Comprehensive Tools for Remediation Support - Can You Measure Progress?

Chlorinated Hydrocarbon Remediation Short Course

2020

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Comprehensive Tools for Remediation Support

- Introduction
- Monitored Natural Attention Parameters
- Compound Specific Isotope Analysis
- Chlorinated Forensics
- Conclusion

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Monitored Natural Attenuation (MNA)

- **Natural attenuation** is "a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater."[1]
- Classified as passive remediation/ passive bioremediation
- Cost effective

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1: Wiedmeier, T, et al., 1999, Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface, p.3

MNA – cont'd

- Limitations
  - Slowest option for site cleanup
  - Regulatory roadblocks
  - Complicated sites require some level of expertise to prove passive remediation is occurring
- Monitoring is key into interpreting the effectiveness
- MNA parameters detail the stage

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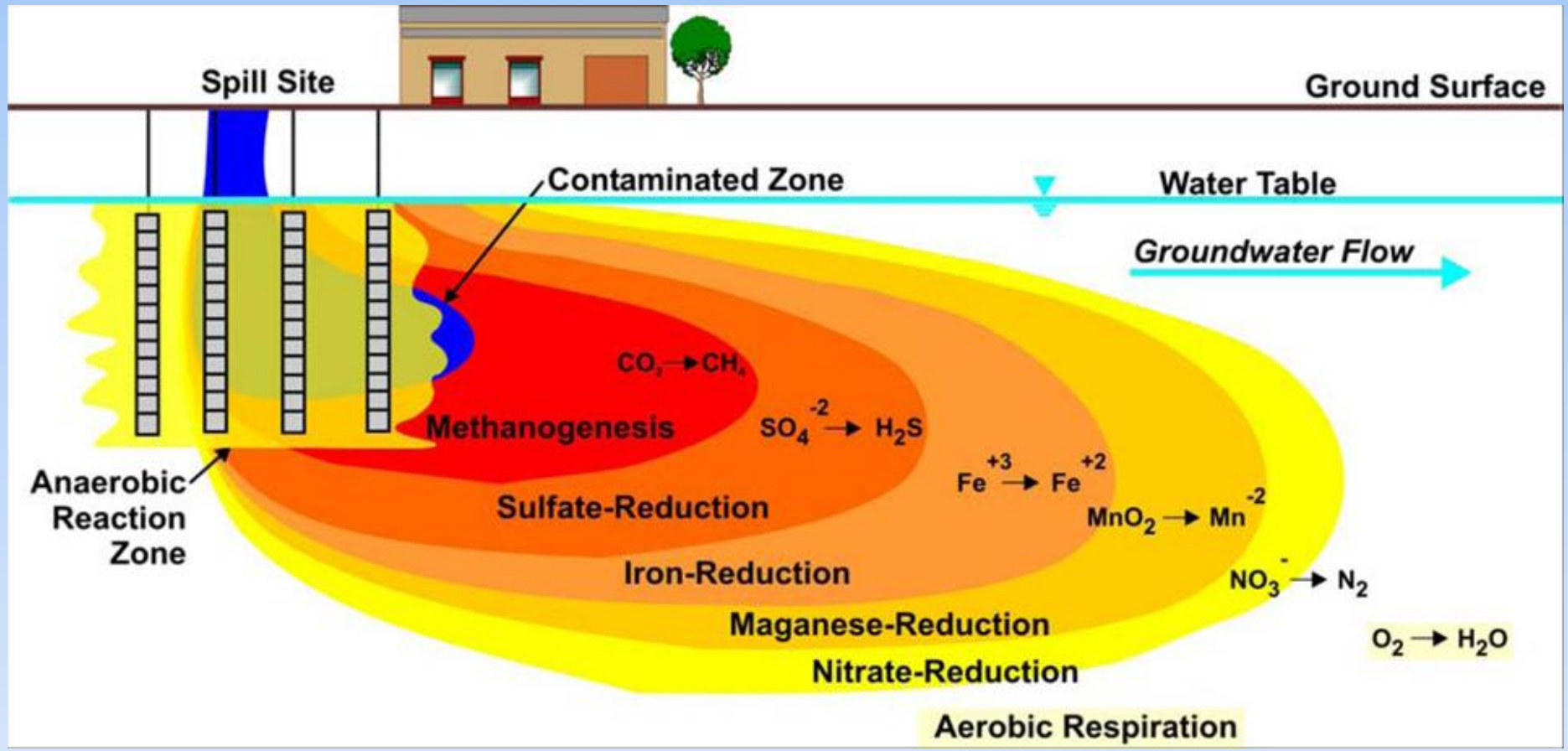
Plume Evolution



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

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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 Fe3+ 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 organic carbon degradation via methanogenesis	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

Source: Adapted from Guidance on Developing a Monitored Natural Attenuation Remedial Proposal for Chlorinated Organics in Ground Water, North Carolina Hazardous Waste Section, October 4, 2000

MNA – Cont'd

- Additional Info Needed
  - Microbial Analysis
    - Qualification and Quantification
    - Ensuring you have the right bugs at the right site – dhc, dhb
  - Electron Donor
    - Re-amendment

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MNA – Cont'd

- Dissolved gases
  - Carbon dioxide – evaluate microbial breakdown of contaminant (aerobic)
  - Hydrogen – monitors degradation
  - Propane, butane(s) – monitors specific breakdown
  - Methane, ethene, ethane (MEE)
    - Methane – by product of the reactions that facilitate reductive dechlorination
    - Ethane/Ethene – end products of dechlorination

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)

- VFAs are created when and injected substrates are broken down by microbial community via fermentation
  - e.g., dichloromethane + dehalobacter $\longrightarrow$ acetate + H = acetic acid
  - e.g., Dichloromethane +dehalobacterium $\longrightarrow$ formate + H = formic acid
- Useful when monitoring breakdown and microbial activity
- Useful when tracing amended water

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VFAs – Reporting Limit Comparison

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

Low Level Reporting Limits

- 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%

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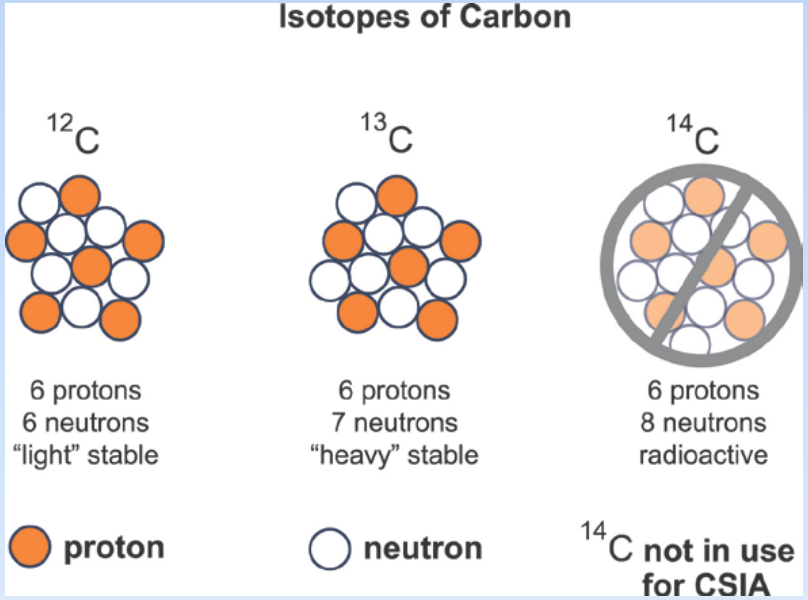
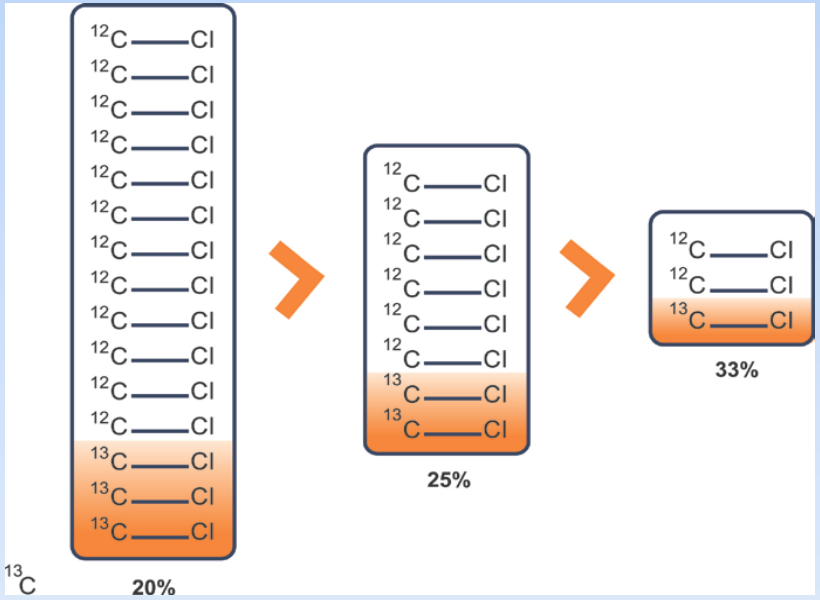
Compound Specific Isotope Analysis (CSIA)

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





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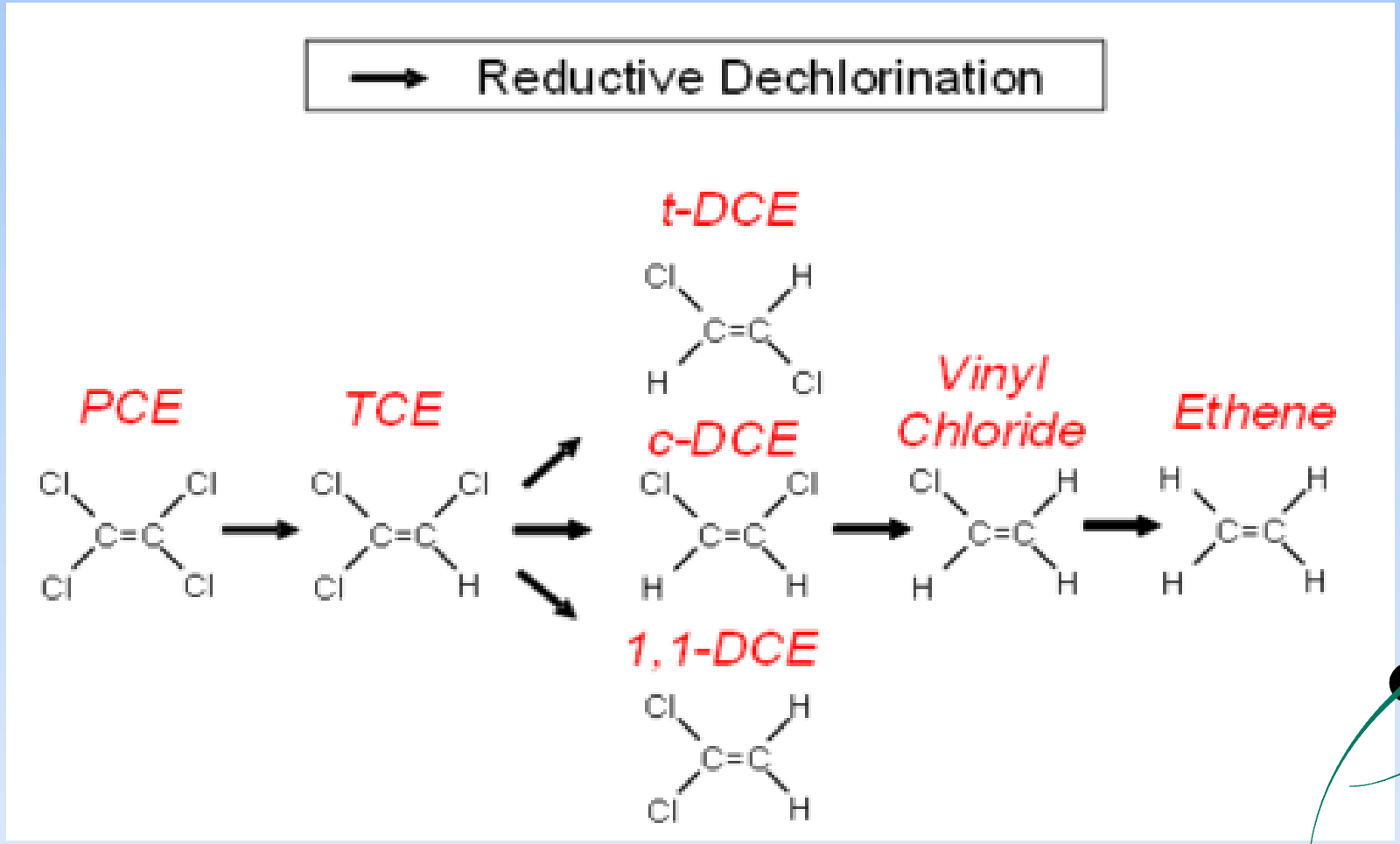
CSIA – Degradation Pathway



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CSIA – cont'd

For remediation efforts:

- Use of carbon isotopes to prove degradation
- Rate of degradation via
  - Microbial degradation with KB-1, for example
  - Recognizes impact of electron donor
- Can be used to understand multiple sources, which could impact perceived MNA success

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CSIA – cont'd

- Additionally, CSIA can add clarification of contaminant rebound
  - 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

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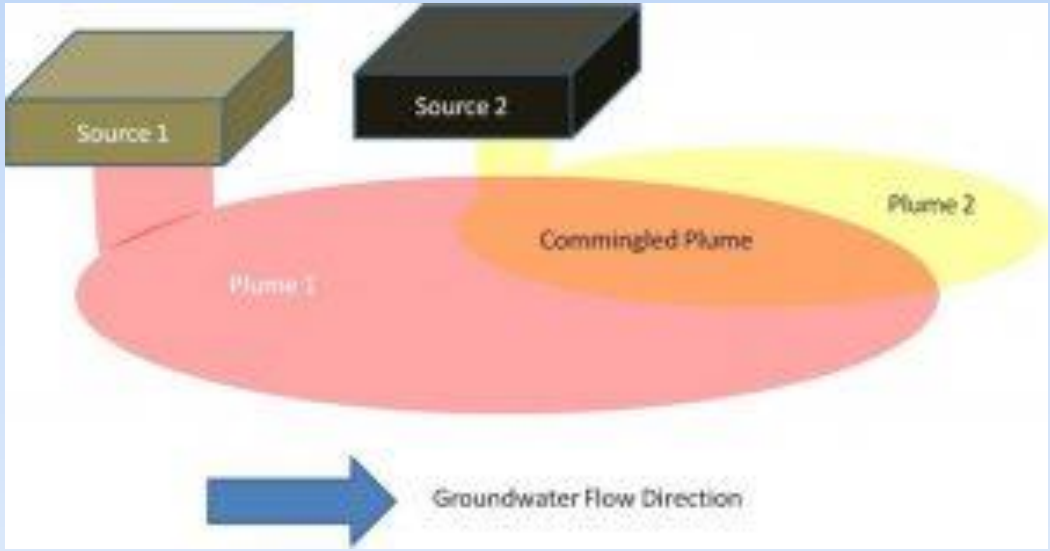
CSIA Forensics

- 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)



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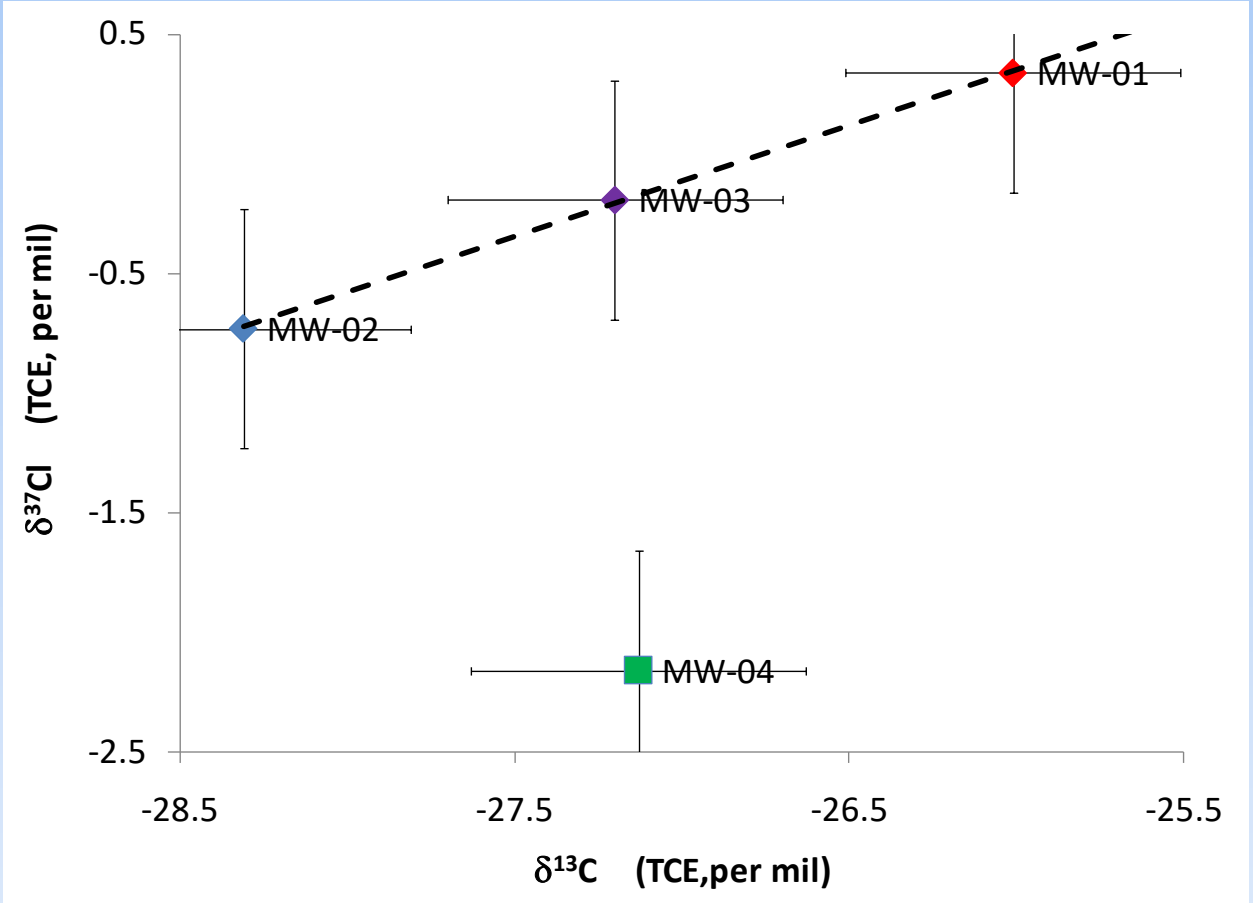
CSIA Forensics – Base Information



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CSIA Forensics – Case Study

- 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

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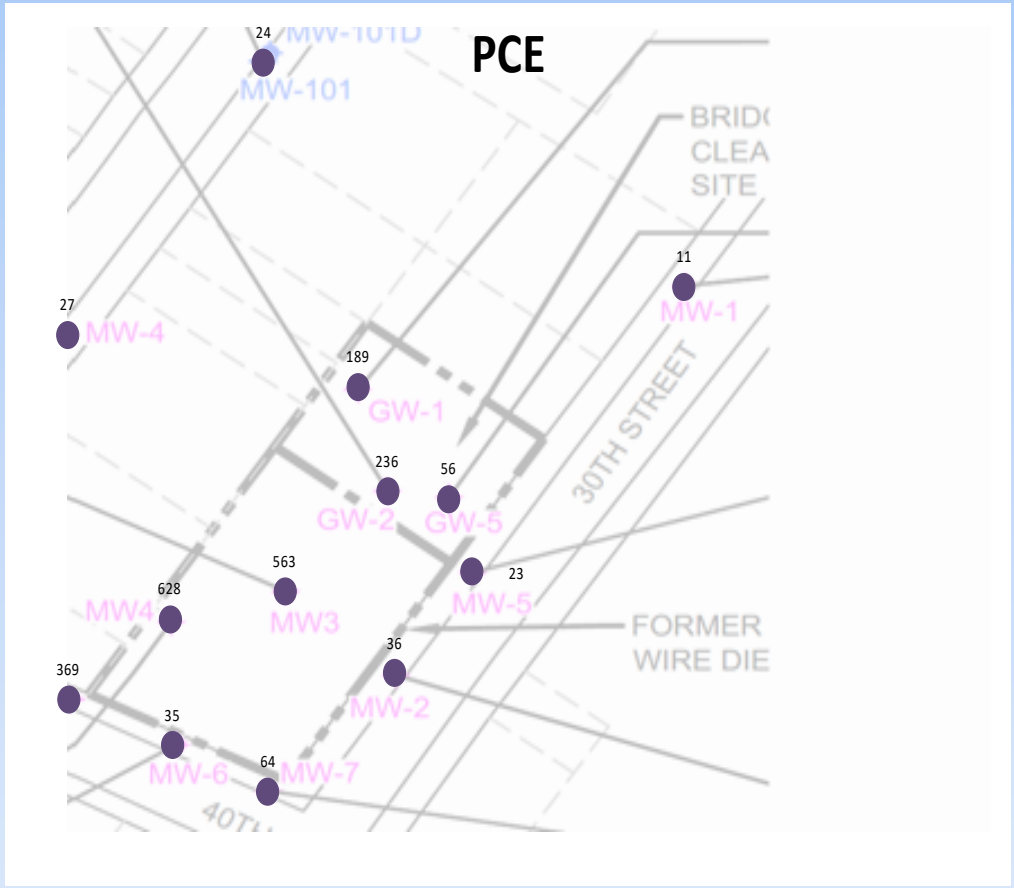
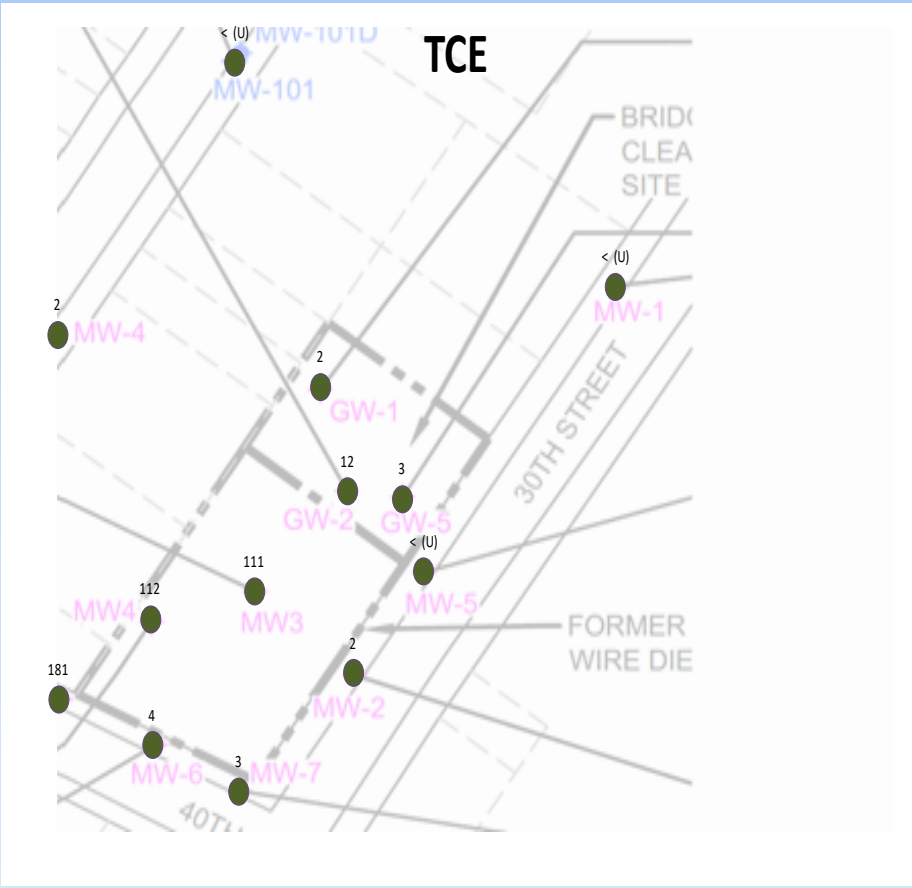
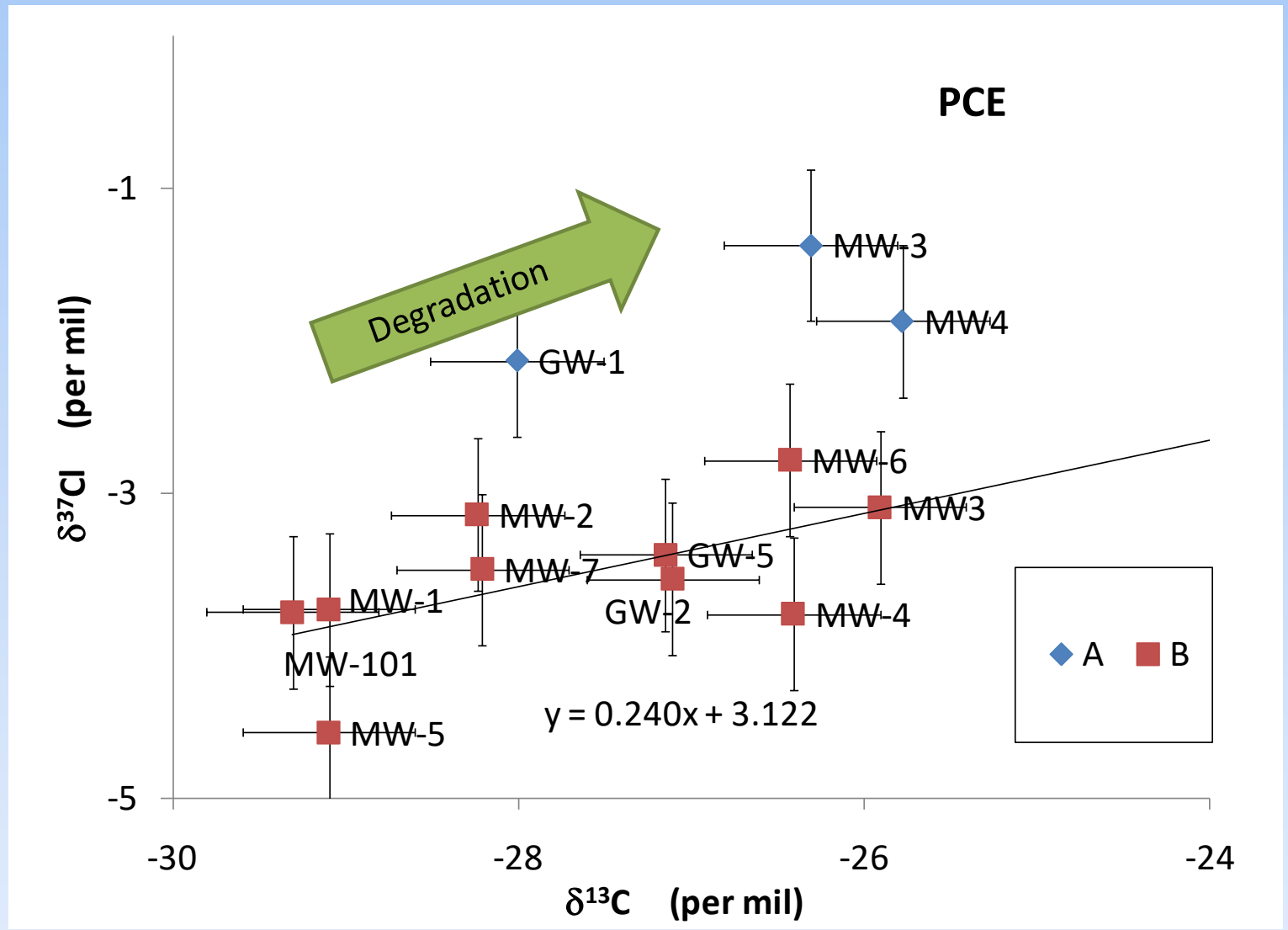
CSIA Forensics – Case Study





CSIA Forensics – Case Study



CSIA Forensics – Case Study

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 seven figures.**

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Conclusions

- Monitoring Natural Attenuation at remediation sites is key to move towards the ultimate goal of closure.
- Utilizing all tools available is fundamental in expediting towards goal
- 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

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Questions?

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