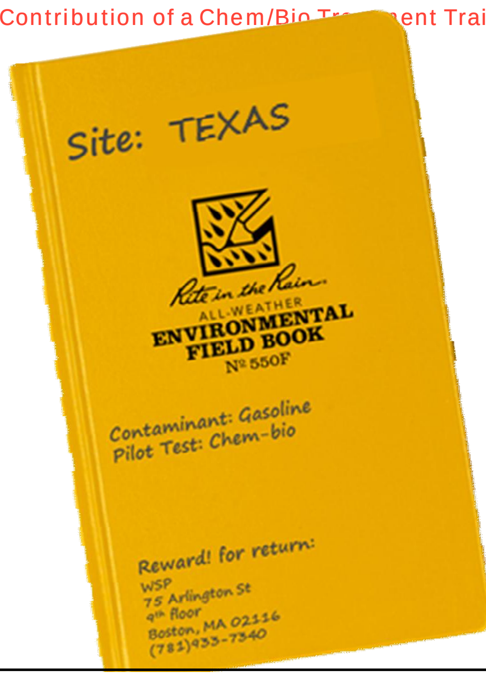
Texas Case Study: Bio Contribution of a Chem/Bio Tr… ent Train of Benzene



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Texas Case Study: Bio Contribution of a Chem/Bio Treatment Train of Benzene

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Texas Case Study: Bio Contribution of a Chem/Bio Treatment Train of Benzene

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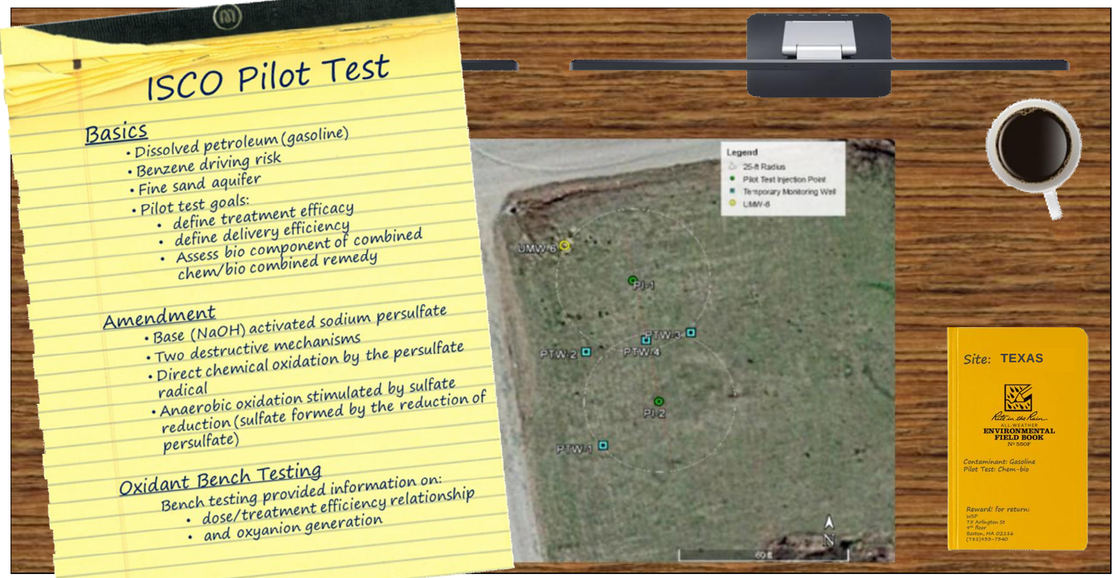
Texas Case Study: Bio Contribution of a Chem/Bio Treatment Train of Benzene



ISCO Pilot Test

Basics
- Dissolved petroleum (gasoline)
- Benzene driving risk
- Fine sand aquifer
- Pilot test goals:
  - define treatment efficacy
  - define delivery efficiency
  - Assess bio component of combined chem/bio combined remedy

Amendment
- Base (NaOH) activated sodium persulfate
- Two destructive mechanisms
- Direct chemical oxidation by the persulfate radical
- Anaerobic oxidation stimulated by sulfate reduction (sulfate formed by the reduction of persulfate)

Oxidant Bench Testing
Bench testing provided information on:
- dose/treatment efficiency relationship
- and oxyanion generation

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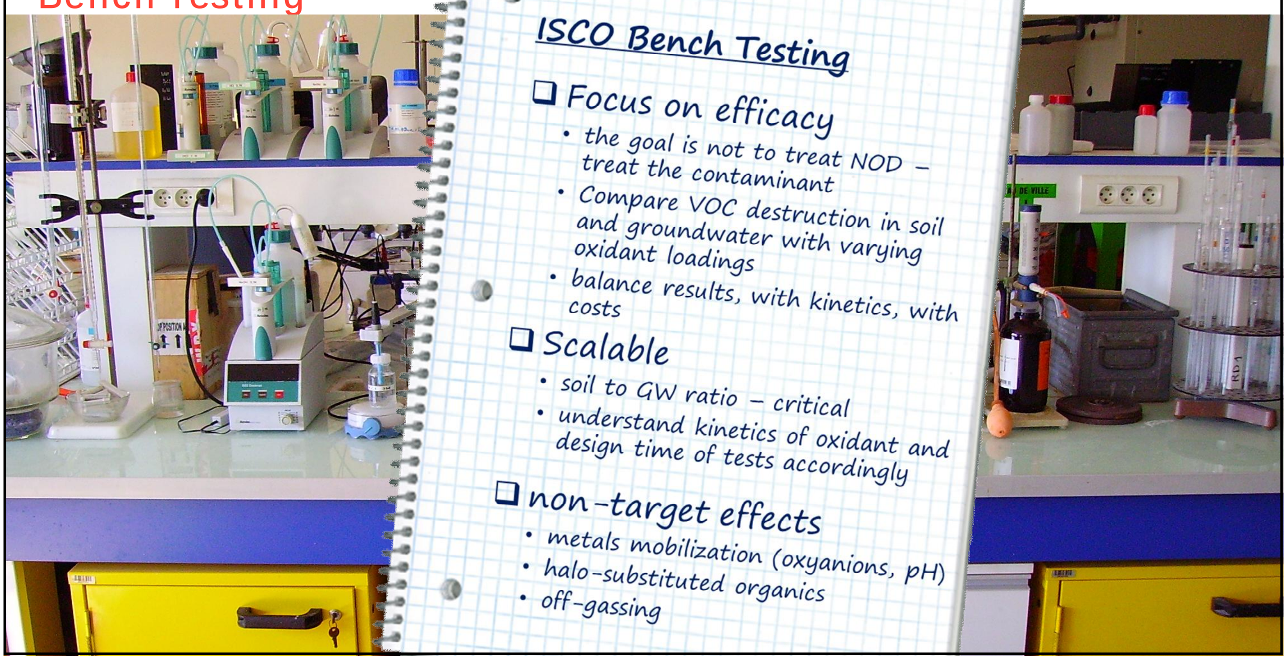
Bench Testing



ISCO Bench Testing

- ❑ Focus on efficacy
  - the goal is not to treat NOD – treat the contaminant
  - Compare VOC destruction in soil and groundwater with varying oxidant loadings
  - balance results, with kinetics, with costs
- ❑ Scalable
  - soil to GW ratio – critical
  - understand kinetics of oxidant and design time of tests accordingly
- ❑ non-target effects
  - metals mobilization (oxyanions, pH)
  - halo-substituted organics
  - off-gassing

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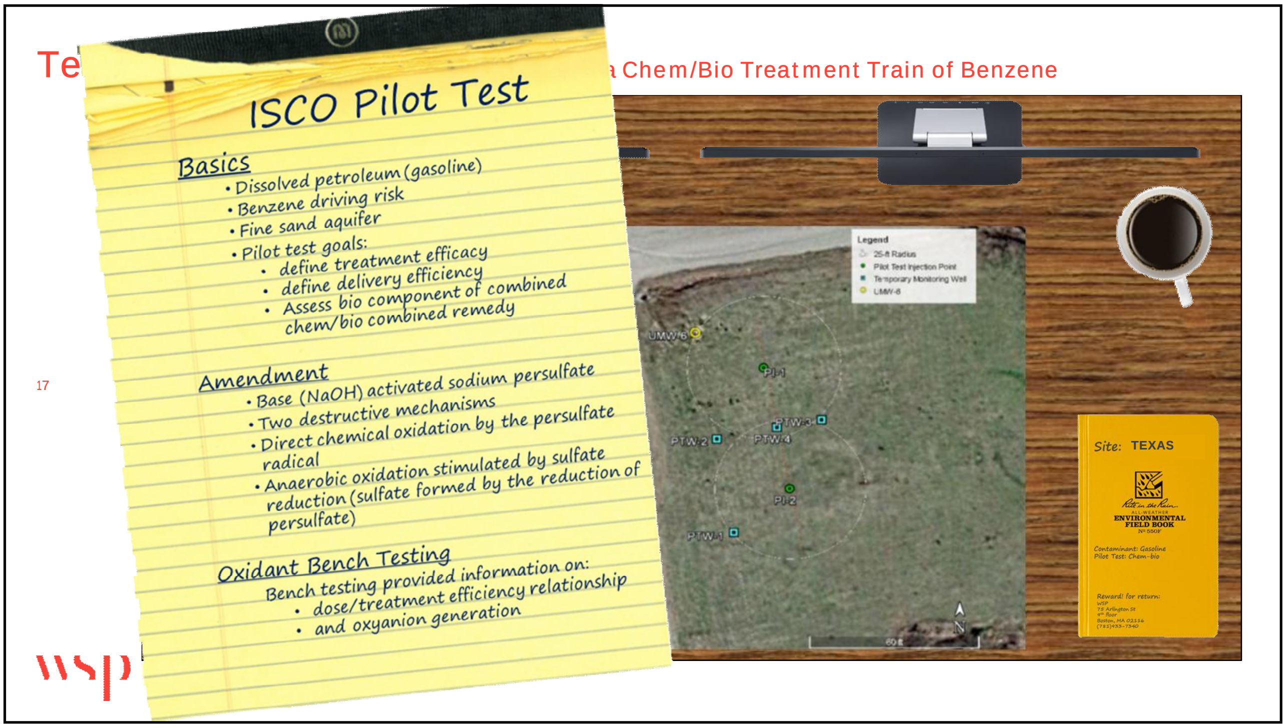
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Chem/Bio Treatment Train of Benzene
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Legend
25-ft Radius
Pilot Test Injection Point
Temporary Monitoring Well
UMW-6
PI-1
PTW-3
PTW-2
PTW-4
PI-2
PTW-1
Site: TEXAS
ENVIRONMENTAL FIELD BOOK
Contaminant: Gasoline
Pilot Test: Chem-bio
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Chem/Bio Treatment Train of Benzene
Plan to Assess Bio Component
• Basic: benzene concentration trends
• ISCO relatively quick – attribute degradation within first month
• Post 1 month = bio
• Correlate bio to decrease in sulfate concentrations
• Advanced Diagnostic – SIP
• Apply amendment
• Monitor for indicators that chemical oxidation complete (ORP & Sulfate)
• When ORP negative, deploy 13C benzene bated biotrap
• Incubate for one month
Legend
25-ft Radius
Pilot Test Injection Point
Temporary Monitoring Well
UMW-6
PI-1
PTW-3
PTW-2
PTW-4
PI-2
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ENVIRONMENTAL FIELD BOOK
Contaminant: Gasoline
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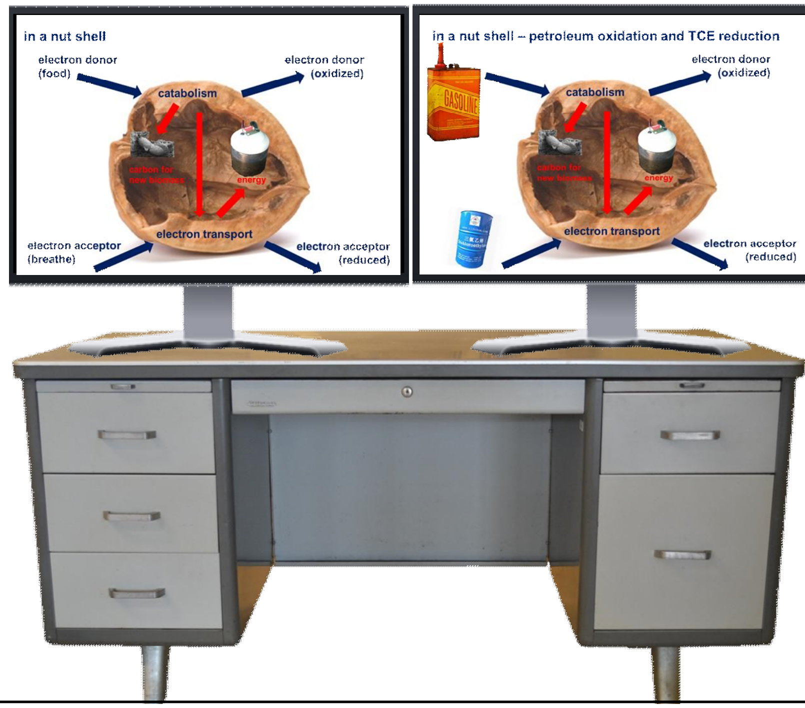
HOW
Stable Isotope Probing



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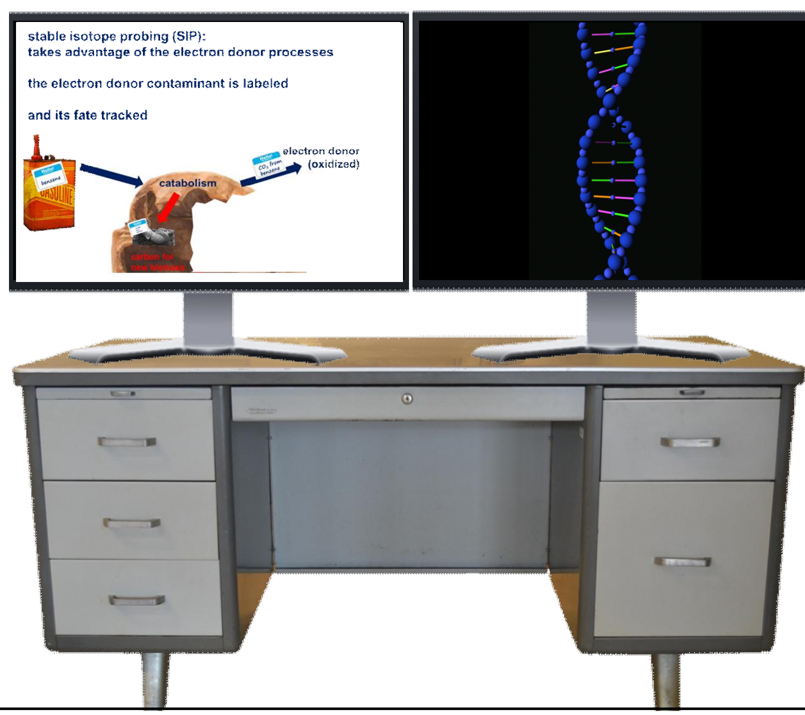
HOW
Stable Isotope Probing



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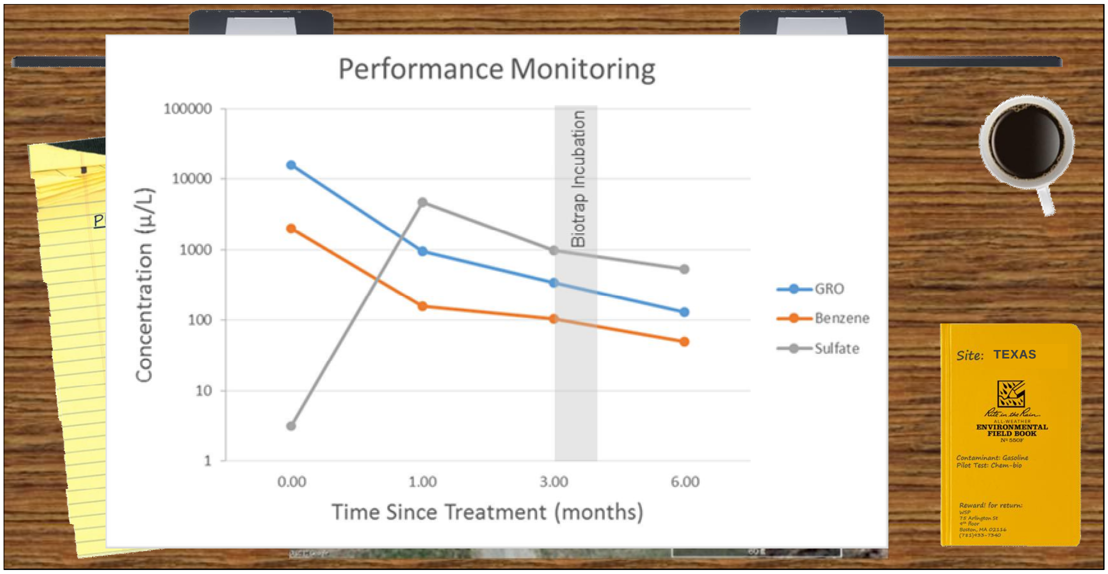
Texas Case Study: Bio Contribution of a Chem/Bio Treatment Train of Benzene



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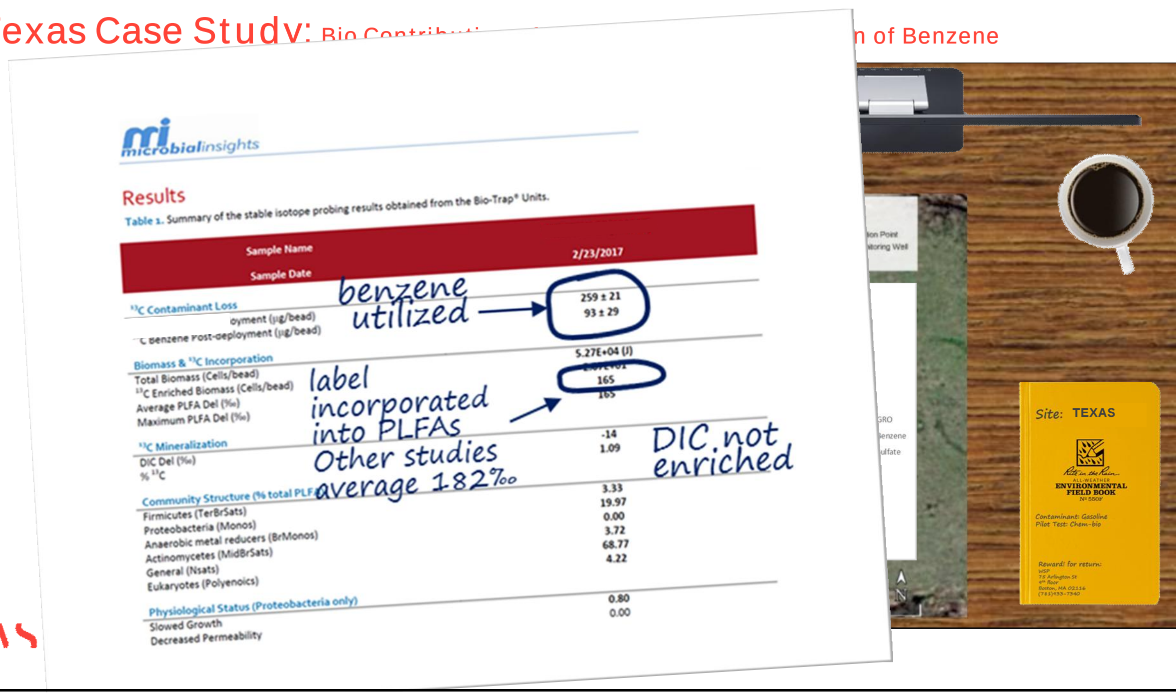
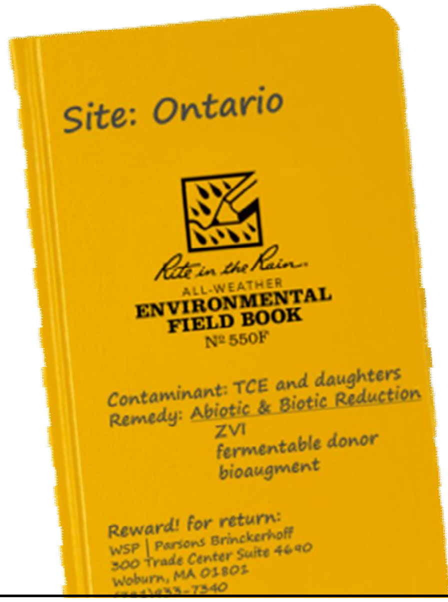
Texas Case Study: Bio Contributi … n of Benzene



Ontario Case Study: Reductive Biotic & Abiotic



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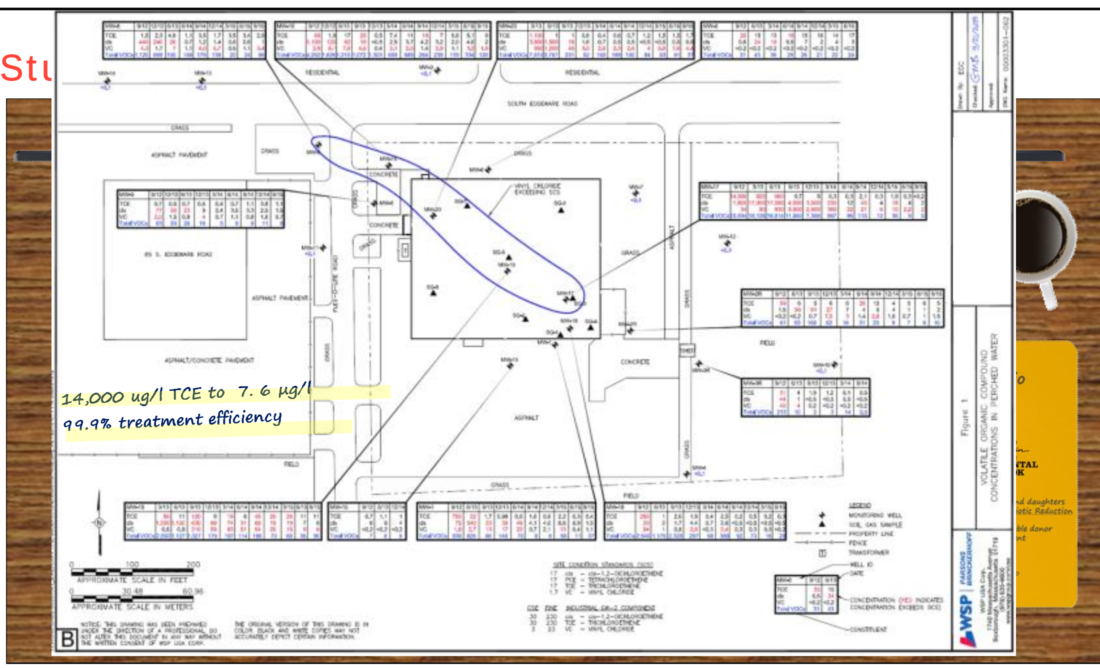
Case Stu



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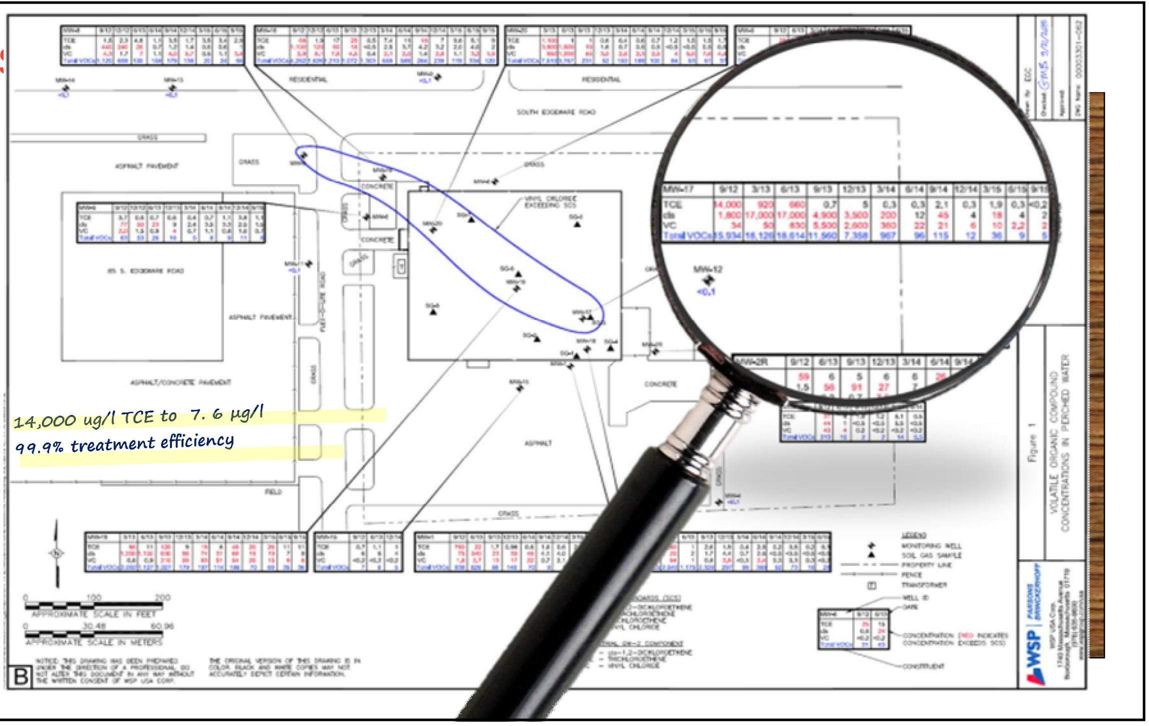
Case S



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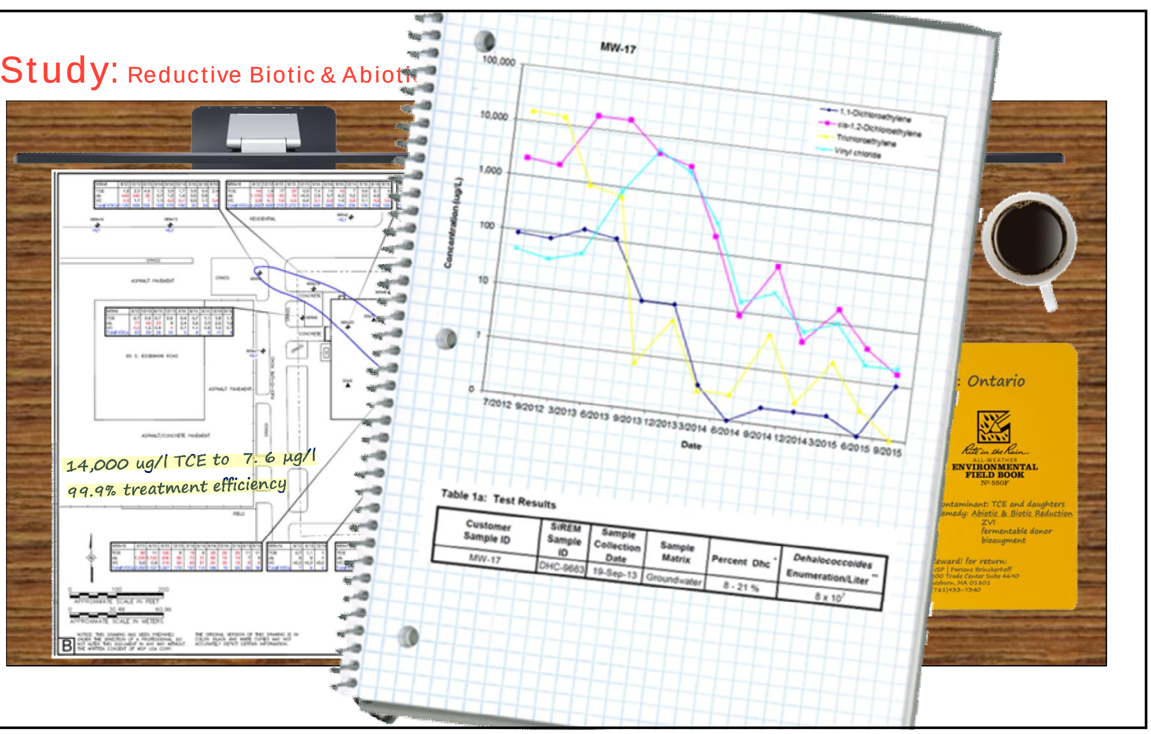
Case Study: Reductive Biotic & Abioti



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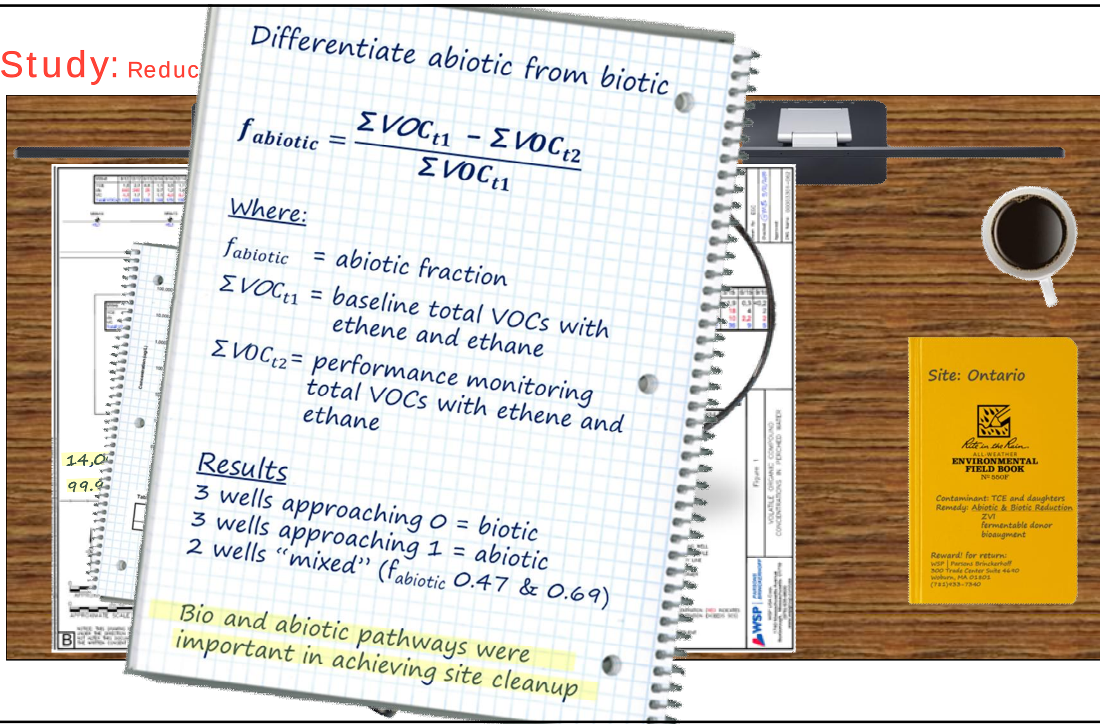
Case Study: Reduc



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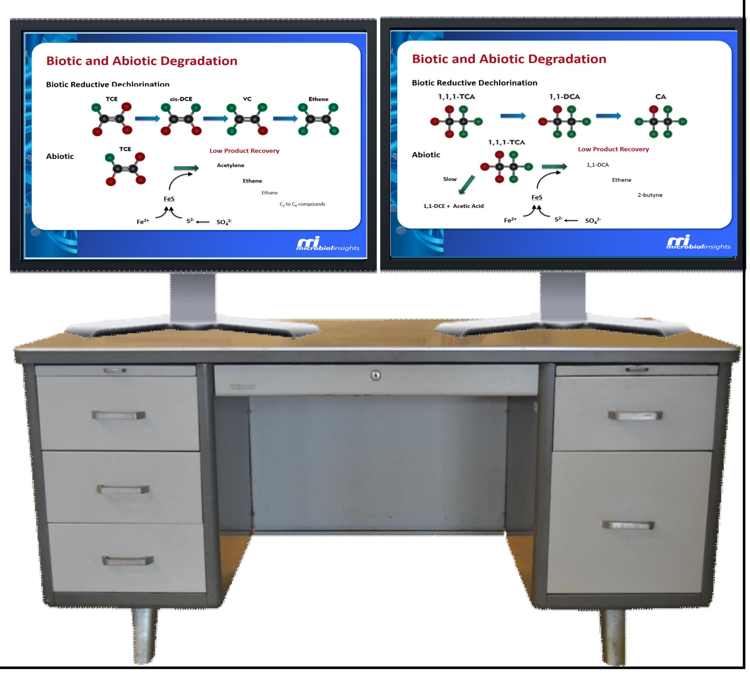
Complex Sites

Degradation Pathways



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Ontario Case S

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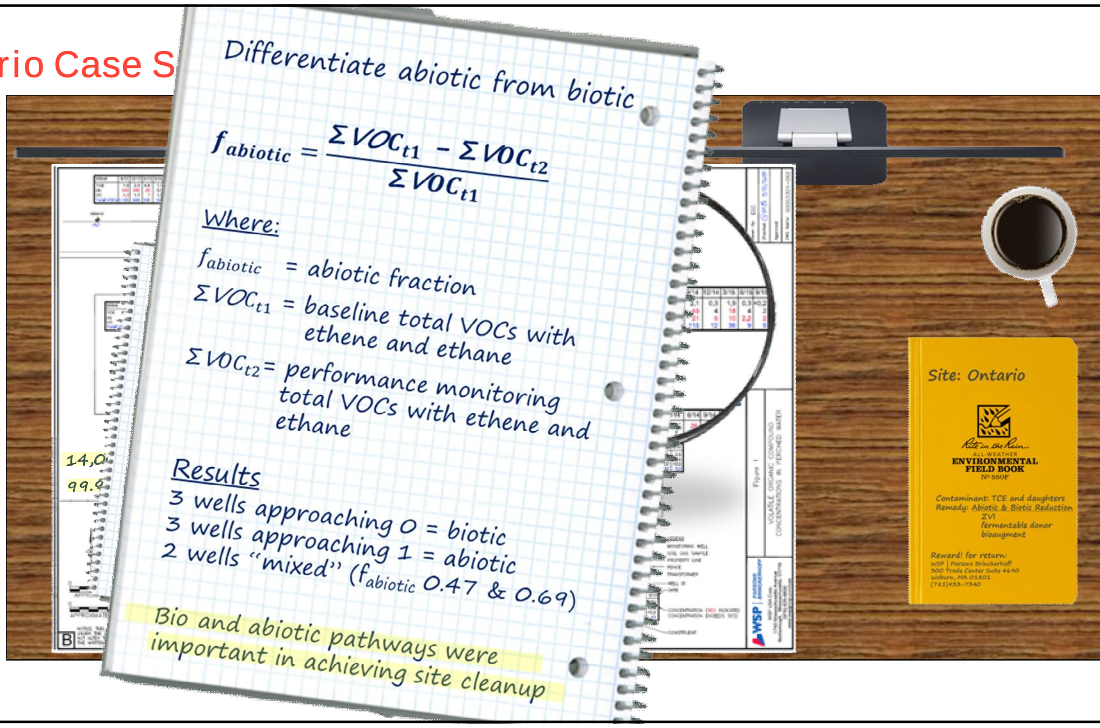

Missouri Case Study: Bio + Biogeochemical Reduction

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Case Study: Missouri

Biogeochemical Reduction

Biogeochemical Reductive Transformation

a.k.a.

- biogeochemical transformation
- Biogeochemical reductive dechlorination (BiRD)

Has been used to remediate chlorinated VOCs and other compounds for about 10 years

It involves abiotic reduction by reactive iron minerals – similar to ZVI. These ferrous iron-containing minerals include:

Mackinawite
Pyrite
Magnetite
Green rust

Can be a mechanism of MNA

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Case Study: Missouri

Biogeochemical Reduc

Engineering Biogenic Iron Sulfide

(1) **Iron Reduction**

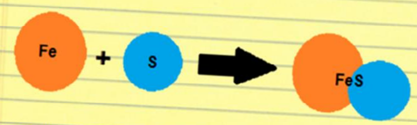
Fe^{3+} + organic matter → $Fe^{2+} + H_2O + CO_2$

(2) **Sulfate Reduction**

SO_4^{2-} + organic matter → $S^{2-} + H_2O + CO_2$

(3) **Iron Sulfide Precipitation**

$HS^- + Fe^{2+} \rightarrow FeS + H^+$



Addition of sulfate to form FeS to treat chlorinated VOCs is a Patented Process:

- Kennedy – US Patent Off. #6,884,352 B1
- Contact Jim Studer of InfraSur
  - jstuder@InfraSUR-LLC.com
  - 505-858-3136

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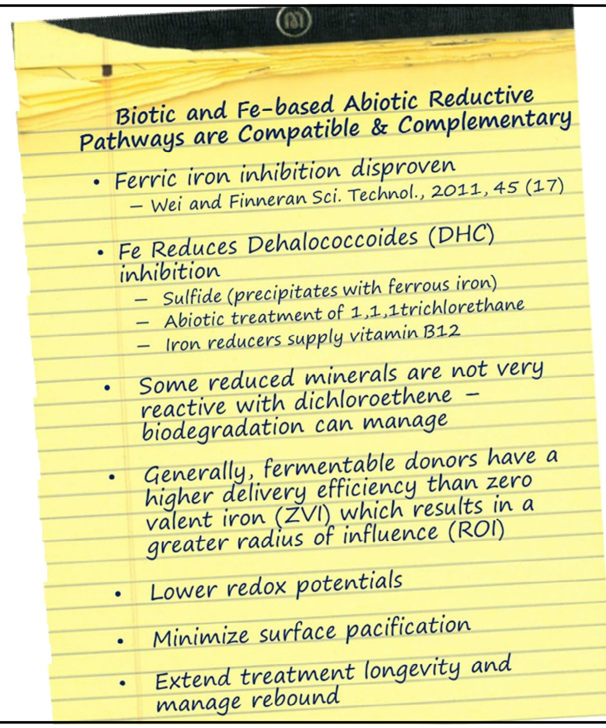
Case Study: Missouri

Synergies

More details including SEFA – in article



Missouri Case Study: Bio + Biogeochemical Reduction

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Missouri Case Study: Bio + Biogeochemical Reduction

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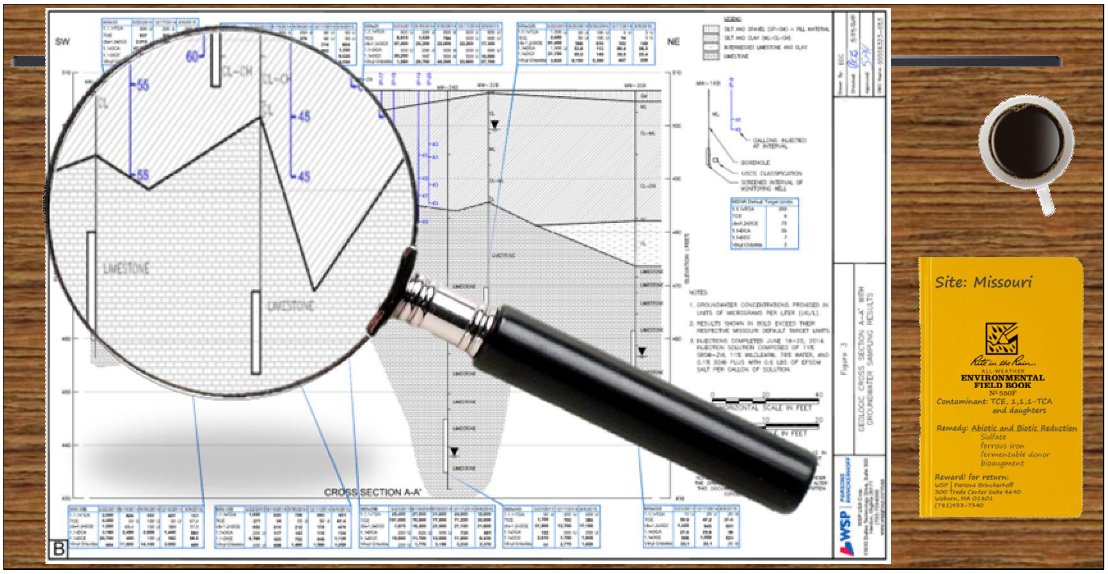

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Missouri Case Study: Bio + Biogeochemical Reduction

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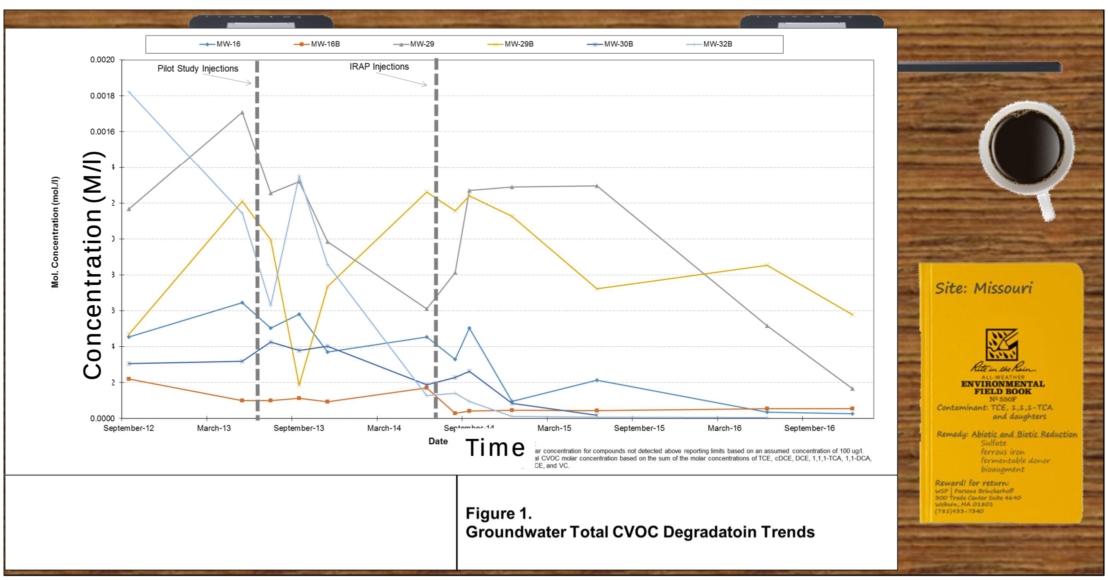

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Missouri Case Study: Bio + Biogeochemical Reduction

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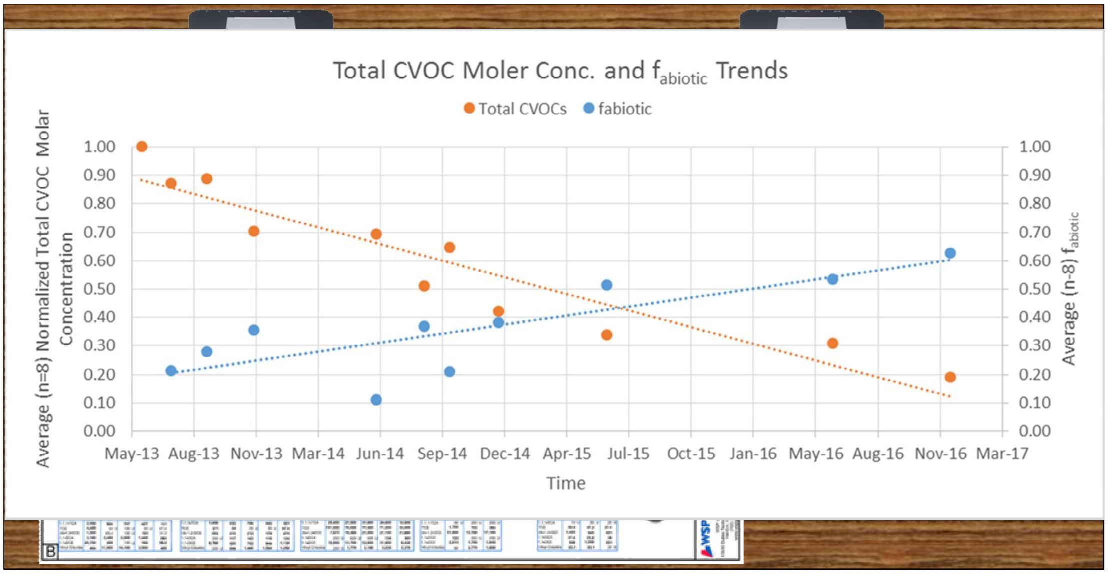

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Recorded Webinar:

On Regenesis Website

Arkansas Site – Fractured Bedrock

Plume Stop + Bio
Biogeochemical + Bio

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REGENESIS

Back Diffusion of VOCs from a Fractured Sandstone Aquifer Treated At Former Industrial Facility

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Project Highlights

Large-scale pilot tests confirm management of chlorinated VOC back diffusion from fractured bedrock aquifer

- Tests concluded degradation along biotic and abiotic reductive pathways
- Advanced sorbent technology extends treatment longevity to manage long-term back diffusion

Project Summary

Fractured bedrock aquifers can be extremely heterogeneous which not only results in complex dissolved plume behavior, but can also hinder *in situ* remediation efforts that rely on an injection of amendments to promote microbial activity and abiotic degradation. However, due to the potentially high cost of a pump and treat remedy at a former industrial site in Arkansas, WSP determined that an *in situ* pilot test with advanced substrates was warranted.

At the Arkansas site, a 2016 pilot study was conducted using a multifunctional amendment formulation. REGENESIS® 3D-Microemulsion®, BDI Plus®, and CRS® were injected to remediate affected groundwater within a fractured sandstone bedrock aquifer impacted by chlorinated solvents. The contaminants at the site included trichloroethene (TCE), 1,1,1-trichloroethane (TCA), and degradation products. The plume on site underlies several developed properties and threatens a stream located approximately 1,500 feet from the source area. Results of the first pilot study yielded an 82% reduction within 9 months was measured approximately 80 feet from the application location.

A second pilot study was undertaken in 2017 to emplace a sorbent technology with long-lasting treatment capacity (PlumeStop®) on bedrock fracture faces to manage back diffusion from the bedrock primary porosity. This test also included the addition of bioremediation amendments to permanently degrade the sorbed contaminants. The 2017 treatment included PlumeStop and bioremediation amendments. After only one month, an 81% reduction was achieved in samples located 50 feet downgradient.

Site Details

Site Type: Former Manufacturing/Industrial Facility
Contaminant of Concern: TCE and 1,1,1-TCA and reductive daughter products
Remediation Approach: Pilot Tests of a combined remedy using multiple ERD processes
Soil Type: Fractured Sandstone
Technology Used: 3DME, HRC, CRS, BDI Plus, PlumeStop Liquid Activated Carbon

3-D MICROEMULSION | HRC HYDROGEN RELEASE COMPOUND | BDI BIO-DECHLOR INOCULUM | CRS CHEMICAL REDUCING SOLUTION | PLUME STOP

Preliminary indications of these amendment formulation tests are extremely promising in treating contaminant back diffusion emanating from the fractured bedrock matrix in this aquifer. WSP is confident that favorable performance monitoring results will continue and the full-scale remedy for this complex geologic setting will include REGENESIS products that extend treatment longevity.

REGENESIS | 1011 Calle Sombra San Clemente, CA 92673 | T: (949) 366-8000 | www.regenesis.com

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Michigan Case Study: Abiotic Reduction + Aerobic Bio

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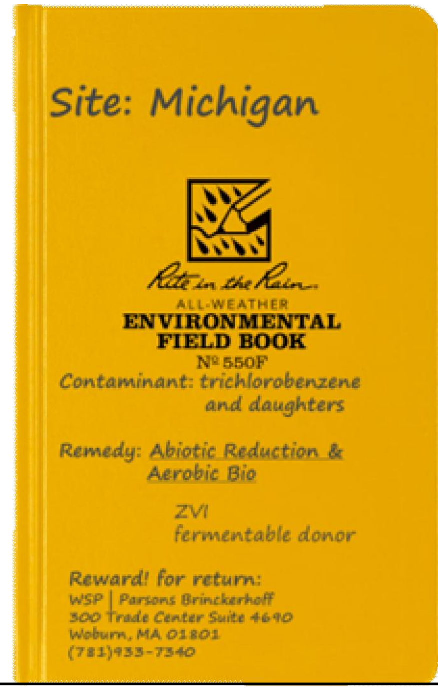

Michigan Case Study: Abiotic Reduction + Aerobic Bio

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Michigan Case Study: Abiotic Reduction + Aerobic Bio

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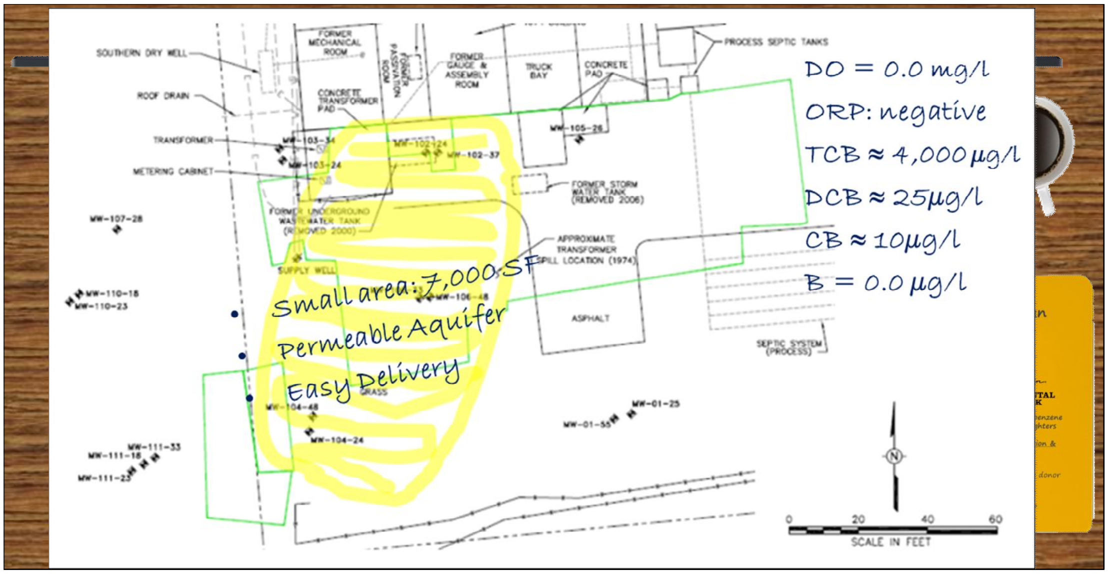

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Michigan Case Study: Abiotic Reduction + Aerobic Bio

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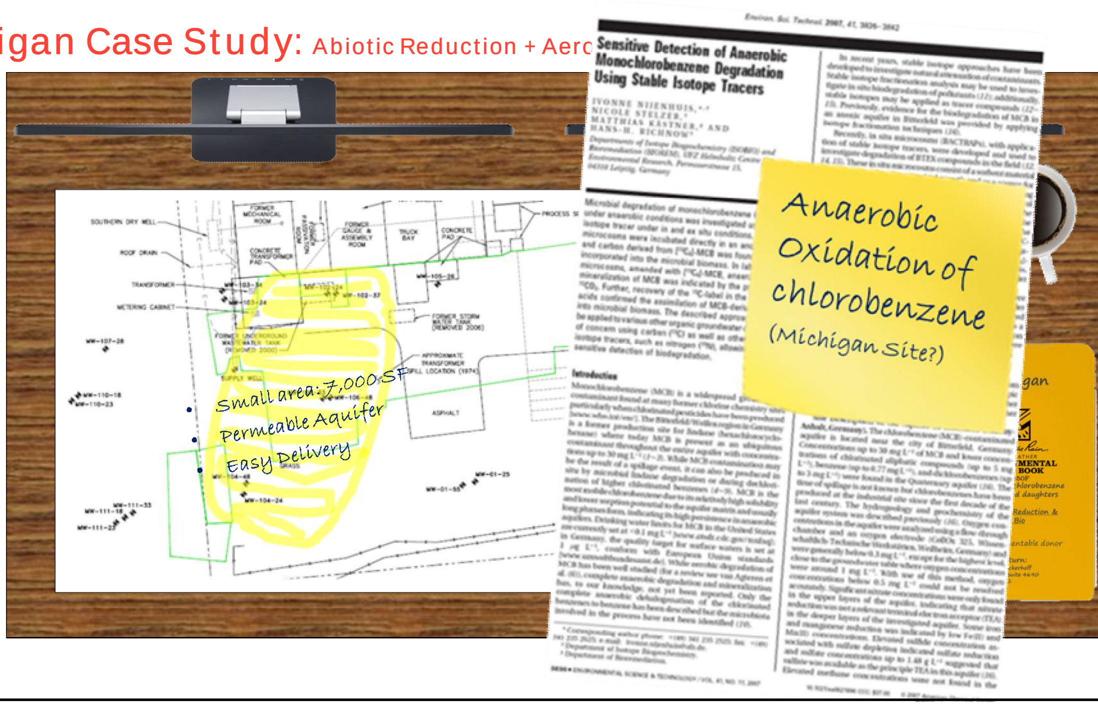

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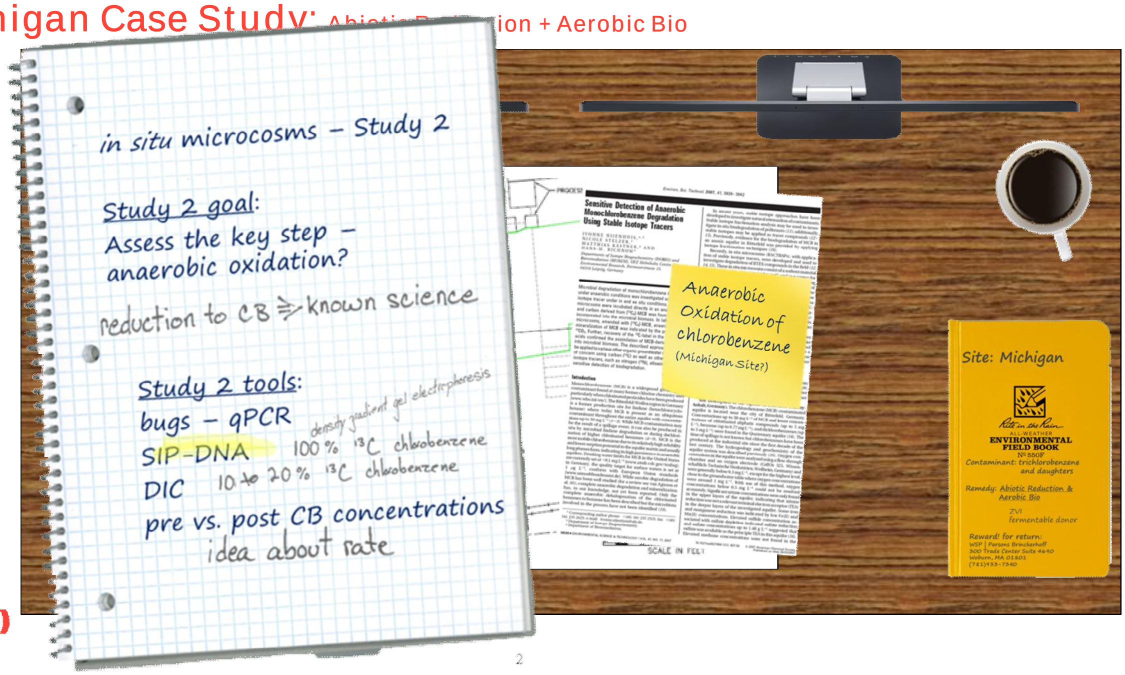
Michigan Case Study: Abiotic Reduction + Aerobic Bio



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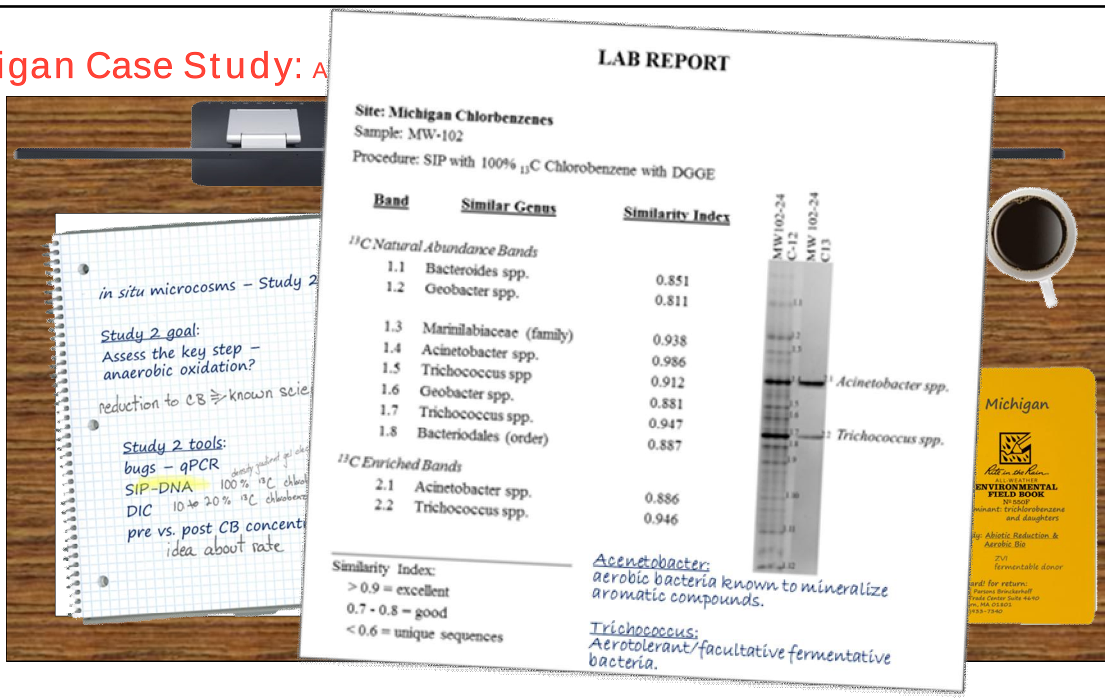
Michigan Case Study: A



LAB REPORT

Site: Michigan Chlorbenzenes
Sample: MW-102
Procedure: SIP with 100% $_{13}$C Chlorobenzene with DGGE

Band	Similar Genus	Similarity Index
^{13}C Natural Abundance Bands		
1.1	Bacteroides spp.	0.851
1.2	Geobacter spp.	0.811
1.3	Marinilabiaceae (family)	0.938
1.4	Acinetobacter spp.	0.986
1.5	Trichococcus spp	0.912
1.6	Geobacter spp.	0.881
1.7	Trichococcus spp.	0.947
1.8	Bacteriodales (order)	0.887
^{13}C Enriched Bands		
2.1	Acinetobacter spp.	0.886
2.2	Trichococcus spp.	0.946

Similarity Index:
> 0.9 = excellent
0.7 - 0.8 = good
< 0.6 = unique sequences

Acenetobacter:
aerobic bacteria known to mineralize aromatic compounds.

Trichococcus:
Aerotolerant/facultative fermentative bacteria.

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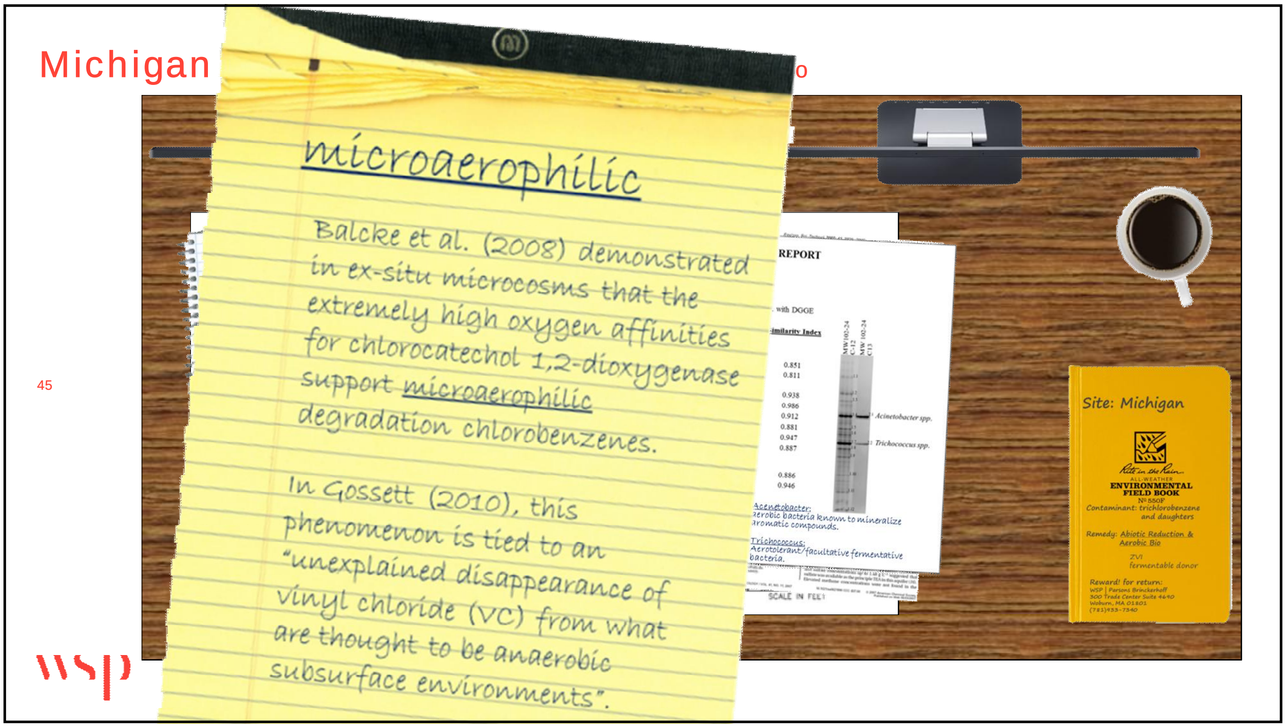
Michigan
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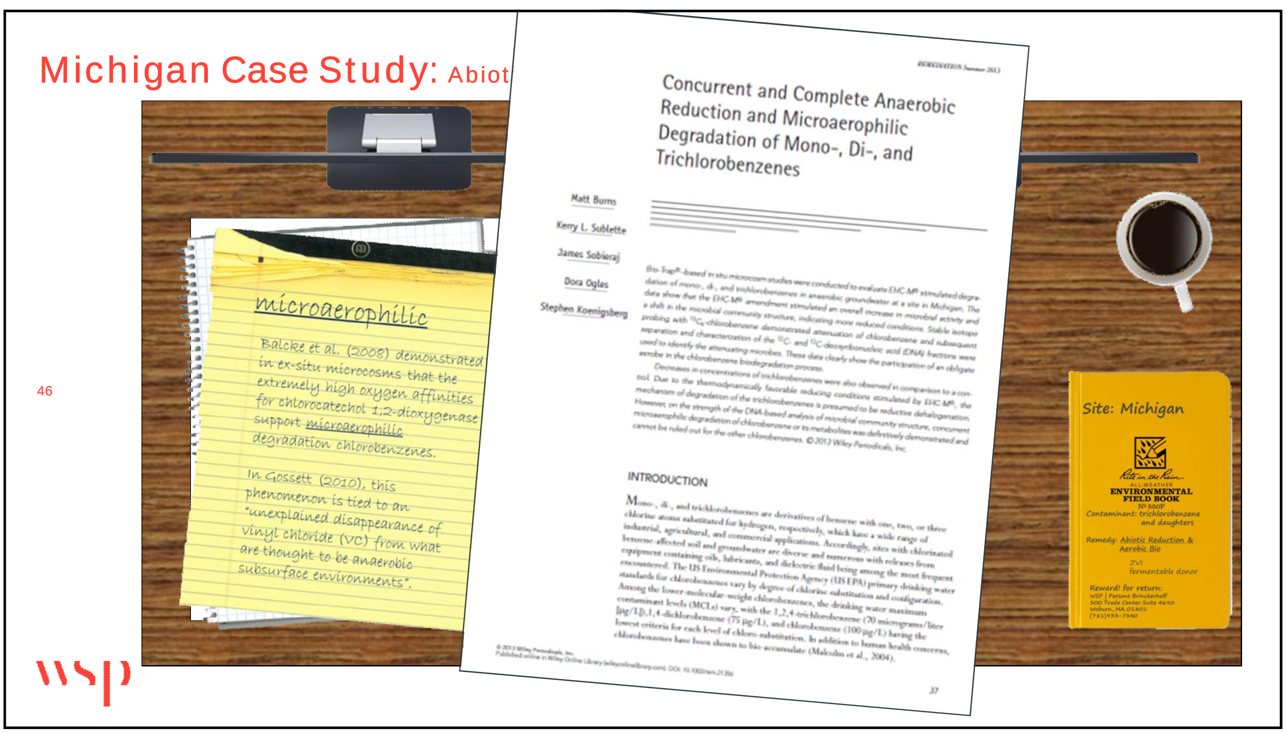
microaerophilic
Balcke et al. (2008) demonstrated in ex-situ microcosms that the extremely high oxygen affinities for chlorocatechol 1,2-dioxygenase support microaerophilic degradation chlorobenzenes.
In Gossett (2010), this phenomenon is tied to an "unexplained disappearance of vinyl chloride (VC) from what are thought to be anaerobic subsurface environments".
REPORT
Acinetobacter spp.
Trichococcus spp.
Acinetobacter: aerobic bacteria known to mineralize aromatic compounds.
Trichococcus: Aerotolerant/facultative fermentative bacteria.
Site: Michigan
Rite in the Rain
ENVIRONMENTAL FIELD BOOK
Contaminant: trichlorobenzene and daughters
Remedy: Abiotic Reduction & Aerobic Bio
ZVI
fermentable donor
Reward! for return:


Michigan Case Study: Abiot
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Concurrent and Complete Anaerobic Reduction and Microaerophilic Degradation of Mono-, Di-, and Trichlorobenzenes
Matt Burns
Kerry L. Sublette
James Sobieraj
Dora Ogles
Stephen Koenigsberg
INTRODUCTION
microaerophilic
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Multi-Component & Multi-Functional Amendments

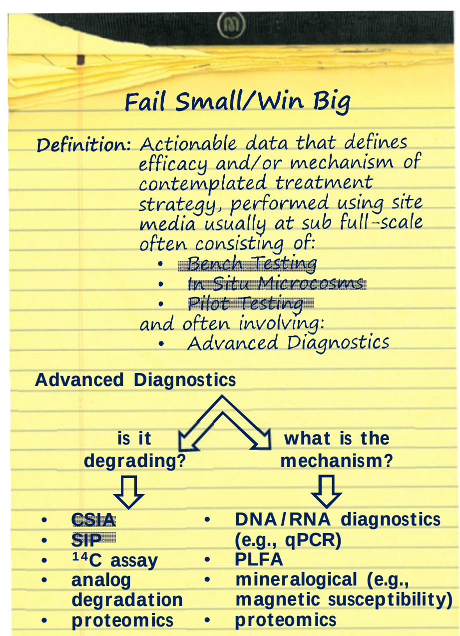
Questions?

Contact: Matt Burns

- 978-844-3907 (mobile)
- matt.burns@wsp.com
- linkedin.com/in/mattburnswsp

Actionable Data

Bonus Material Actionable Data



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CSIA

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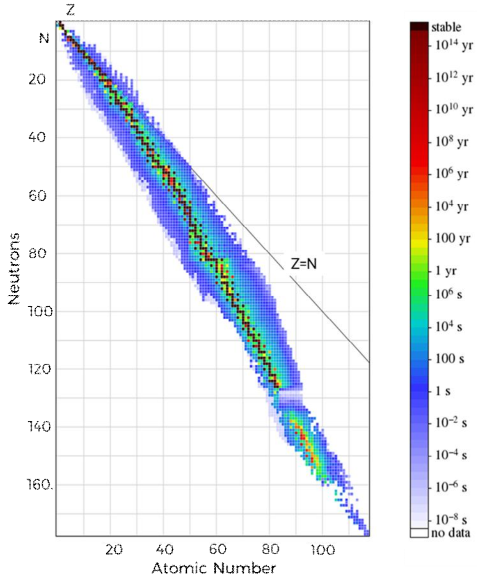
CSIA

CS: Compound Specific (i.e., contaminant)

I: Isotope – a form of the same element that contain an equal number of protons but differ in number of neutrons (i.e, differ in atomic mass)

A: Isotope Analysis (i.e., elements that make up the contaminant)

Stable: Don't deal with radioactive isotopes



By BenRG - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=7900237

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CSIA

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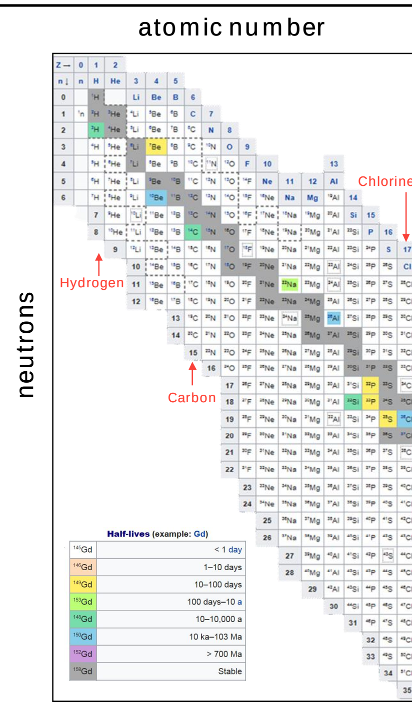
CSIA

Figure to Right: shows isotopes of elements that comprise most chemicals of interest to remediation professionals (e.g., Carbon has 2 stable isotopes ^{12}C and ^{13}C).

Relevance: Chemical bonds of lighter isotopes are slightly more reactive than bonds involving heavier isotopes. So compounds with heavier isotopes tend to accumulate in residual contaminated matrix.

Definitive: Enrichment of heavier isotopes, referred to as fractionation, is definitive evidence of chemical degradation as non-destructive processes like dilution and dispersion generally do not have significant disparate effects on isotopes.



Brookhaven National Laboratory which has an interactive Table of Nuclides

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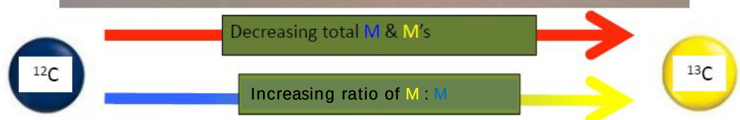
^{13}Chocolate Fractionation



Chocolate Fractionation used with permission from
Dr. Mike Hyman, Department of Microbiology
North Carolina State University

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CSIA

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Reporting: data are expressed in relation to an international standard (i.e., δ) and multiplied by 1,000 (i.e., ‰).

International Standard
Pee Dee River Belemnite

http://atoztheusa.blogspot.com/2013/03/delaware-state-fossil.html

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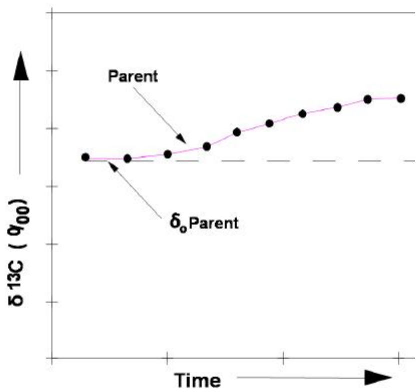
Isotopic Effects of Parent Compound Degradation



Parent compound fractionation is unequivocal proof of degradation

CSIA

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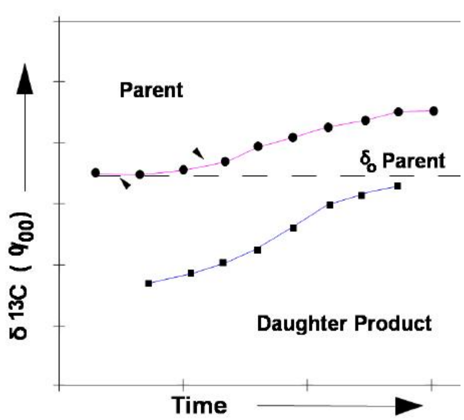
CSIA

Isotopic Effects of Parent Compound Degradation



The undegraded daughter product can get no heavier than the initial signature of the parent

for daughter products, fractionation alone does not prove daughter product degradation

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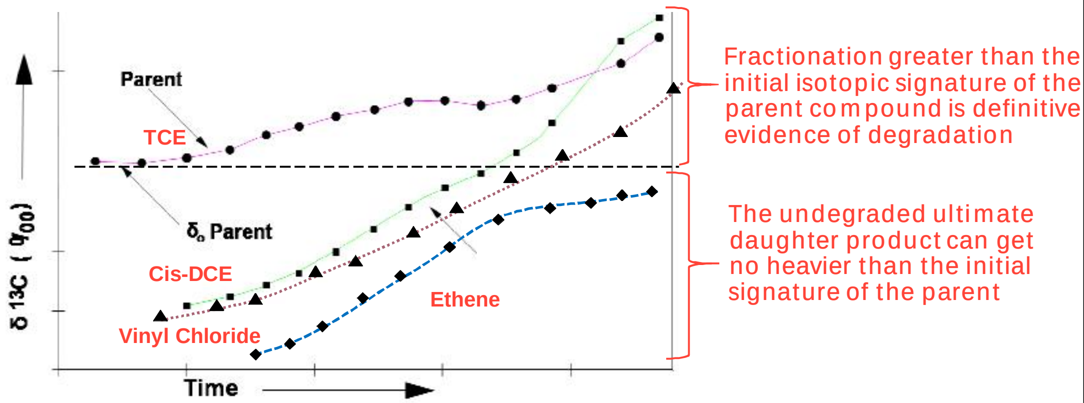
Isotopic Effects of Degrading
Daughter Product



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Permanganate Treatment at MA Site

Sample	MW-1 Pre-ISCO	MW-1 Post-ISCO	MW-2 Pre-ISCO	MW-2 Post-ISCO
TCE Concentration (µg/l)	3,000	80	400	500
TCE CSIA, $\delta^{13}C$ (‰)	-29.6	-3.7	-34.4	-25.7

MW-1:
- large decrease in TCE concentration
- corresponding large isotopic fractionation

MW-2:
- increase in TCE concentration
- significant isotopic fractionation with
- treatment effective

CSIA

Activated Persulfate Treatment at Swiss Site

	MW-4 Pre-ISCO	Post-ISCO 1	Post-ISCO 2
PCE Concentration (µg/l)	6,100	480	1,700
PCE CSIA, $\delta^{13}C$ (‰)	-25.8	-23.7	-24.5

- large decrease in PCE concentration
- isotopic fractionation

- Large concentration rebound
- isotopic rebound too
- Consistent with mixing of treated and untreated groundwater

CSIA

Permanganate Treatment at Texas Site

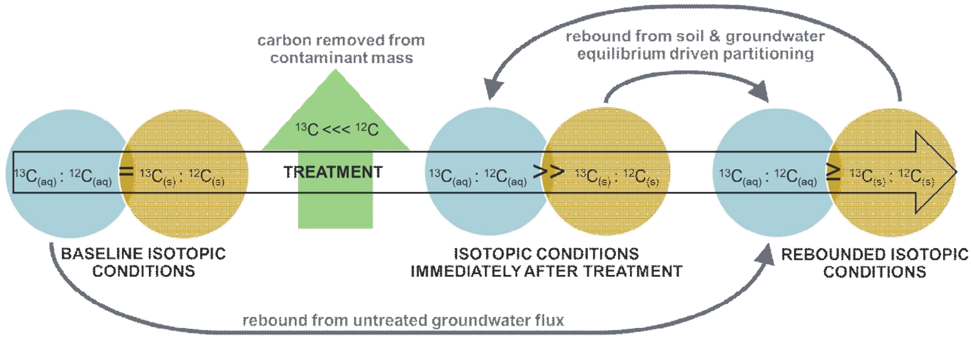
	MW-1 Pre-ISCO	Post-ISCO 1	Post-ISCO 2
PCE Concentration (µg/l)	6,000	80	600
PCE CSIA, $\delta^{13}C$ (‰)	-27.3	-16.8	-33.1

- large decrease in PCE concentration
- isotopic fractionation

- concentration rebound
- Isotopic signature lighter than pre-ISCO.
- Consistent with non-treatment (pushing water around)

At a glance

CSIA Rebound Summary



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Multi-Component & Multi-Functional Amendments

Questions?

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