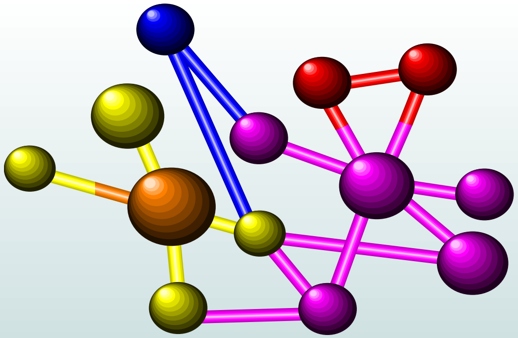

# Optimizing *In-Situ* Chemical Oxidation Performance Monitoring and Project Management Using Compound Specific Isotope Analysis

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microseeps insight

WSP

# CSIA

- A powerful tool to document in-situ degradation
- Validated academic sector and regulatory agencies
- Newly available services widening the use of CSIA
- provides new information completely independent of concentration.
- Isotopic composition measures the type of molecules that make up a VOC
- Concentration measures the number of those molecules.

## CSIA can guide remediation decisions by:

- Identifying cost reduction opportunities
- Assessing the effectiveness of existing remediation strategies
- Providing a new kind of data that helps avoid un-necessary or redundant controls

## CSIA provides valuable insights about:

- degradation mechanisms.
- degradation versus dilution.
- extent of degradation.

# Applications of CSIA

- In-Situ Remediation
  - Chemical Oxidation and Reduction
  - Biological Oxidation and Reduction
- Remedial Forensic Investigations
- Source Forensic Investigations

# Stable Isotopes in In-Situ Degradation

- Focus on carbon and hydrogen isotopes
- Can be determined in continuous flow mode
- Applicable to environmentally interesting concentrations

# Stable Isotopes in In-Situ Degradation

- Compounds with Light isotopes in the reactive position degraded more rapidly than compounds with Heavy isotopes in the reactive position
- Product remaining becomes isotopically heavier
- Process of isotopic change is called fractionation

# Stable Isotopes in In-Situ Degradation

Any process which breaks a bond…..

biological oxidation or reduction

chemical oxidation or reduction

……causes isotopic 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

# Stable Isotopes in In-Situ Degradation

- Light isotopes degraded more rapidly than heavy isotopes
- Product remaining becomes isotopically heavier
- Process of isotopic change is called fractionation
- 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

# The Stable Isotope Ratio

**Ratio = R = ([heavy] / [light])**

$$R = ([^{13}C] / [^{12}C])$$

$$R = ([^{2}H] / [^{1}H])$$

# The Stable Isotope Parameter δ

**We define a parameter "del" ≡ δ**

**and for a compound X**

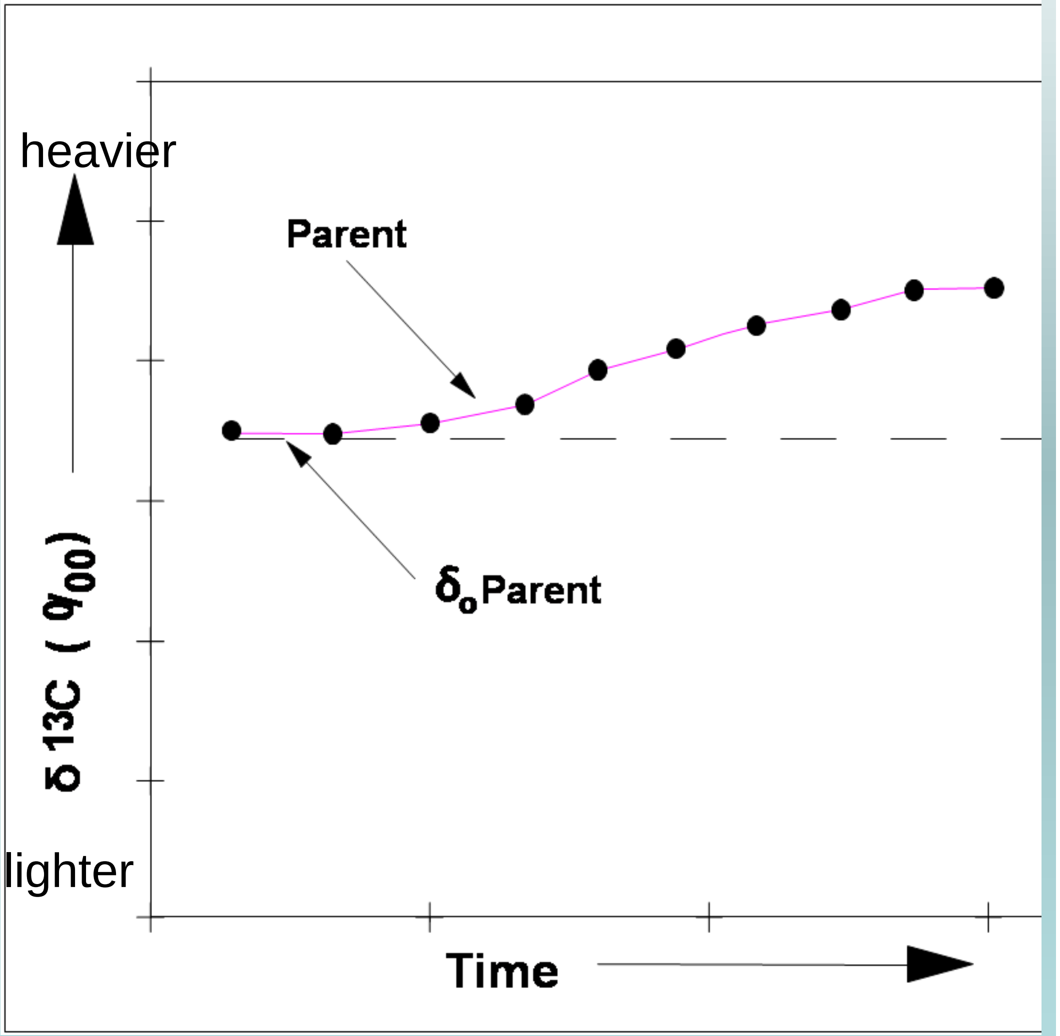
$$\delta_x = \{(R_x - R_{std}) / R_{std}\} \times 1000$$

**The units of $\delta_x$ are ppt or "per mil"…..**

**often denoted by the symbol "‰"**

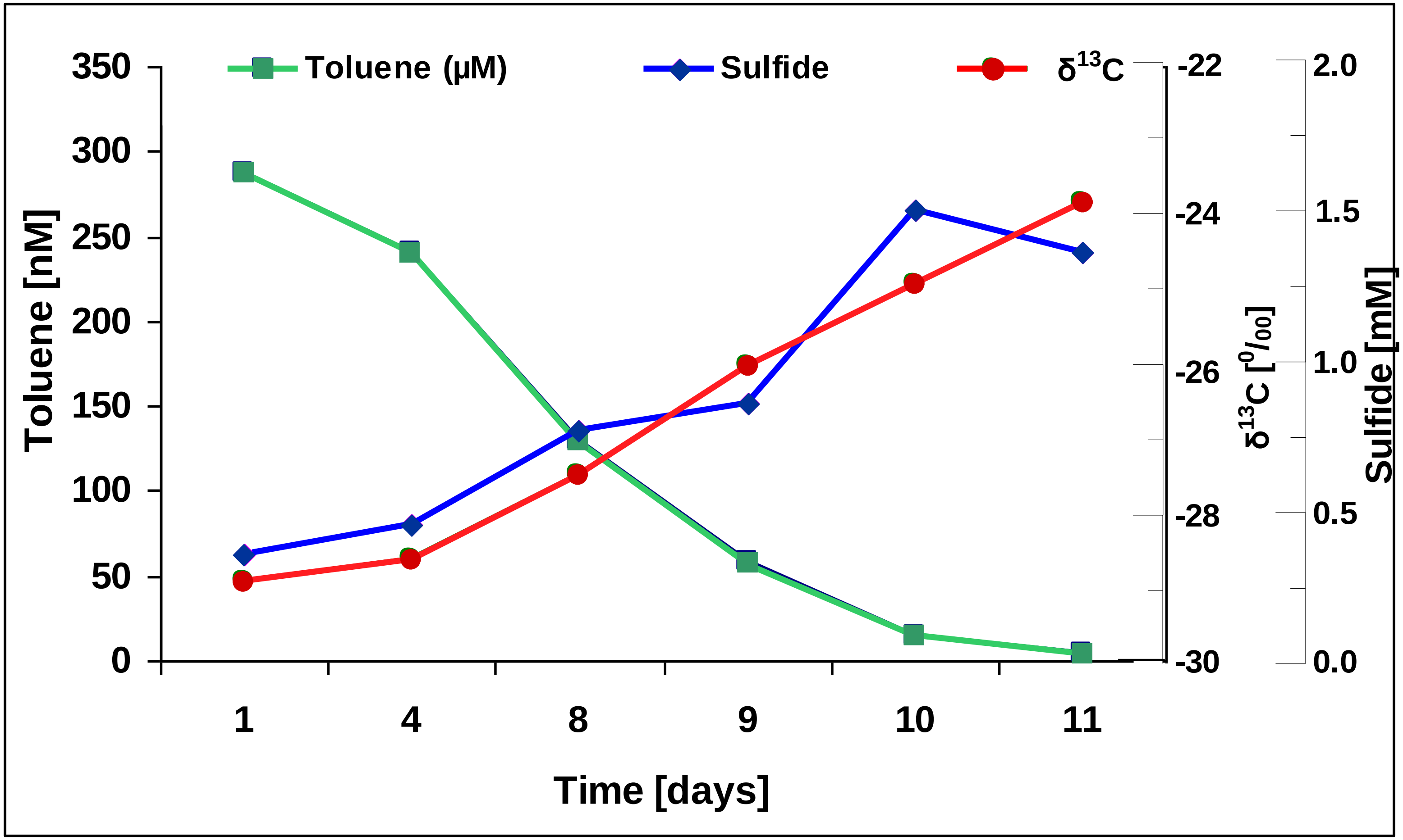
# CSIA and Degradation

- Degradation "chews" away at the lightest stuff, leaving behind the heavy stuff.
- This is called "fractionation."
- For parent molecules (*i.e.* what was originally released, typically PCE or TCE) fractionation is unequivocal proof of degradation.



# Anaerobic Degradation of Toluene under Sulfate Reducing Conditions

Meckenstock, et al., 1999.



# CSIA and In-Situ Degradation

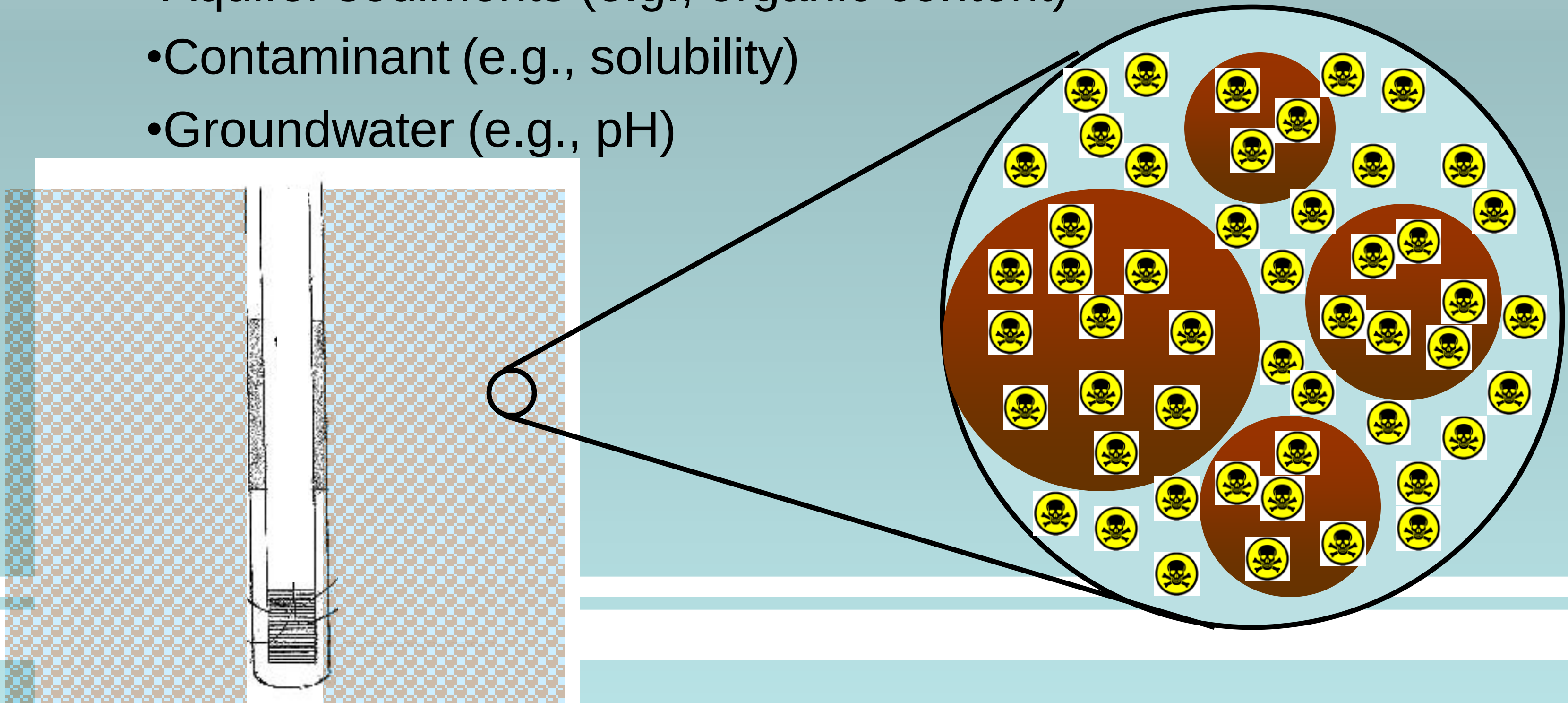
- WSP has used CSIA at approximately 30 sites world wide to make better decisions that have expedited site closure and minimized costs. Applications include:
  - Monitored Natural Attenuation (MNA)
  - Enhanced In-Situ Remediation
  - In Situ Microcosm Studies
  - In-Situ Chemical Oxidation (ISCO)

# CSIA & ISCO

- The use of CSIA to track ISCO remedial progress is an emerging application of the CSIA technology
- WSP has used CSIA to monitor remedial progress and optimize performance at 4 ISCO sites
  - Remediation is ongoing at all 4 sites
  - Tests were paid for by clients. Results were expected to provide actionable data and achieve closure as rapidly and cost effectively as possible
- CSIA has been found to be beneficial to:
  - Confirm contaminant destruction where contaminant concentration data is inconclusive
  - Identify delivery limitations
  - Better target/time supplemental ISCO applications

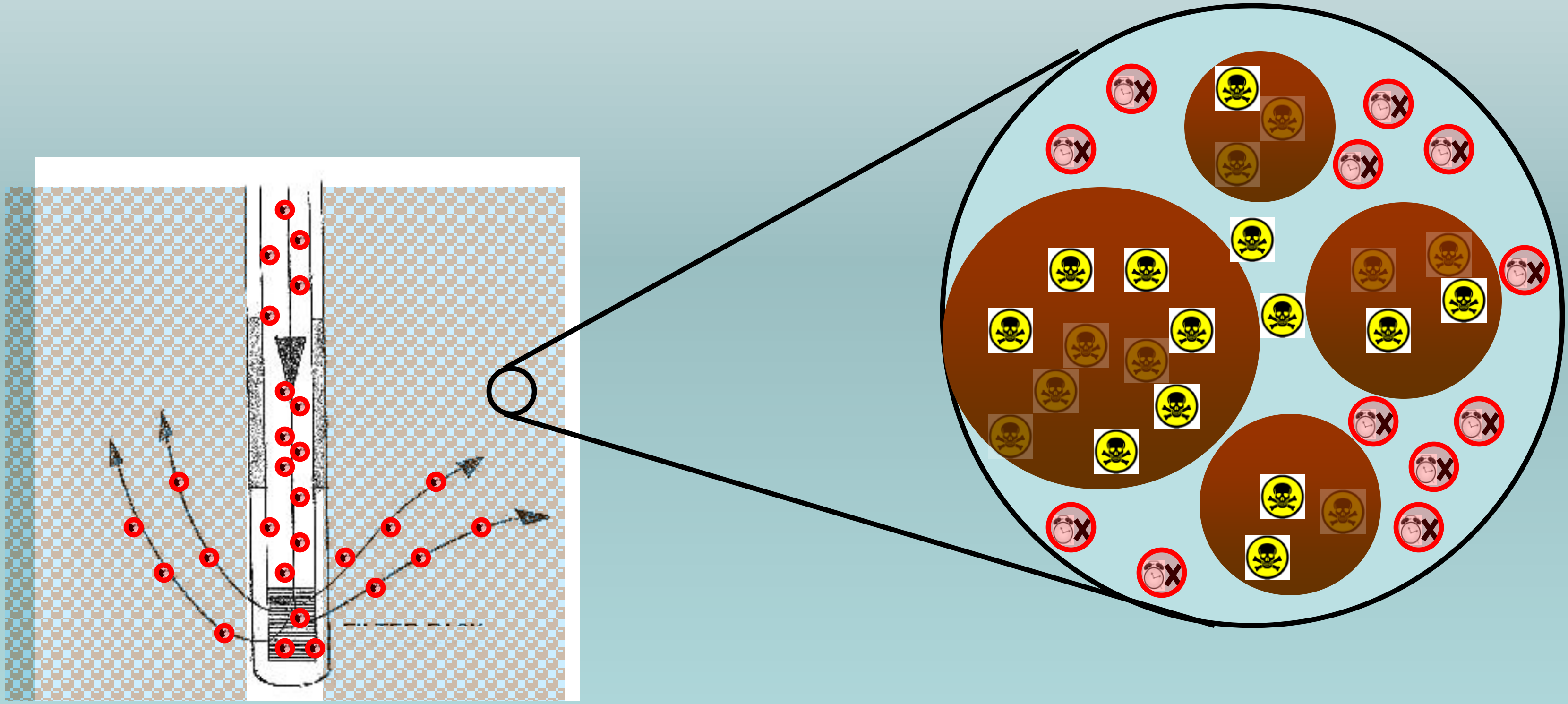
# Pre-ISCO Application

- 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)



# Post-ISCO Application

Immediately following oxidant application, dissolved contaminant concentrations decrease



# Post-ISCO Application

ISCO effect on carbon isotopic ratios:

**Baseline Isotopic Conditions**

$$^{13}C_{(aq)} : {}^{12}C_{(aq)} = {}^{13}C_{(s)} : {}^{12}C_{(s)}$$

$$Ox + {}^{12}C_{(aq)} \rightarrow \text{oxidized } {}^{12}C_{(aq,\, g)} + \text{reduced Ox}$$

**(inorganic $^{12}C_{(aq, g)}$ removed from system)**

**Post-ISCO Isotopic Conditions**

$$^{13}C_{(aq)} : {}^{12}C_{(aq)} >> {}^{13}C_{(s)} : {}^{12}C_{(s)}$$

# Post-ISCO Application

Site data show significant fractionation immediately following ISCO application

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

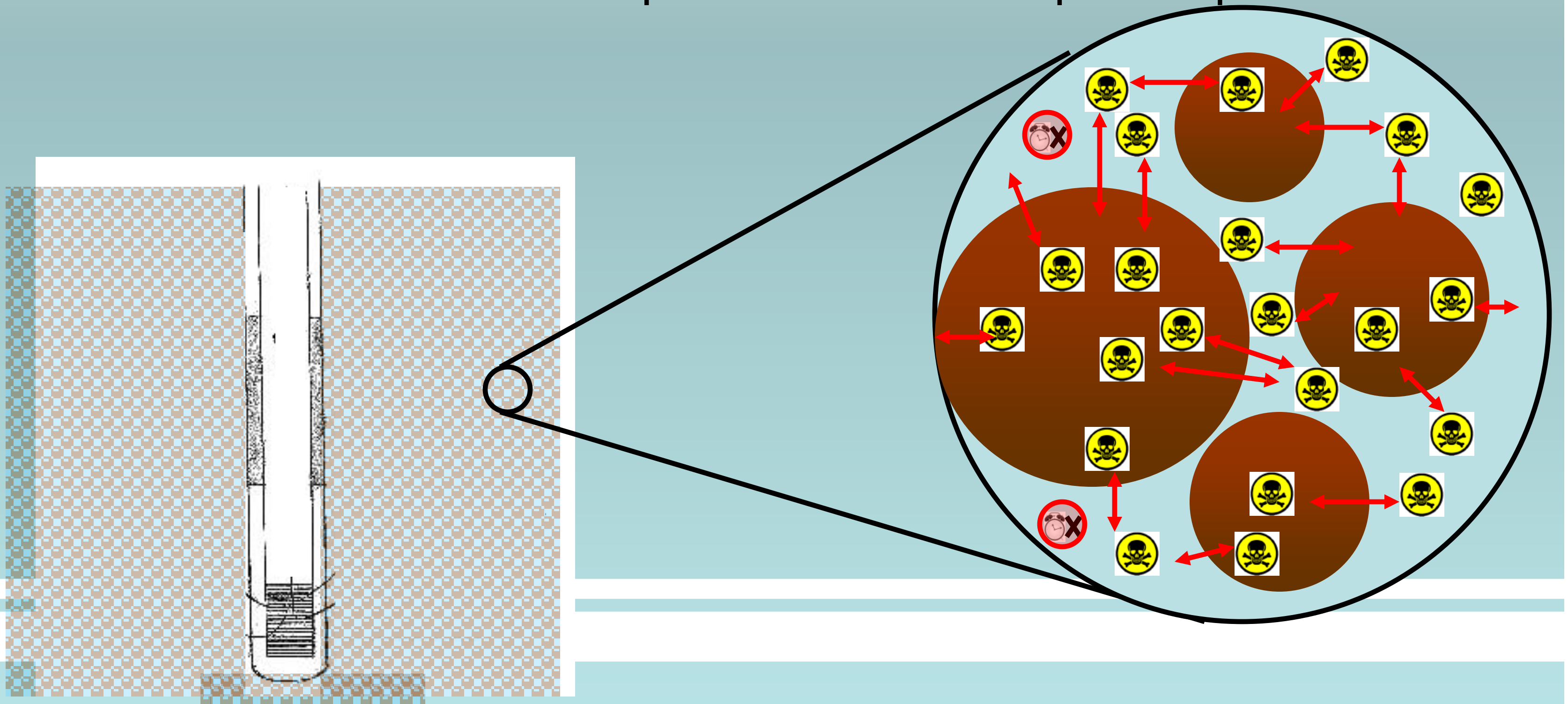
Very large isotopic fractionation (enrichment of $^{13}$**C/** $^{12}$**C** within the dissolved carbon pool comprising TCE) with very large **decrease** in TCE concentration

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

# Rebound

With the depletion of the oxidant, a flux of “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**

$$^{13}C_{(aq)} : {}^{12}C_{(aq)} = {}^{13}C_{(s)} : {}^{12}C_{(s)}$$

$$Ox + {}^{12}C_{(aq)} \rightarrow \text{oxidized } {}^{12}C_{(aq,\ g)} + \text{reduced } Ox$$

**Post-ISCO Isotopic Conditions**

$$^{13}C_{(aq)} : {}^{12}C_{(aq)} >> {}^{13}C_{(s)} : {}^{12}C_{(s)}$$

**Isotopic Fractionation Shifts During Rebound**

desorption

dissolution

$$^{13}C_{(aq)} : {}^{12}C_{(aq)} > {}^{13}C_{(s)} : {}^{12}C_{(s)}$$

# Rebound

Isotopic evidence interpreted as desorption rebound

**Switzerland Site**

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

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

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

# Rebound

## Isotopic effects of a chem/bio application

**Florida Site**

Baseline/Pre-ISCO sample not collected

| MW-5 | Post-ISCO T-1 | Post-ISCO T-2 | Post-ISCO T-3 |
|---|---|---|---|
| Benzene: CSIA, $\delta^{13}C$ (‰) | -24.6 | -26.4 | -25.5 |
| Benzene Concentration (µg/l) | 200 | 800 | 151 |
| MTBE: CSIA, $\delta^{13}C$ (‰) | -24.6 | -26.3 | -25.6 |
| MTBE Concentration (µg/l) | 70 | 40 | 10 |

Assume enrichment of $^{13}C$ or increase of $\delta^{13}C$

Decrease of $\delta^{13}C$ within the dissolved contaminant plume

A contaminant degradation rate greater than the rate of contaminant desorption/dissolution leads to increase in $\delta^{13}C$.

Typical $\delta^{13}C$ of benzene and MTBE in gasoline:

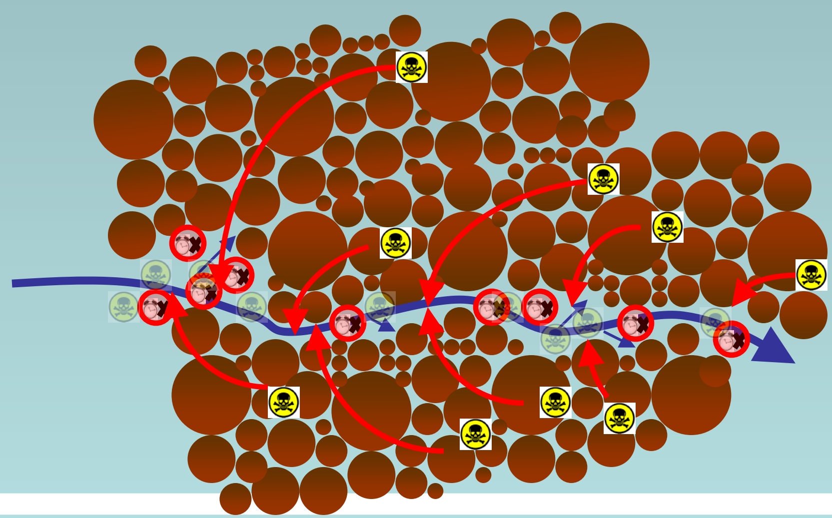
- Benzene: -23.5 ‰ to -31.5 ‰
- MTBE: -27.5 ‰ to -33.0 ‰

# Rebound

Inefficient oxidant delivery can also cause “rebound”

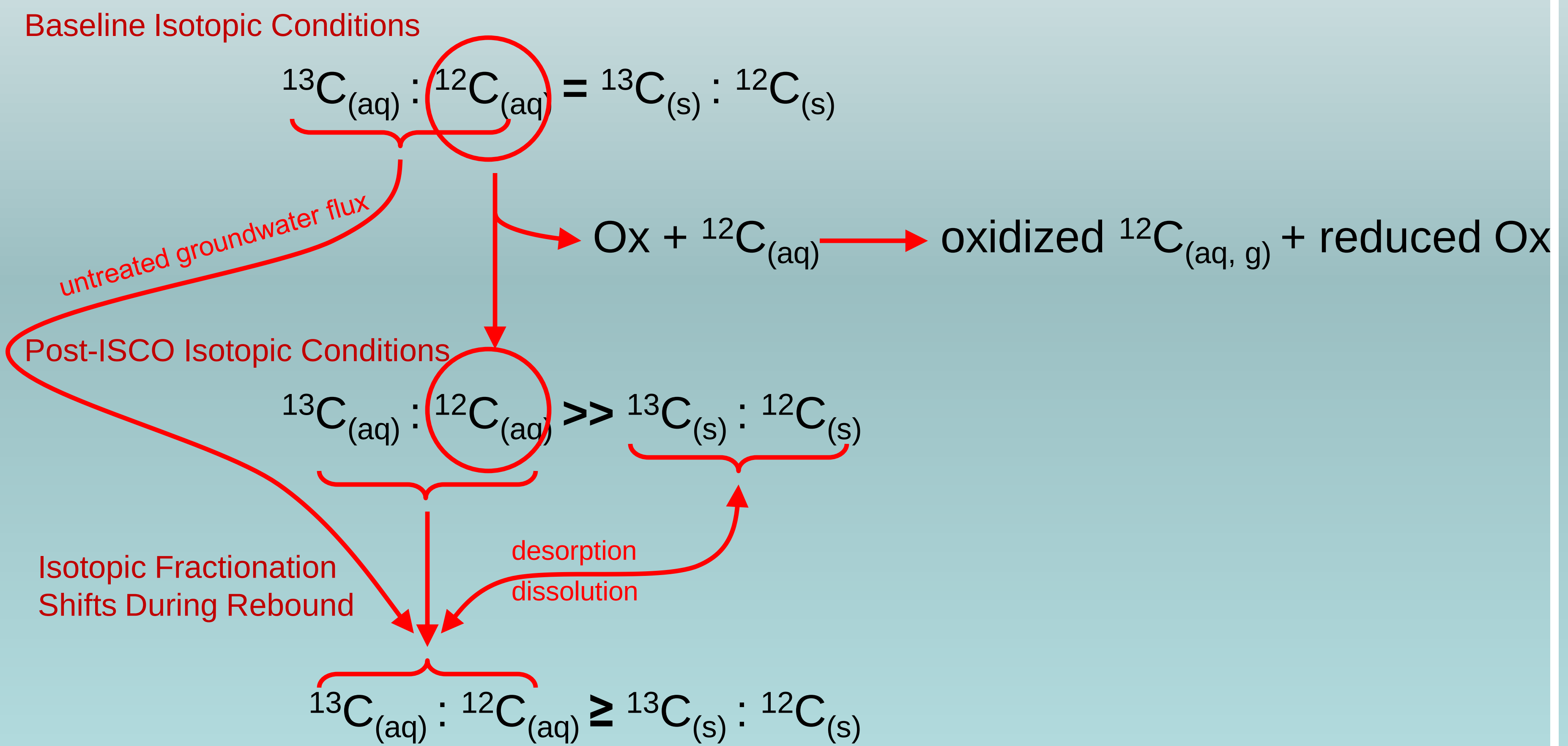
- Preferential flow paths limit treatment to a fraction of the affected volume
  - Desorption rebound occurs from area where oxidant was delivered
  - Delivery rebound occurs when untreated water moves into treated zones.

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



# Rebound

Delivery rebound effect on carbon isotopic ratios:



# Rebound

Site data show isotopic evidence of delivery rebound

**New Jersey Site**

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

large isotopic fractionation

large isotopic rebound

# CSIA and ISCO Summary

- The presented information shows the potential for CSIA to aid in:
  - Confirmation of contaminant destruction where contaminant concentration data are inconclusive
  - Identify delivery limitations
  - Better target/time supplemental ISCO applications

# Case Study – New Jersey Site

Injections Feb & May '08 | Injection Aug '08 | Injection Dec '08 | Pneumatic Fracturing & Injection Apr '09

**MW-1**

| | Nov-07 | Jul-08 | Dec-08 | Mar-09 | Jun-09 |
|---|---|---|---|---|---|
| CSIA, δ13C (‰) | | | | | |
| PCE | -27.27 | -16.84 | -33.1 | -34.69 | -23.55 |
| TCE | -29.55 | -3.74 | -27.03 | -25.04 | -26.99 |
| cis-DCE | -29.84 | -7.42 | -30.45 | -26.25 | -26.2 |
| VCl | -38.37 | NR | -35.76 | -33.22 | -37.65 |
| Concentration (μg/l) | | | | | |
| PCE | 6,000 | 80 | 600 | 300 | 3,000 |
| TCE | 3,000 | 80 | 1,000 | 1,000 | <500 |
| cis-DCE | 20,000 | 2,000 | 30,000 | 30,000 | 10,000 |
| VCl | 600 | <5 | 900 | 40 | 800 |

Large isotopic shift and concentration decrease followed by large rebound

Baseline isotopic conditions effected by biodegradation

**MW-3**

| | Nov-07 | Jul-08 | Dec-08 | Mar-09 | Jun-09 |
|---|---|---|---|---|---|
| CSIA, δ13C (‰) | | | | | |
| PCE | -28.50 | -27.69 | -28.71 | NS | -25.75 |
| TCE | -32.31 | -30.51 | -31.04 | NS | -31.03 |
| cis-DCE | -31.31 | -29.38 | -31.34 | NS | -37.21 |
| VCl | -33.83 | -34.18 | -36.94 | NS | NR |
| Concentration (μg/l) | | | | | |
| PCE | 30,000 | 20,000 | 9,000 | NS | 60,000 |
| TCE | 7,000 | 1,000 | 5,000 | NS | 5,000 |
| cis-DCE | 7,000 | 20,000 | 10,000 | NS | 700 |
| VCl | 500 | 500 | <500 | NS | 30 |

Limited isotopic shift given the large concentration decrease

- PCE rebounded/ $\delta^{13}C$ decrease greater than baseline conditions can not be explained by bond-breaking reactions. Likely mobilized non-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)
- 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

**THE END**