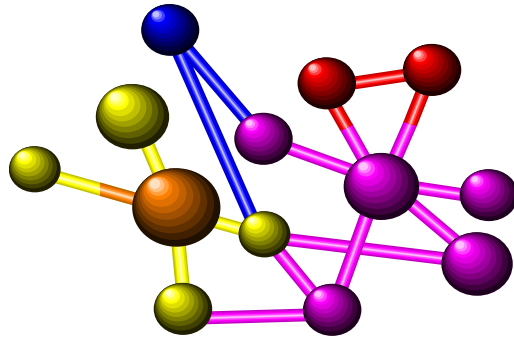


# The Use of Compound Specific Isotope Analysis to Manage Remediation by ISCO



**Robert J. Pirkle and Patrick W. McLoughlin , Microseeps, Pittsburgh, PA**

**Matt Burns, WSP Environment and Energy, Woburn, MA**

**Railroad Environmental Conference 2014**



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# Stable Isotopes in In-Situ Degradation

- Early focus on carbon and hydrogen isotopes
  - Can be determined in continuous flow mode
- Chlorine isotope capability more recently available
- Applicable to environmentally interesting concentrations



# Stable Isotopes in In-Situ Degradation

- ❑ Compounds with Light isotopes degrade more rapidly than compounds with Heavy isotopes
- ❑ Product remaining becomes isotopically heavier
- ❑ Process of isotopic change is called fractionation



# $^{13}\text{C}$ Chocolate Fractionation



Decreasing total  $M$  &  $M$ 's

Increasing ratio  $M : M$

$^{13}\text{C}$

$^{12}\text{C}$



# Stable Isotopes in In-Situ Degradation

- ❑ Compounds with Light isotopes degrade more rapidly than compounds with Heavy isotopes
- ❑ Product remaining becomes isotopically heavier
- ❑ Process of isotopic change is called fractionation

# Stable Isotopes in In-Situ Degradation

## Significant Fractionation Occurs in:

- ❑ Biological Oxidation
- ❑ Biological Reduction
- ❑ Abiotic Degradation
- ❑ In-Situ Chemical Oxidation
- ❑ In-Situ Chemical Reduction

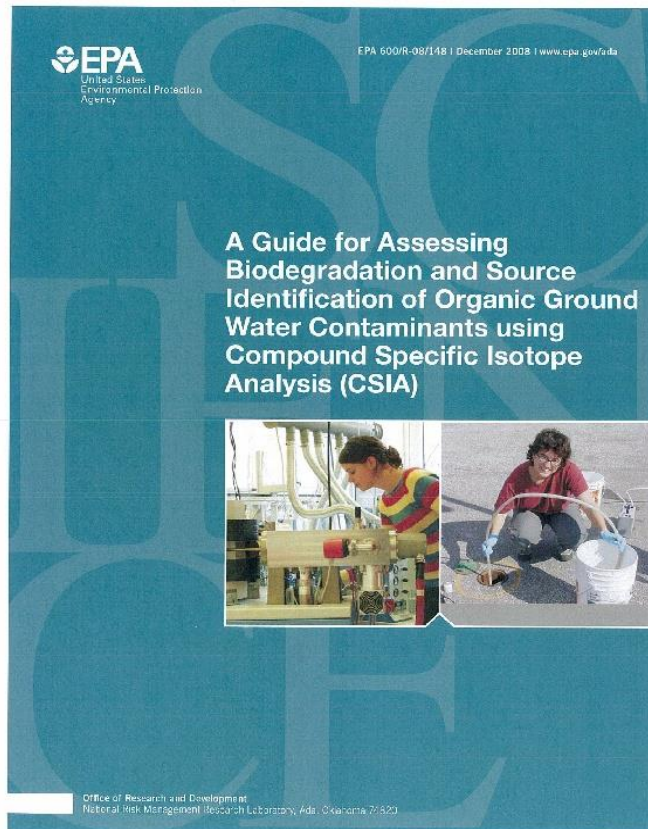
# Stable Isotopes in In-Situ Degradation

## Little or No Fractionation Occurs in:

- ❑ Dilution
- ❑ Volatilization
- ❑ Sorption



# USEPA Guide for CSIA



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# USEPA Chapters

1. Introduction
2. Data Quality Issues
3. Collection, Preservation and Storage of Samples
4. Interpretation of Stable Isotope Data from Field Sites
5. Strategies for Field Investigations
6. Use of Stable Isotopes for Source Identification
7. Derivation of Equations to Describe isotope Fractionation
8. Stable Isotope Enrichment Factors
9. Recommendations for the Application of CSIA
10. References



# The Stable Isotope Parameters

## Ratio

$$R = ([\text{heavy}] / [\text{light}]) = ([^{13}\text{C}] / [^{12}\text{C}])_x$$

## The “Del” Function

$$\delta_x = \{ (R_x - R_{\text{std}}) / R_{\text{std}} \} \times 1000 \text{ ‰}$$

# The Stable Isotope Parameters

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$$\delta_o^{13}\text{C} = -29 \text{ ‰}$$

# The Stable Isotope Parameters

## Ratio

$$R = ([\text{heavy}] / [\text{light}]) = ([^{13}\text{C}] / [^{12}\text{C}])_x$$

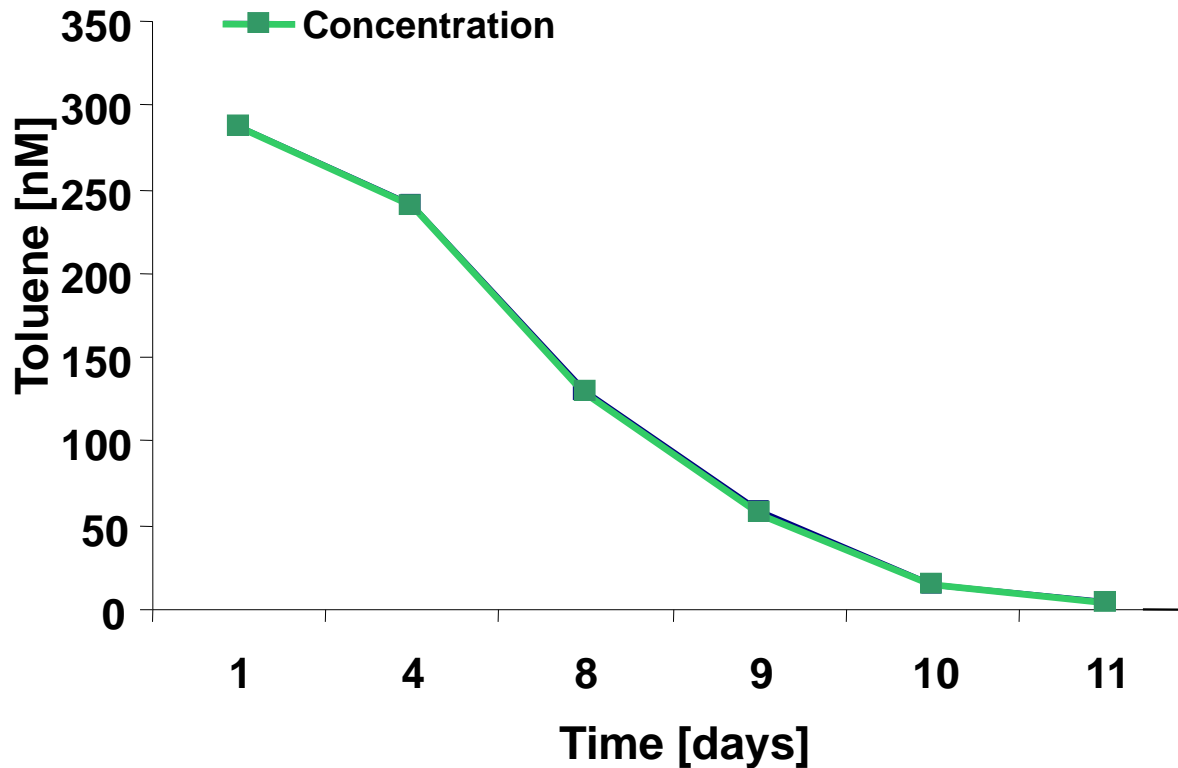
## The “Del” Function

$$\delta_x = \left\{ (R_x - R_{\text{std}}) / R_{\text{std}} \right\} \times 1000 \text{ ‰}$$

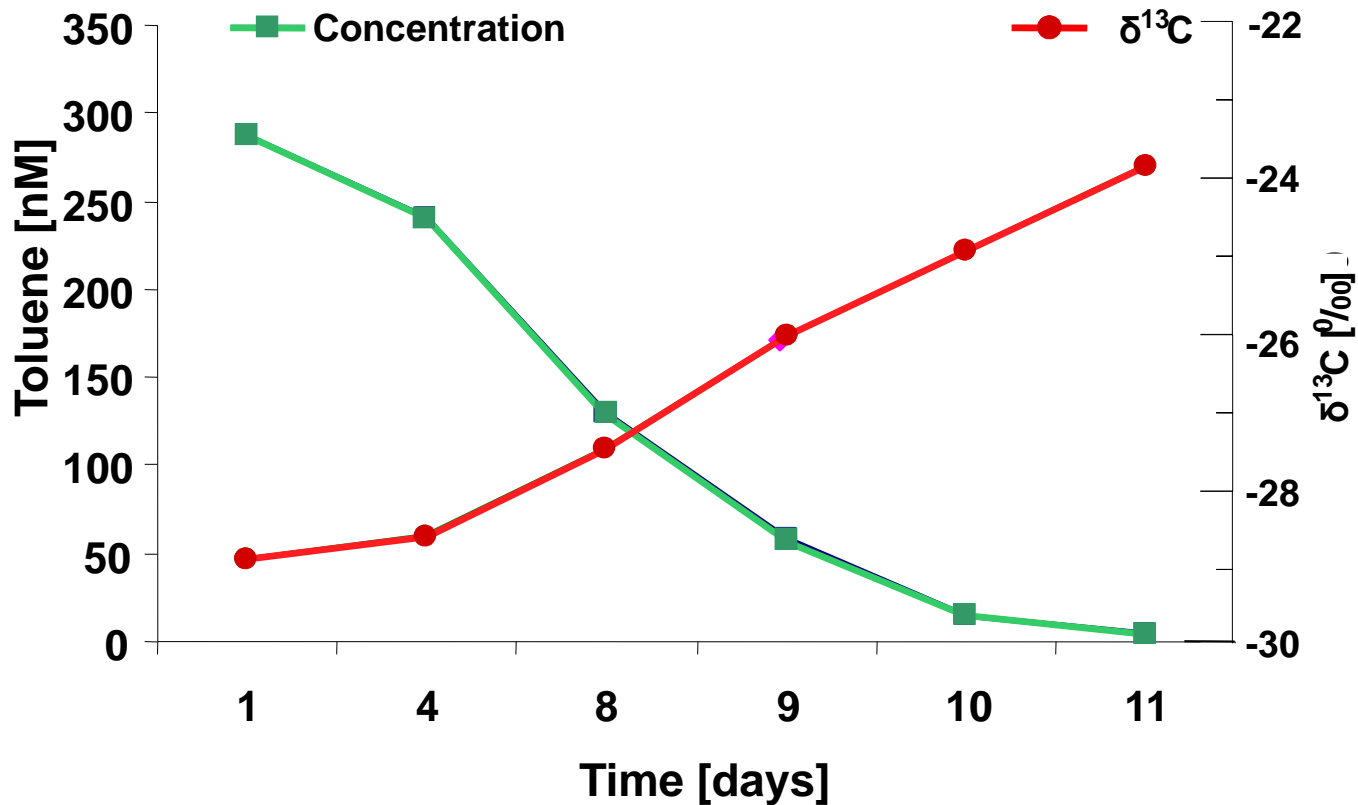
$$\delta_0^{13}\text{C} = - 29 \text{ ‰} \qquad \delta_1^{13}\text{C} = - 24 \text{ ‰}$$

$$\pm 0.5 \text{ ‰}$$

# Degradation of Toluene under Sulfate Reducing Conditions

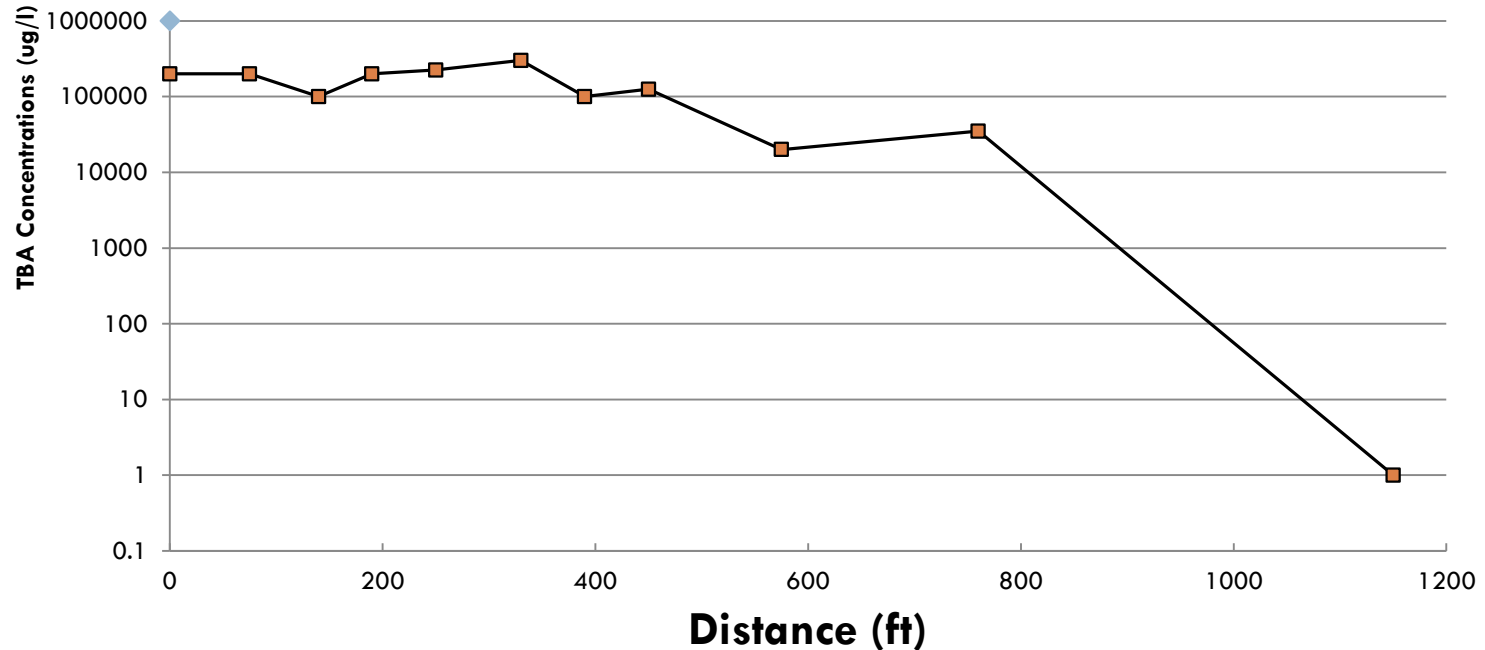


# Degradation of Toluene under Sulfate Reducing Conditions



# Application to Recalcitrant Compounds

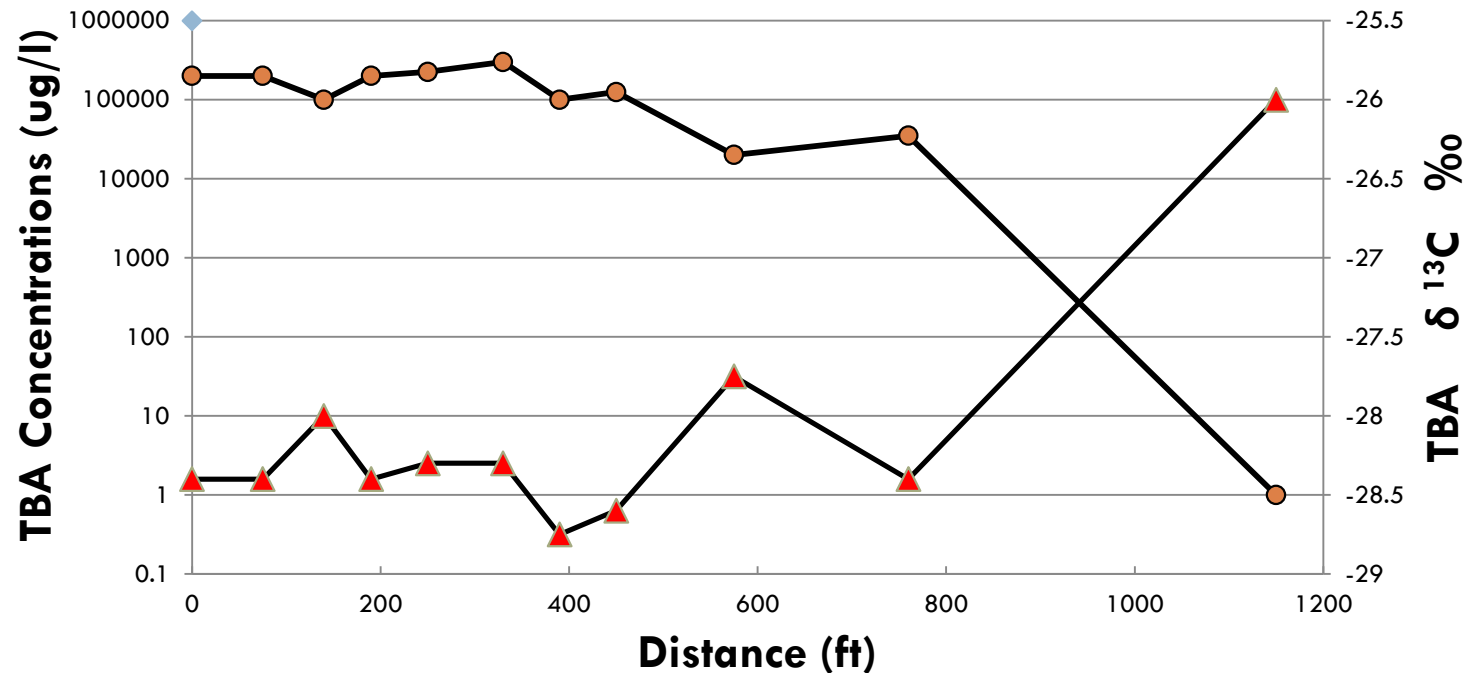
## tert-butyl Alcohol (TBA) Concentration



Day, et.al. (2003); Gulliver (2003)

# Application to Recalcitrant Compounds

## tert-butyl alcohol (TBA) Concentration and Isotopic Composition



Day, et.al. (2003); Gulliver (2003)



# Stable Isotopes in In-Situ Degradation

- Fractionation is unequivocal proof of in-situ degradation
- Related to the mechanism of degradation
- Related to the fraction of component degraded
- Related to the rate of degradation
- Used in groundwater modeling





# Environmental Molecular Diagnostics

New Tools for Better Decisions



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## Welcome

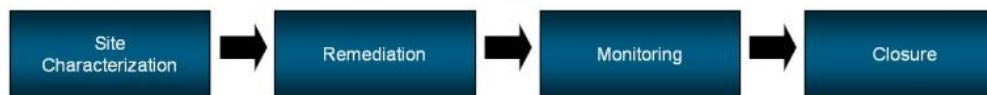
Environmental molecular diagnostics (EMDs) are a group of advanced and emerging techniques used to analyze biological and chemical characteristics of environmental samples. Many of these techniques were originally developed for applications in medicine, defense, and industry. Over the last decade, however, EMDs have proven effective in environmental site management. EMDs have applications in each phase of environmental site management and provide additional lines of evidence for making better decisions.

This online guidance document will help you to understand how EMDs might benefit your site management decisions. If you are reading this document for the first time, please review the following [FAQs](#).

You can review this guidance following the navigation at the left (beginning with the [Executive Summary](#)), or you can use the **Questions** tab at the top of the navigation window to directly access specific questions that EMDs can help to answer. The **Topics** tab summarizes parts of this document that are of particular interest to specific audiences.

If you are trying to determine if EMDs can benefit your site, then you may wish to start with [Figure 2-2](#).

You can also click on one of the project stages below to begin:



If you are interested in specific EMD methods, you can start here:

[Compound Specific Isotope Analysis](#)

[Quantitative Polymerase Chain Reaction](#)



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# EMD Guidance Document Contents

Summary of EMDs and guidance on data interpretation  
Case Studies  
Survey Results  
Science Refreshers (Isotope chemistry,  
Microbiology)  
Regulatory, Public and Tribal Stakeholder  
Acceptance and Issues  
Data Quality Considerations



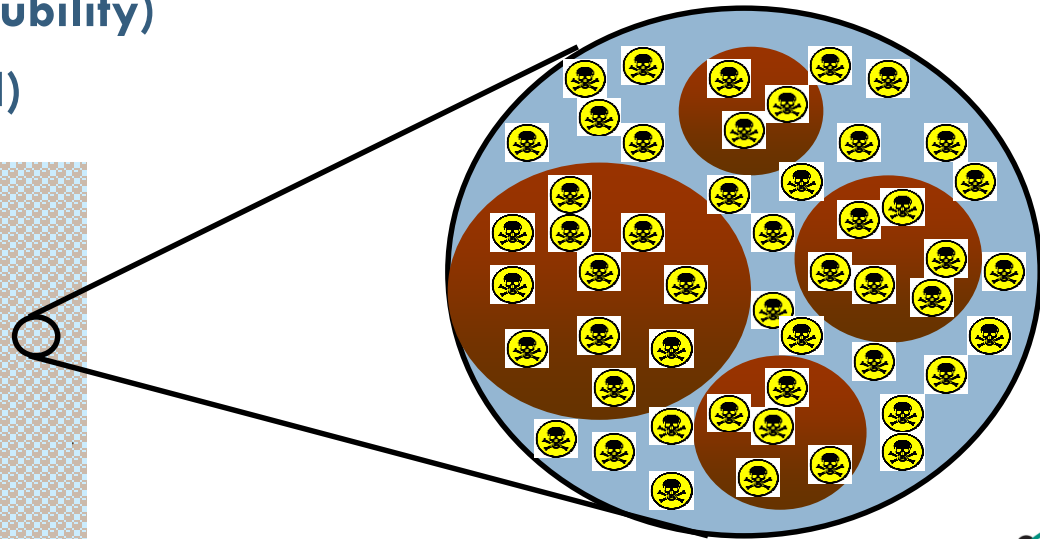
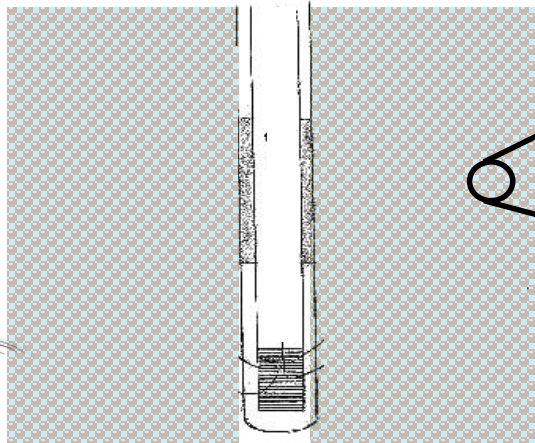
# CSIA & ISCO

- The use of CSIA to track ISCO remedial progress is an emerging application of the CSIA technology
- CSIA has been found to be beneficial to:
  - **Confirm contaminant destruction where contaminant concentration data is inconclusive**
  - **Identify delivery limitations**
  - **Better time supplemental ISCO applications**



# Pre-ISCO Application

- Contaminant mass can be present dissolved in groundwater, sorbed to aquifer sediment, and as a separate non-aqueous phase
- Partitioning between these phases is equilibrium-based and dependent on characteristics of:
  - **Aquifer sediments (e.g., organic content)**
  - **Contaminant (e.g., solubility)**
  - **Groundwater (e.g., pH)**



# Stable Isotopes in In-Situ Degradation

## Little or No Fractionation Occurs in:

- Dilution
- Volatilization
- Sorption

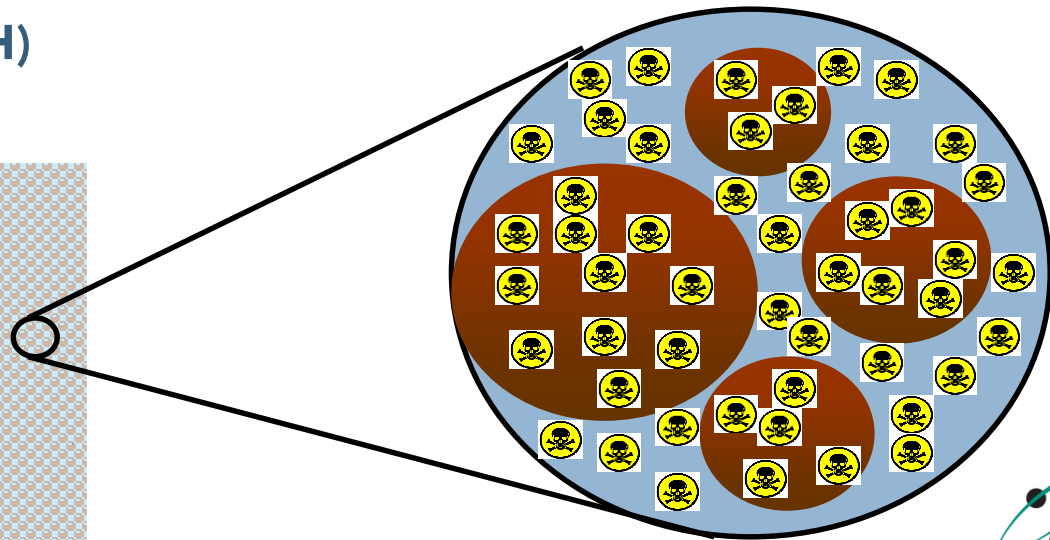
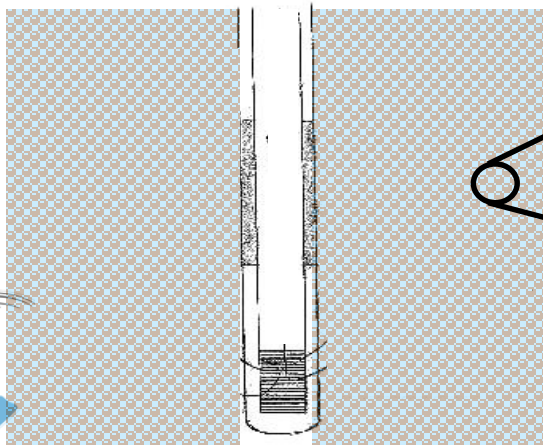
# Baseline Isotopic Conditions

$$^{13}\text{C}_{(\text{aq})} : ^{12}\text{C}_{(\text{aq})} \approx ^{13}\text{C}_{(\text{s})} : ^{12}\text{C}_{(\text{s})}$$

**aqueous ratio  $\approx$  sorbed ratio**

# Pre-ISCO Application

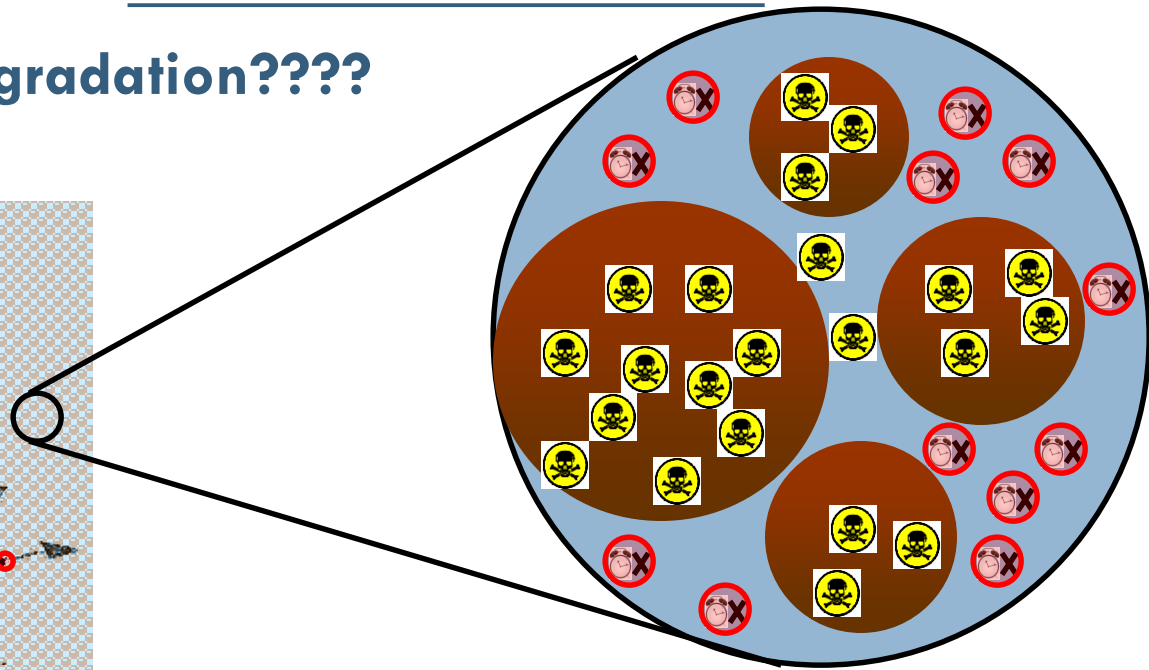
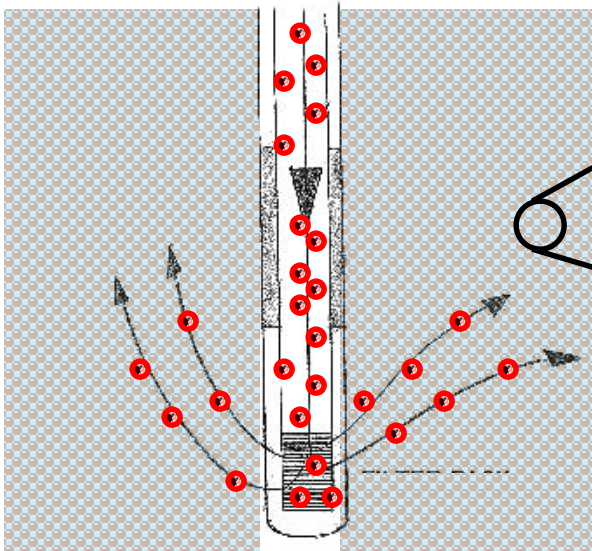
- Contaminant mass can be present dissolved in groundwater, sorbed to aquifer sediment, and as a separate non-aqueous phase
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  - **Aquifer sediments (e.g., organic content)**
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# Post-ISCO Application

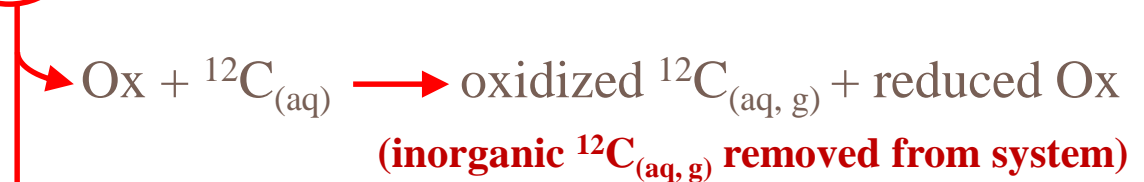
Immediately following oxidant application,  
aqueous contaminant concentrations decrease  
.....dilution or degradation???



# ISCO Application

## ISCO effect on carbon isotopic ratios:

Baseline  
Isotopic Conditions



Post-ISCO  
Isotopic Conditions



# ISCO Application

Site data show significant fractionation immediately following ISCO application

## New Jersey Site

	MW-1		MW-2	
	<u>Pre-ISCO</u>	<u>Post-ISCO</u>	<u>Pre-ISCO</u>	<u>Post-ISCO</u>
TCE: CSIA, $\delta^{13}\text{C}$ (‰)	-29.6	-3.7	-34.4	-25.7
TCE Concentration ( $\mu\text{g/l}$ )	3,000	80	400	500

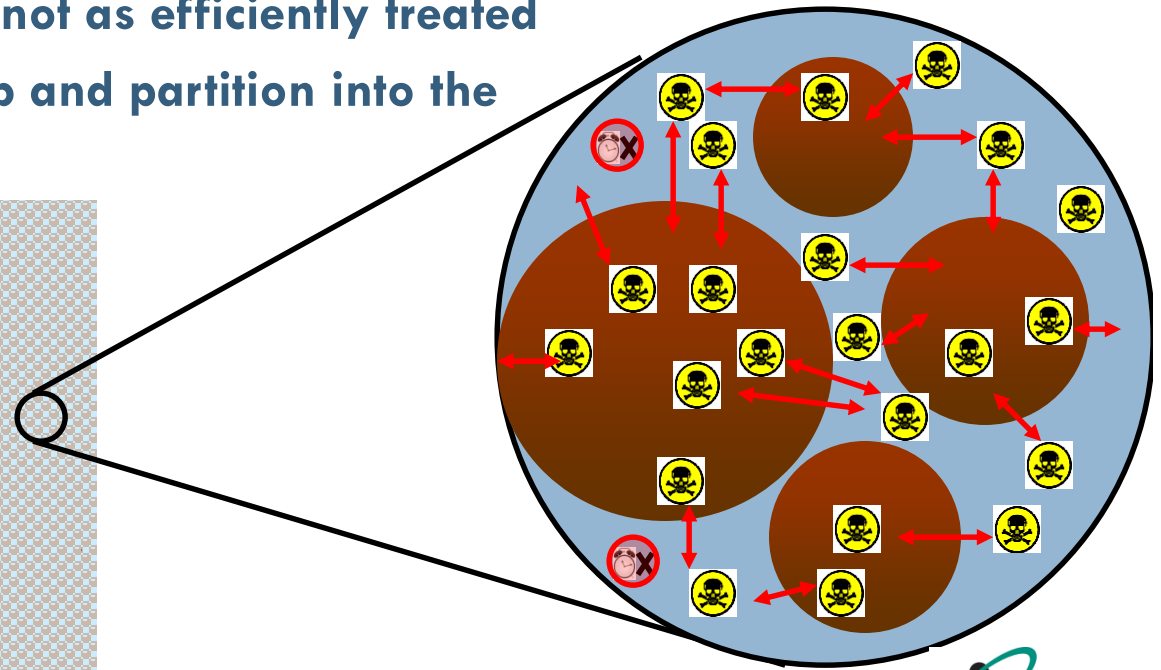
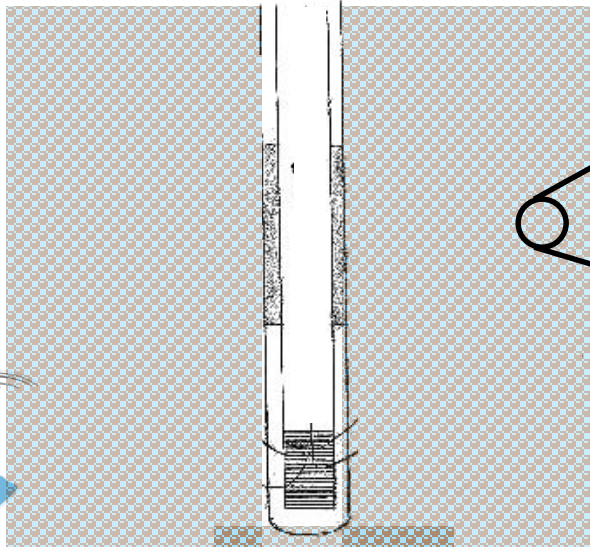
Very large isotopic fractionation (enrichment of  $^{13}\text{C}/^{12}\text{C}$  within the dissolved carbon pool comprising TCE) with very large **decrease** in TCE concentration

Significant isotopic fractionation with **increase** in TCE concentration

# Rebound

With the depletion of the oxidant, a flux of “relatively untreated” contaminant enters the treated groundwater. Desorption is typically the primary mechanism of “rebound”:

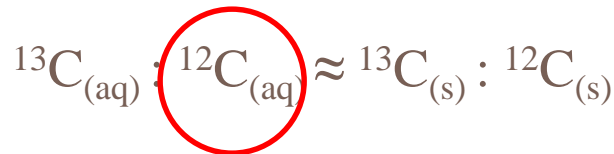
- Contaminant oxidation reactions are believed to be more efficient in the aqueous phase
- Sorbed contaminant not as efficiently treated
- Contaminants desorb and partition into the aqueous phase



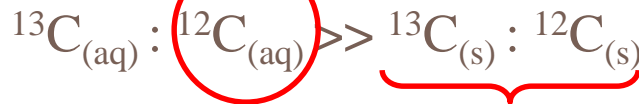
# Rebound

Rebound effect on carbon isotopic ratios:

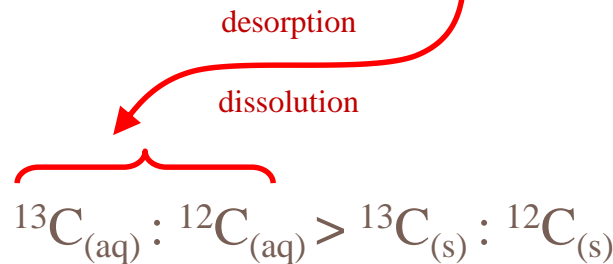
Baseline  
Isotopic Conditions



Post-ISCO  
Isotopic Conditions



Isotopic  
Fractionation Shifts  
During Rebound



# Rebound

## Isotopic evidence interpreted as desorption rebound

### Switzerland Site

Pre-ISCO                      MW-4  
Post-ISCO T-1                      Post-ISCO T-2

PCE: CSIA,  $\delta^{13}\text{C}$  (‰)

-25.8

-23.7

-24.5

PCE Concentration ( $\mu\text{g/l}$ )

6,100

480

1,700

Increase of  $\delta^{13}\text{C}$   
and lower PCE  
concentration  
following ISCO  
application

Decrease of  $\delta^{13}\text{C}$   
and increased PCE  
concentration with time  
following ISCO  
application

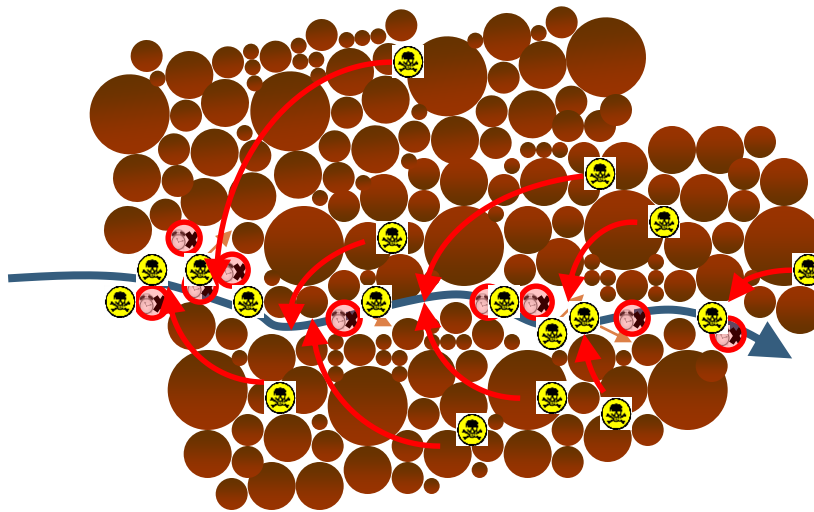
# Rebound

## Inefficient oxidant delivery can also cause “rebound”

- Preferential flow paths limit treatment to a fraction of the affected volume
  - Desorption rebound occurs from area where oxidant was delivered
  - Delivery rebound occurs when untreated water moves into treated zones.

In-situ longevity of oxidant limits transport into less permeable areas

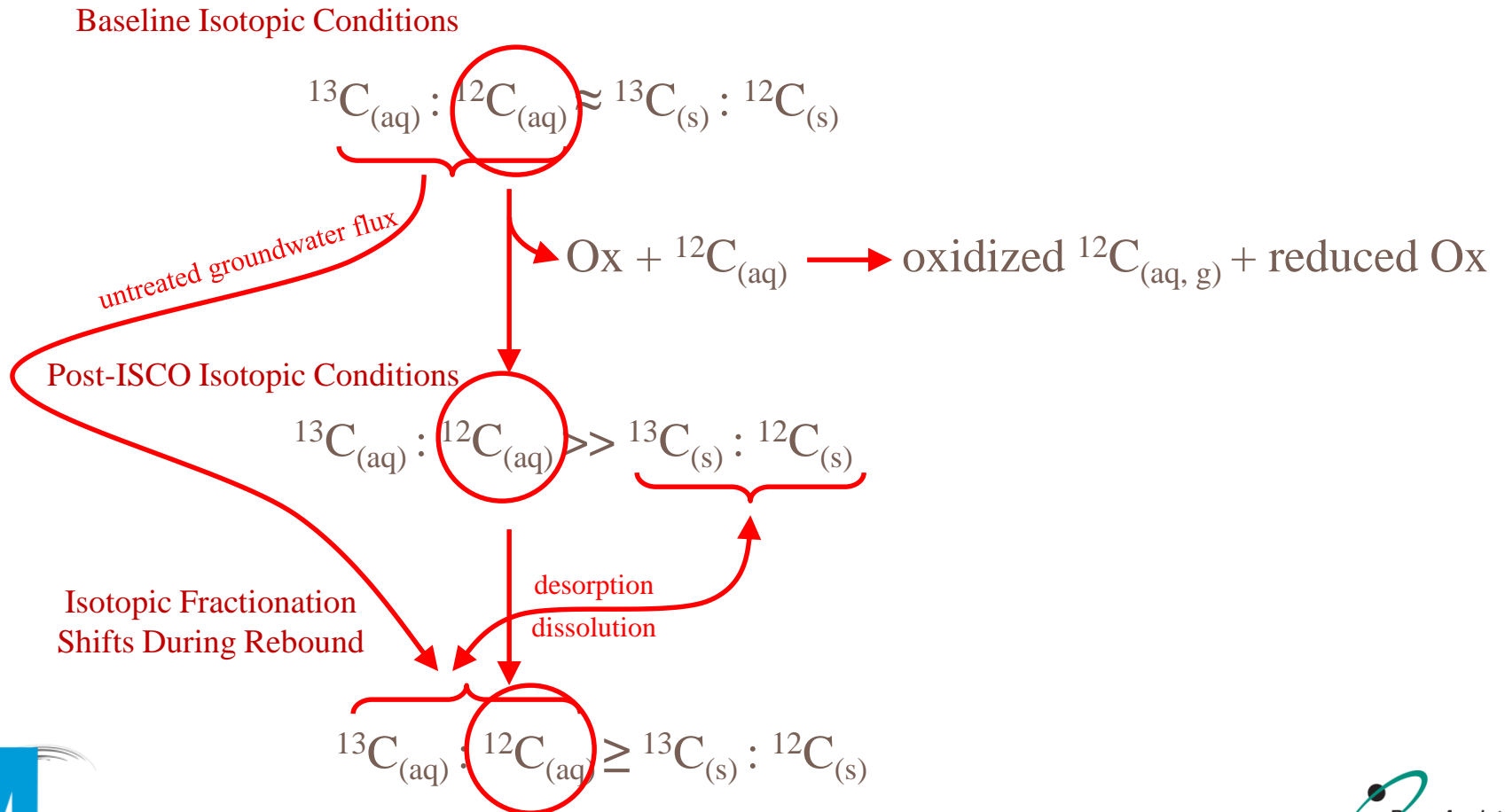
Preferential Flow Path



Contaminants move from less permeable areas to more permeable treated areas

# Rebound

## Delivery rebound effect on carbon isotopic ratios:





# Rebound

## Site data show isotopic evidence of delivery rebound

### New Jersey Site

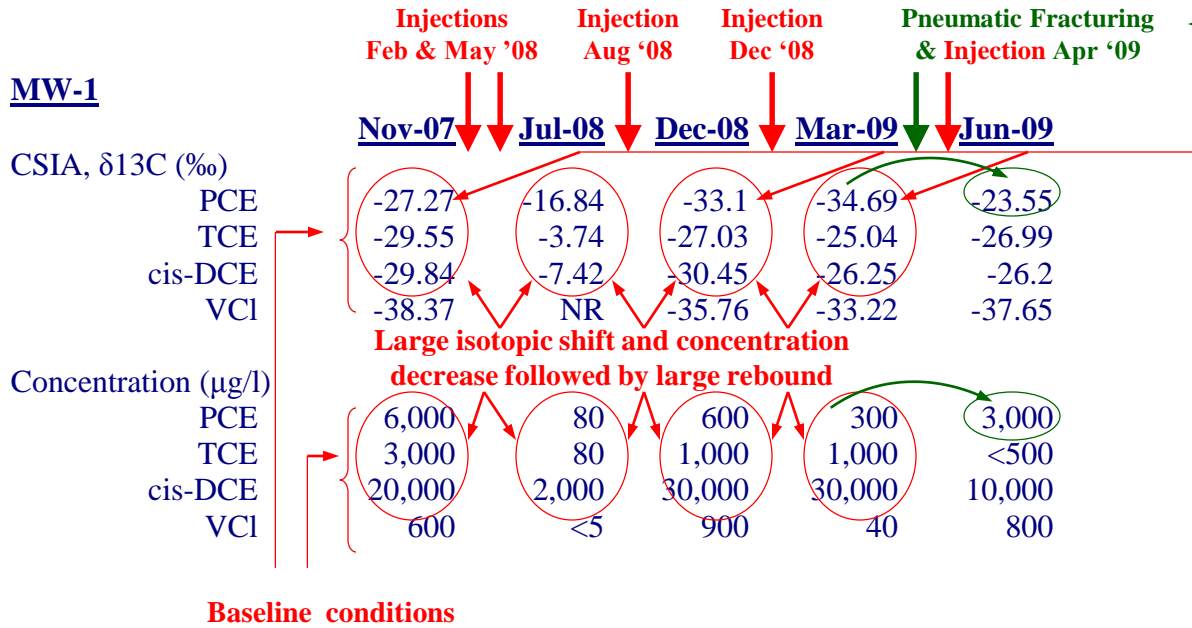
	<u>Pre-ISCO</u>	<u>MW-1</u> <u>Post-ISCO T-1</u>	<u>Post-ISCO T-2</u>
PCE: CSIA, $\delta^{13}\text{C}$ (‰)	-27.3	-16.8	-33.1
PCE Concentration ( $\mu\text{g/l}$ )	6,000	80	600

large isotopic fractionation

large isotopic rebound

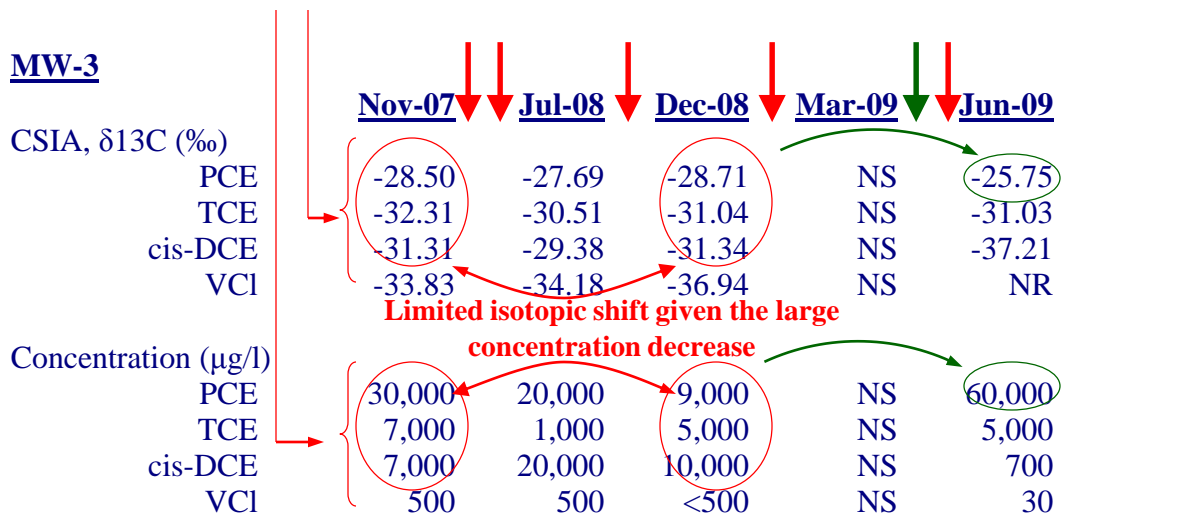
# Case Study – New Jersey Site

## MW-1



- PCE rebounded/  $\delta^{13}\text{C}$  decrease greater than baseline conditions can not be explained by bond-breaking reactions. Likely mobilized un-degraded PCE
- Conclude that although the concentrations are decreasing the remediation is not progressing adequately. Isotopic data suggests water is being pushed around
- Enhance delivery by pneumatically fracturing the saturated soils
- Post enhanced delivery results show large contaminant concentration increases accompanied by significant fractionation (i.e., the larger contaminant mass is being treated)

## MW-3



- **Conclusions:**
  - CSIA data identified delivery inefficiencies where concentration data alone were inconclusive
  - Enhancing delivery has increased contaminant destruction efficiency and will reduce oxidant and application costs significantly (20% estimated) over the duration of the project

# CSIA and ISCO Summary

The data presented shows the potential for CSIA to aid in:

- **Confirmation of contaminant destruction where contaminant concentration data are inconclusive**
- **Identify delivery limitations**
- **Better target and/or time supplemental ISCO applications**



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# Questions???



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