



# Comprehensive Tools for Remediation Support - Can You Measure Progress?

**Optimization and Monitoring for Remediation of Chlorinated and Related Compounds**

**Virtual Seminar Series - April 29<sup>th</sup> 2020**



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# AGENDA

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1. Introduction
2. Monitored Natural Attenuation Parameters
3. Compound Specific Isotope Analysis
4. Chlorinated Forensics
5. Conclusion

# Basis of Breakdown

$e^-$  donors +  $e^-$  acceptors  $\longrightarrow$  by products + energy

Tersus products

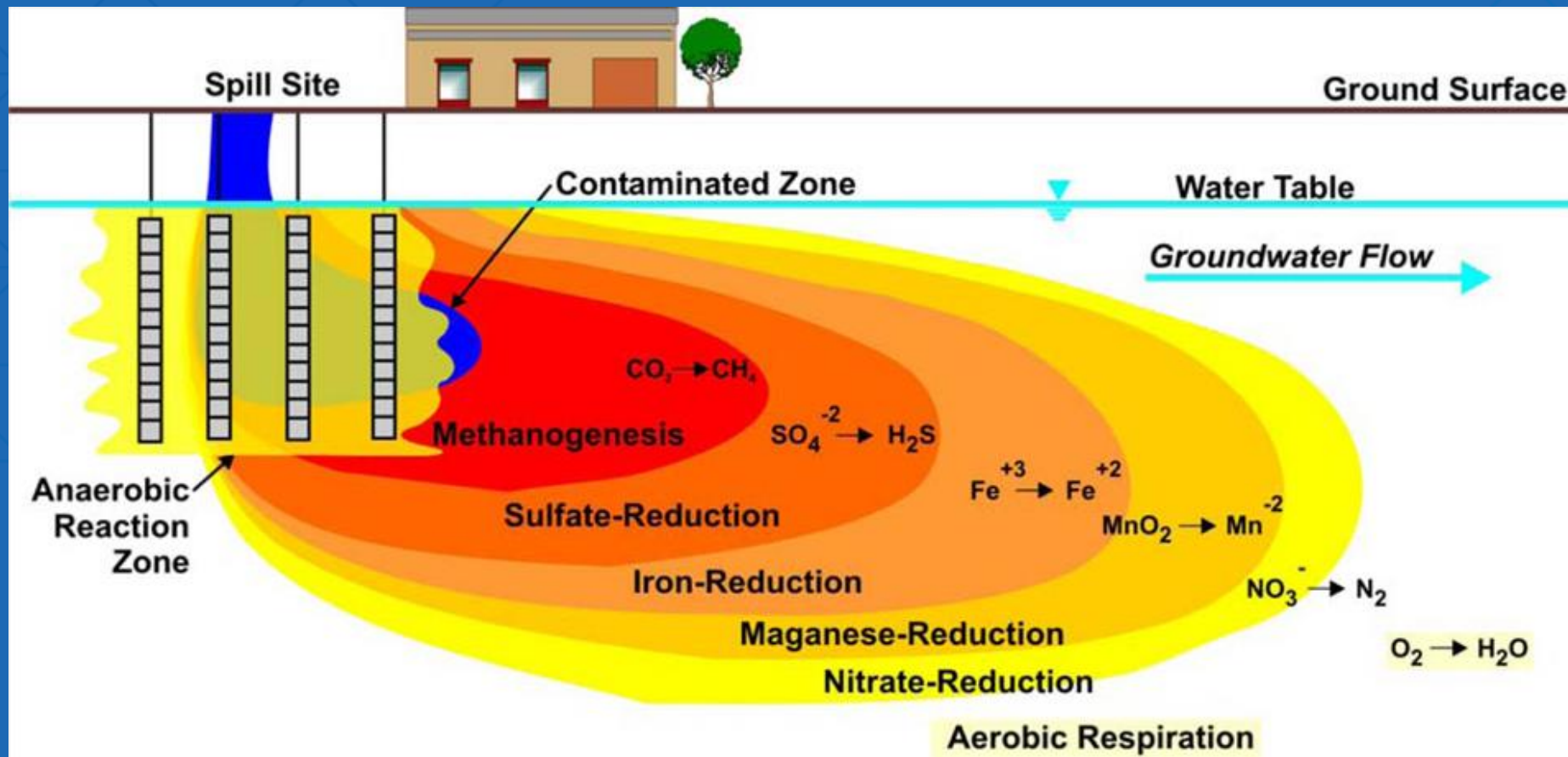
TCE, PCE, etc.

Dis. gas,  $Cl^-$

$H_2$

Existing available  
carbon in GW

# Plume Evolution Model



Source: Parsons. 2004. Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents. AFCEE, NFEC, ESTCP 457 pp, August 2004

# Common MNA Parameters

Parameter	Data use	Analyte trend	Values of Degrade.	Process
Dissolved Oxygen	Generally indicate anaerobic pathway	Decreases	<0.5 mg/L	Aerobic Respiration
Nitrate	Electron acceptor for microbial resp.	Decreases	<1 mg/L	Denitrification
Fe 2+	Indication of Fe <sup>3+</sup> reduction during microbial degradation of organic compounds in the absence of dissolved oxygen, nitrate, and Mn(IV).	Increases	> 1 mg/L	Fe 3+ reduction
Sulfate	Electron acceptor for anaerobic respiration	Decreases	<20 mg/L	Sulfate Red.
Methane	The presence of methane suggests the geochem of the water is favorable for RD	Increases	>0.5 mg/L	Methanogenesis
Chloride	General water quality parameter used as a marker to verify that site samples are obtained from the same ground water system. Final product of chlorinated solvent reduction	Increases	>2 times background	Reductive Dechlorination or Direct Oxidation of Chlorinated Compound

# MNA – Cont'd

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What to do if a stall happens?

- Microbial Analysis

Qualification and Quantification

Ensuring you have the right bugs at the right site – dhc,  
dhb

- Electron Donor  
Re-amendment

# MNA – Dissolved gases

- Methane, ethene, ethane (MEE)
  - Methane – by product of the reactions that facilitate reductive dechlorination
  - Ethane/Ethene – end products of dechlorination
- Hydrogen – monitors degradation of specific redox processes
  - Concentration lends better understanding of stage
- Carbon dioxide – Petroleum hydrocarbons (aerobic)

# Dissolved Gases – Reporting Limit Comparison

Analyte	RSK-175 Method	Pace Energy – AM 20 GAX
Methane	10 µg/L	0.5 µg/L
Ethane	10 µg/L	0.1 µg/L
Ethene	10 µg/L	0.1 µg/L
Acetylene	N/A	0.5 µg/L
Carbon Dioxide	N/A	5 mg/L
Carbon Monoxide	N/A	1 mg/L
Nitrogen	N/A	2 mg/L
Oxygen	N/A	0.5 mg/L
Propane	N/A	0.1 µg/L
Propene	N/A	0.1 µg/L
Iso-Butane	N/A	0.2 µg/L
N-Butane	N/A	0.2 µg/L



# MNA – Volatile Fatty Acids (VFAs)

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Volatile Fatty Acids (VFAs) are created when and injected substrates are broken down by microbial community via fermentation

e.g.,  $\text{CH}_2\text{Cl}_2$  + dehalobacter  $\longrightarrow$  acetate + H = acetic acid

e.g.,  $\text{CH}_2\text{Cl}_2$  + dehalobacter  $\longrightarrow$  formate + H = formic acid

# MNA – Cont'd

Analyte	LL VFA – AM23 G
Acetic	0.2 mg/L
Propionic	0.1 mg/L
Butyric	0.1 mg/L
Pyruvic	0.1 mg/L
Lactic	0.1 mg/L
Iso-Pentanoic	0.1 mg/L
Pentanoic	0.1 mg/L
iso-Hexanoic	0.2 mg/L
Hexanoic	0.2 mg/L
Formic	0.1 mg/L

# MNA – Cont'd

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Pace Energy provides the lowest detection limits for MEE and VFAs in the industry

What does this mean?

- Edge of plume amendment detection

- Is degradation still occurring?

- Is plume properly constrained


- Monitoring of hardest 5-10%

# Compound Specific Isotope Analysis (CSIA)

Using isotopic ratios of certain elements within distinct compounds provides information that analytical concentrations cannot  
 Ratios reflect relationship of heavier isotopes to lighter isotopes


**Isotopes of Carbon**

<sup>12</sup>C




6 protons  
6 neutrons  
"light" stable

<sup>13</sup>C





6 protons  
7 neutrons  
"heavy" stable

<sup>14</sup>C



6 protons  
8 neutrons  
radioactive

 **proton**

 **neutron**

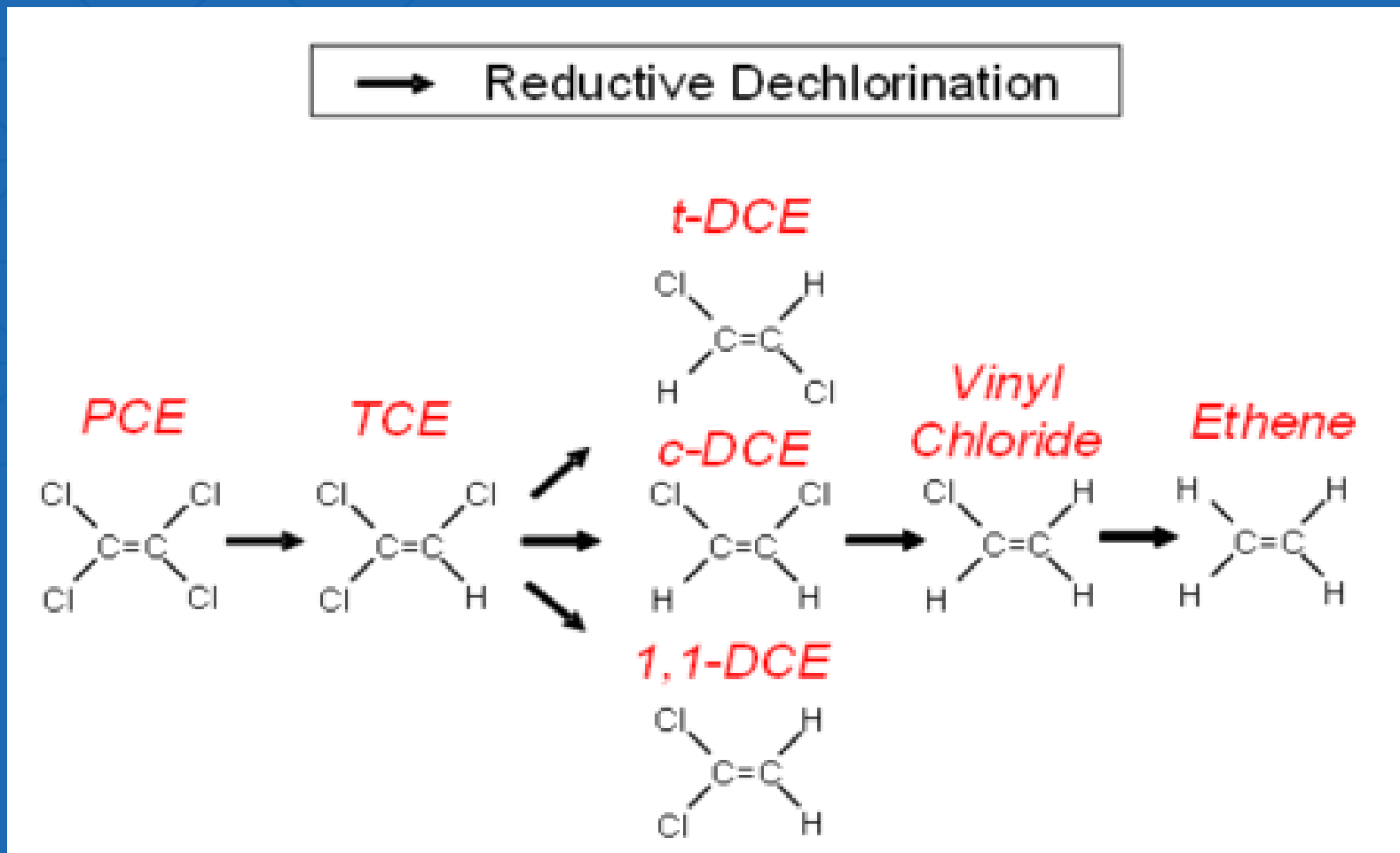
<sup>14</sup>C not in use  
for CSIA

<sup>12</sup>C—Cl  
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<sup>12</sup>C—Cl  
<sup>12</sup>C—Cl  
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<sup>13</sup>C 33%

# CSIA – Degradation Pathway



# CSIA – cont'd

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For remediation efforts:

Use of carbon isotopes to prove degradation

Rate of degradation via

Microbial degradation

Recognizes impact of electron donor

Can be used to understand multiple sources, which could impact perceived MNA success

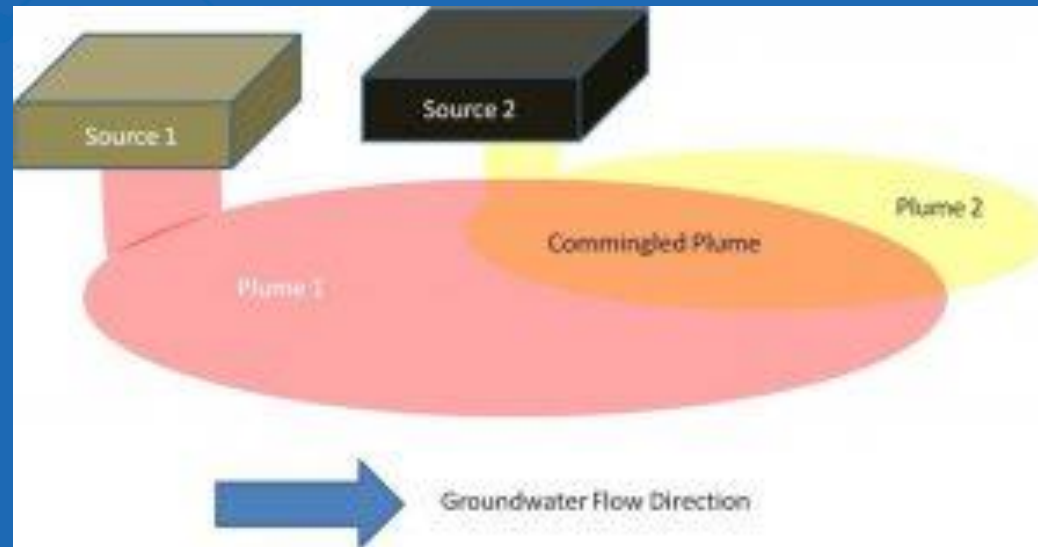
# CSIA – cont'd

- - Additionally, CSIA can add clarification of contaminant rebound – i.e., desorbed mass
  - Ideal implementation for 1-D CSIA is center plume analysis tying near source samples with edge of plume samples
  - Additionally, CSIA can supplement data detailing plume evolution – earlier slide

# CSIA Forensics

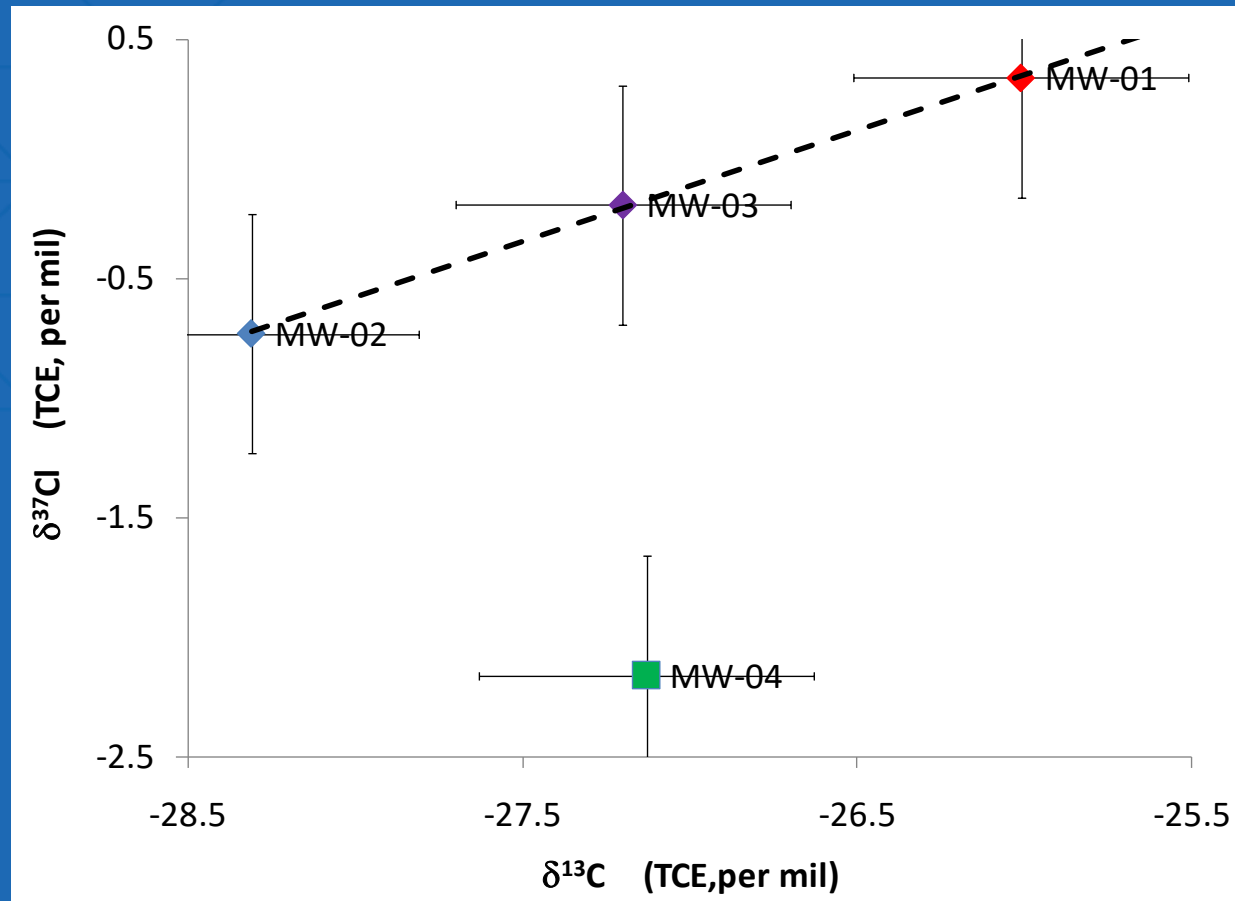
By adding additional isotopes to the analysis, isotopic signatures (fingerprints) can be determined

Adding the forensic aspect provides support in identification of multiple sources, off site contribution (co-mingled plumes)





# CSIA Forensics – Base Information



# CSIA Forensics – Case Study

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Site near New York City

Industrial area

PCE and TCE issues

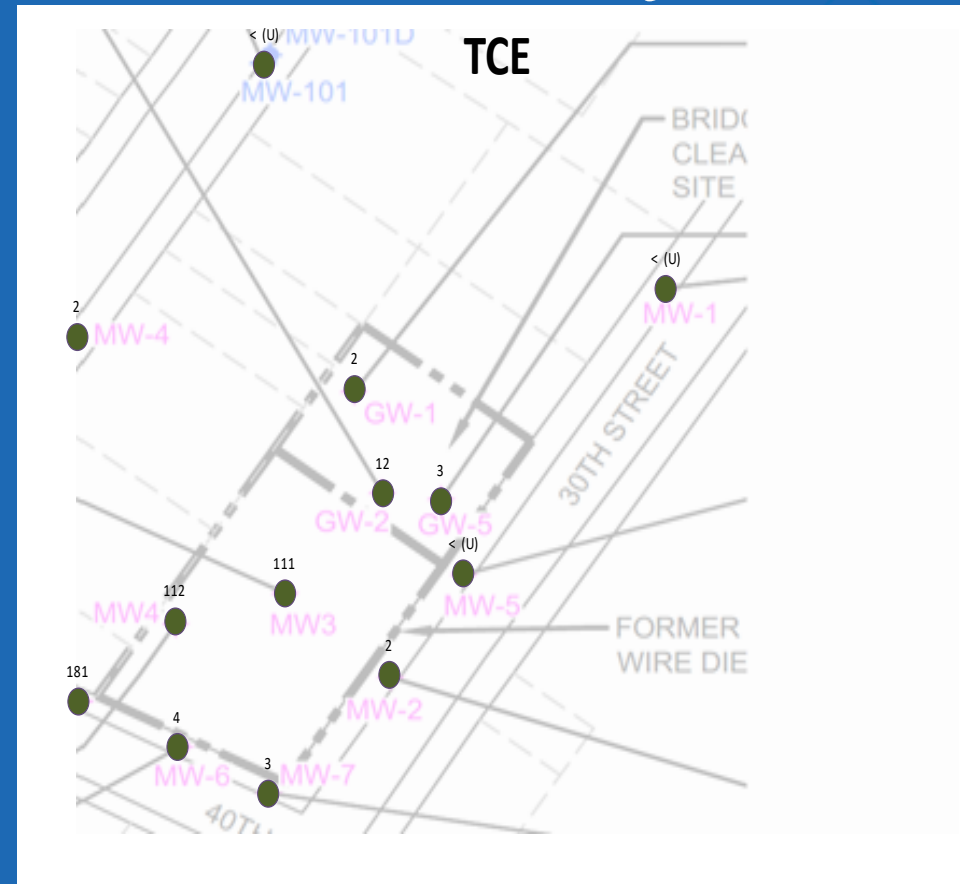
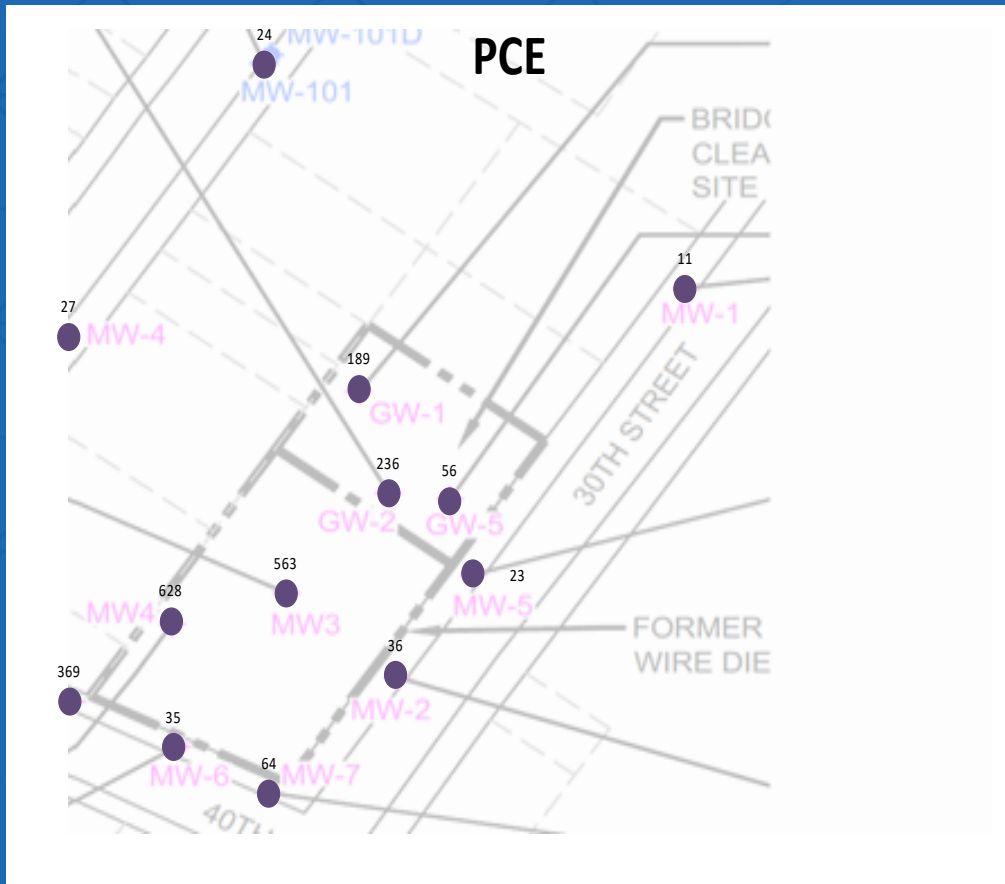
Associated vapor intrusion issue

Groundwater flow complex both vertically and horizontally

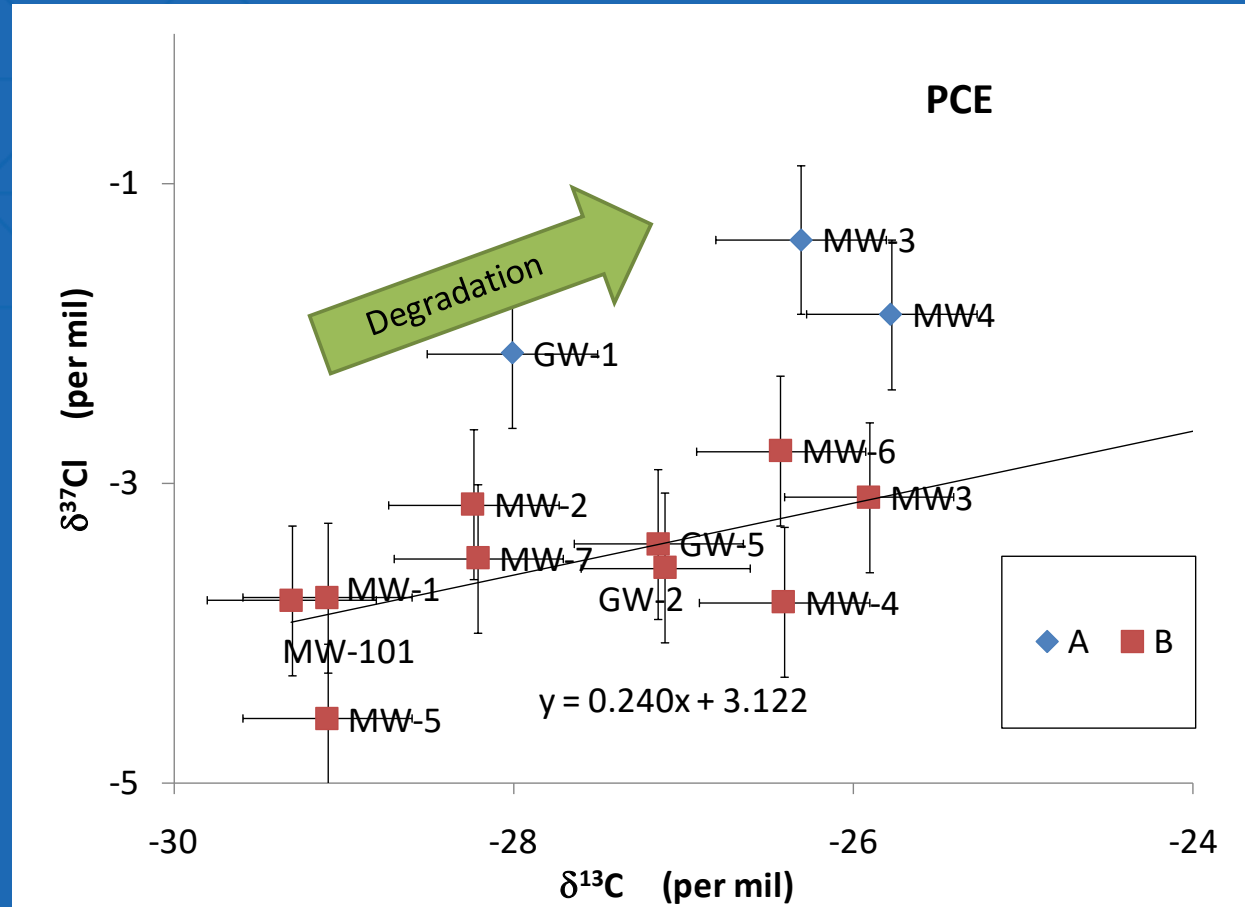
Inconsistent concentrations lead to CSIA being evaluated

Questions to be answered

# CSIA Forensics – Case Study



# CSIA Forensics – Case Study



# CSIA Forensics – Case Study

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Conclusions – cont'd:

Physical location of the two PCE sources suggested the client was not the responsible party.

**Cost of analysis and interpretive reporting was around \$26,000.**

**The cost of the remediation was shared saving the client upwards of six figures.**

# Conclusions

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Monitoring Natural Attenuation at remediation sites is key to move towards the ultimate goal of closure and ensuring efforts are streamlined

Low level analysis provides a more distinct picture than standard analysis with high reporting limits

CSIA can facilitate information for CSM data gaps and streamline remediation efficiency

Use of forensic analysis can contribute to understanding “outside” influences



Pace will deliver unmatched value and customer service. We will develop our talents and innovative culture to become the clear choice for our customers, employees and business partners.

# THANK YOU

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## Course Code: CHMM

