Compound Specific Isotope Analyses to Support Monitored Natural Attenuation for Chlorinated Ethenes and Ethanes

Advanced Tools Webinar Series:
Fundamentals of Compound Specific Isotope Analysis
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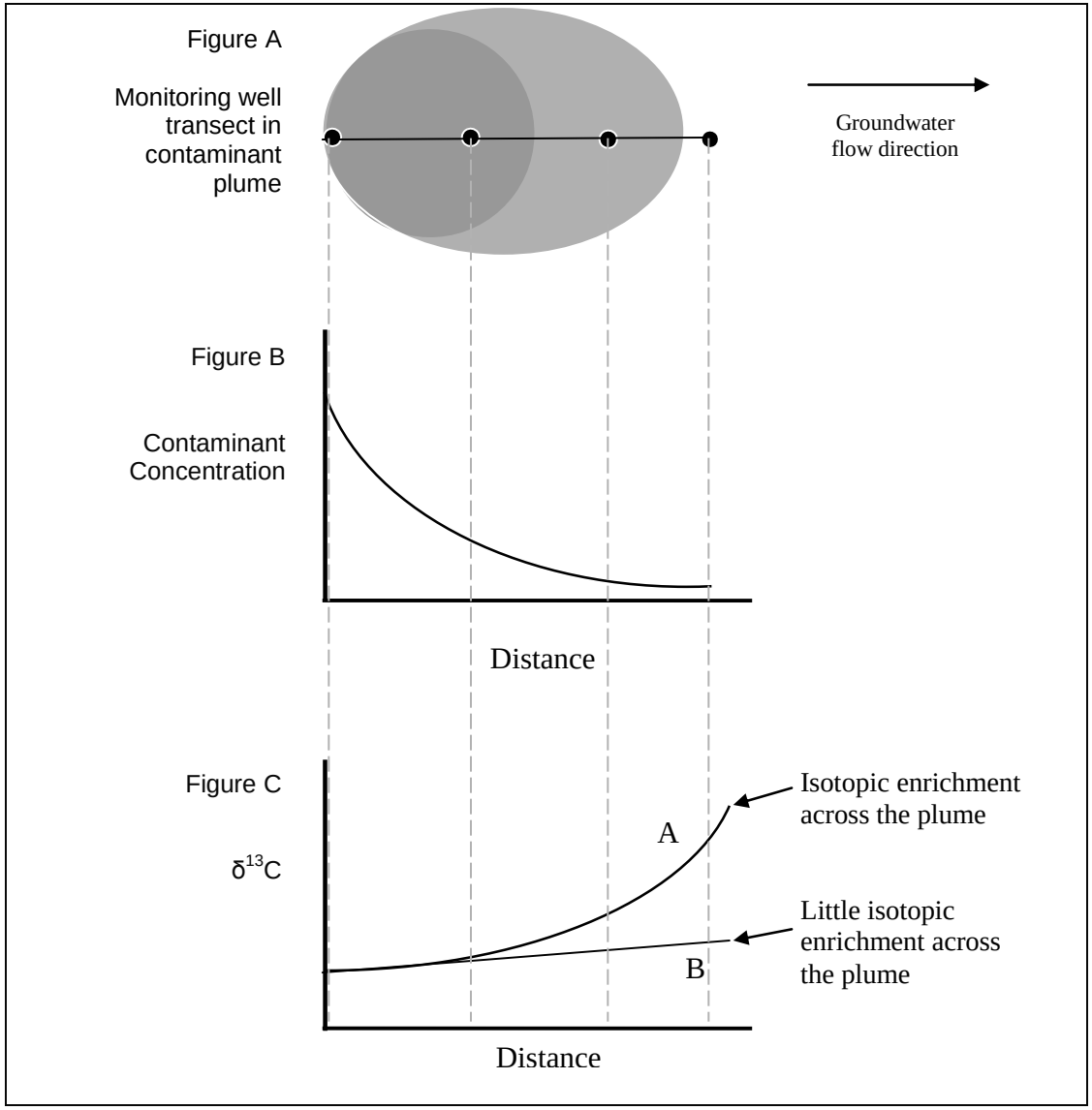
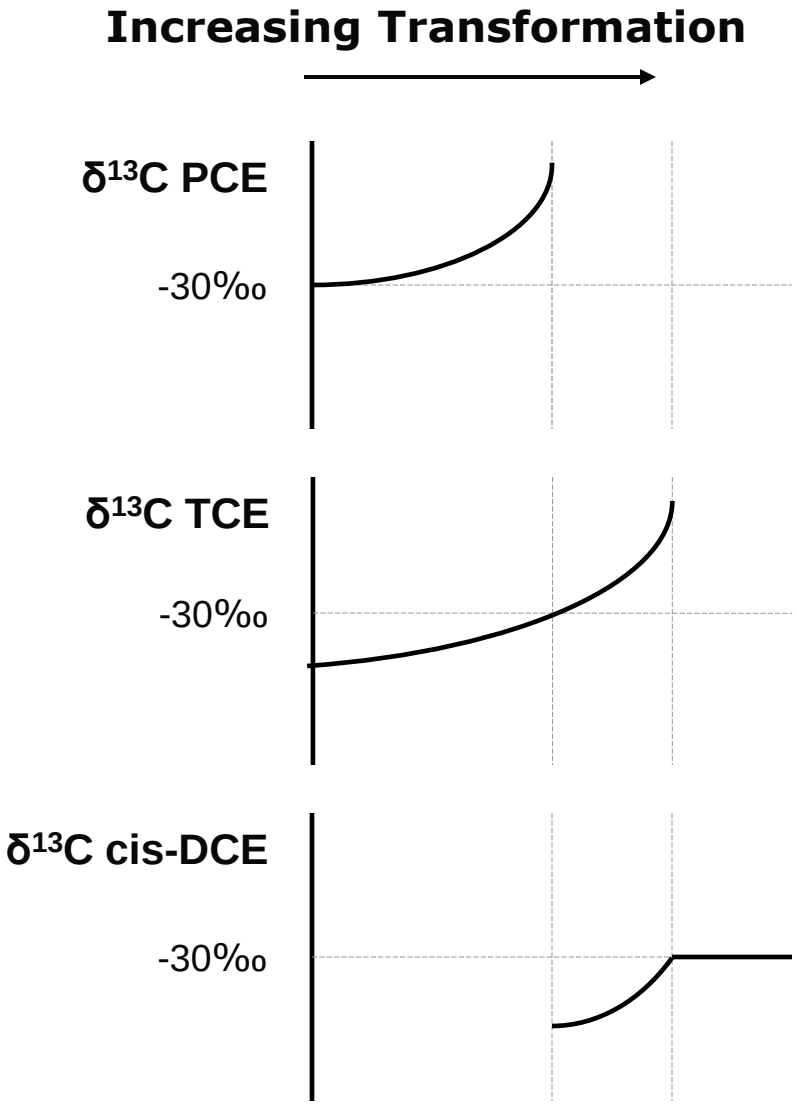
Isotopic Enrichment Across a Contaminant Plume

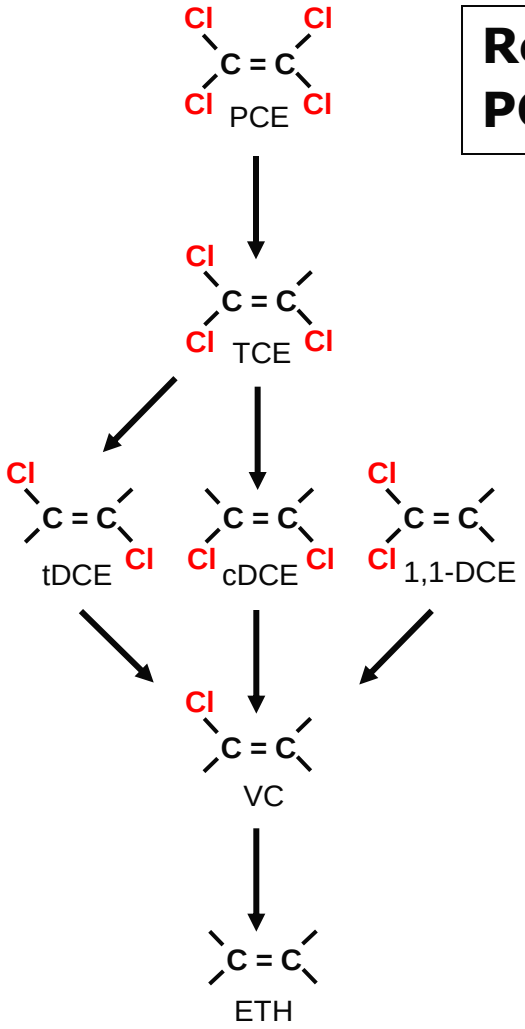


Isotopic Enrichment with Transformation



- Assume that cis-DCE is the end product of PCE degradation
- Benchmark $\delta^{13}C$ value for undegraded parent (PCE)
- Newly generated degradation product (TCE and cis-DCE) is depleted in ^{13}C (more negative)
- When the transformation of TCE exceeds its formation, $\delta^{13}C$ becomes more positive than benchmark
- Final $\delta^{13}C$ value for product (cis-DCE) is the same as benchmark

Transformation Pathways for Chlorinated Ethenes and Ethanes



Reductive Dechlorination: PCE and TCE

tDCE (trans-DCE): trans-dichloroethene

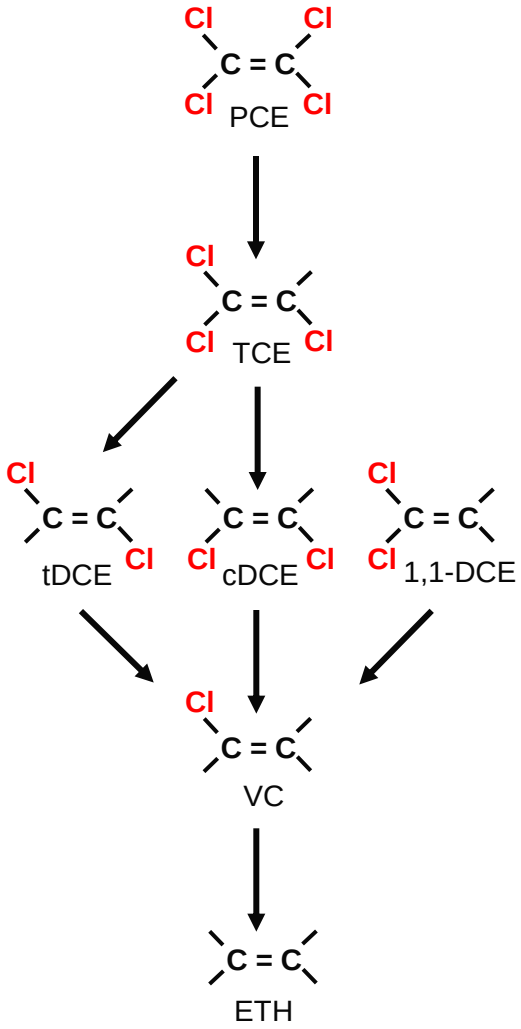
cDCE (cis-DCE): cis-dichloroethene

1,1-DCE: 1,1-dichloroethene

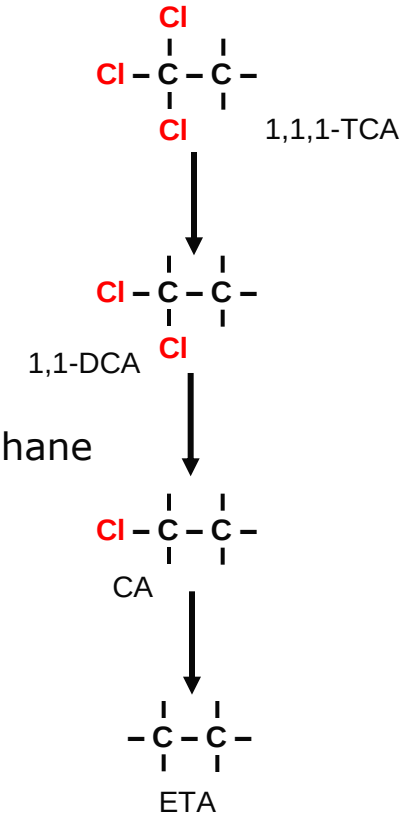
VC: vinyl chloride

ETH: ethene

Transformation Pathways

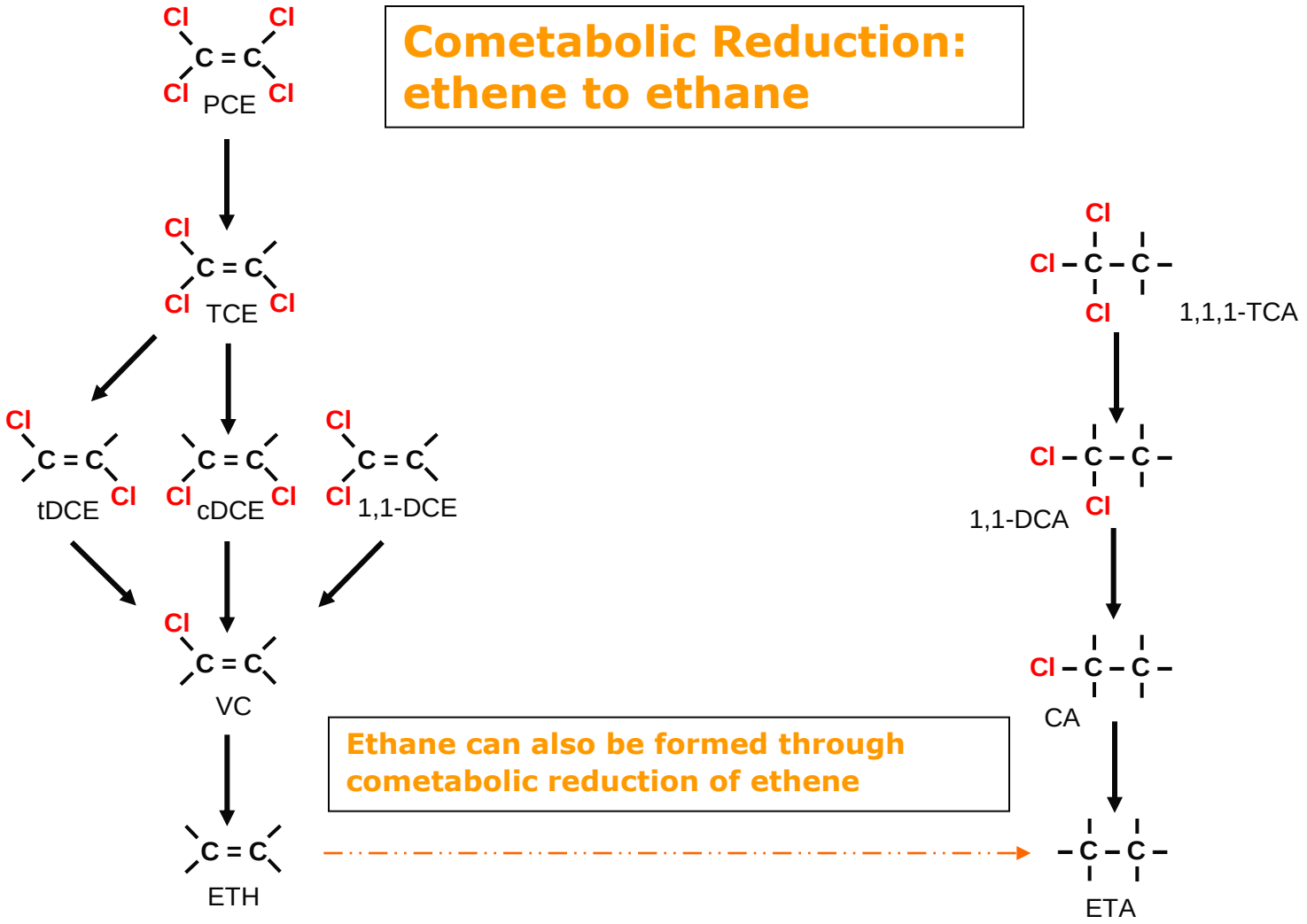


Reductive Dechlorination: 1,1,1-TCA

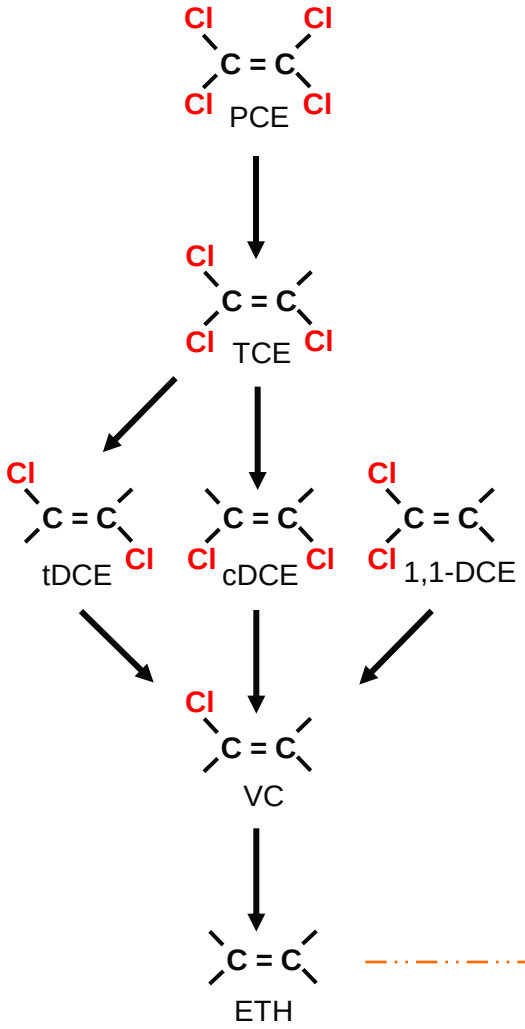


1,1-DCA: 1,1-dichloroethane
CA: chloroethane
ETA: ethane

Transformation Pathways

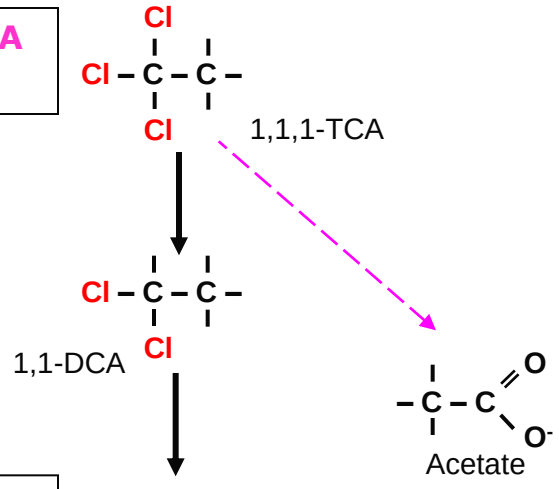


Transformation Pathways

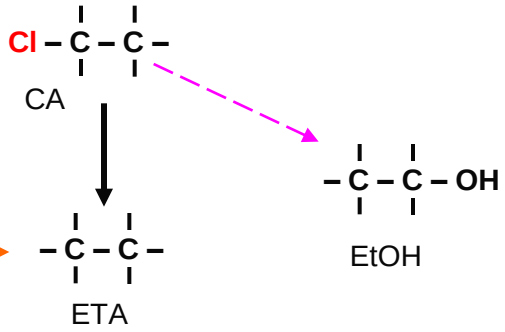


Hydrolysis: 1,1,1-TCA and CA

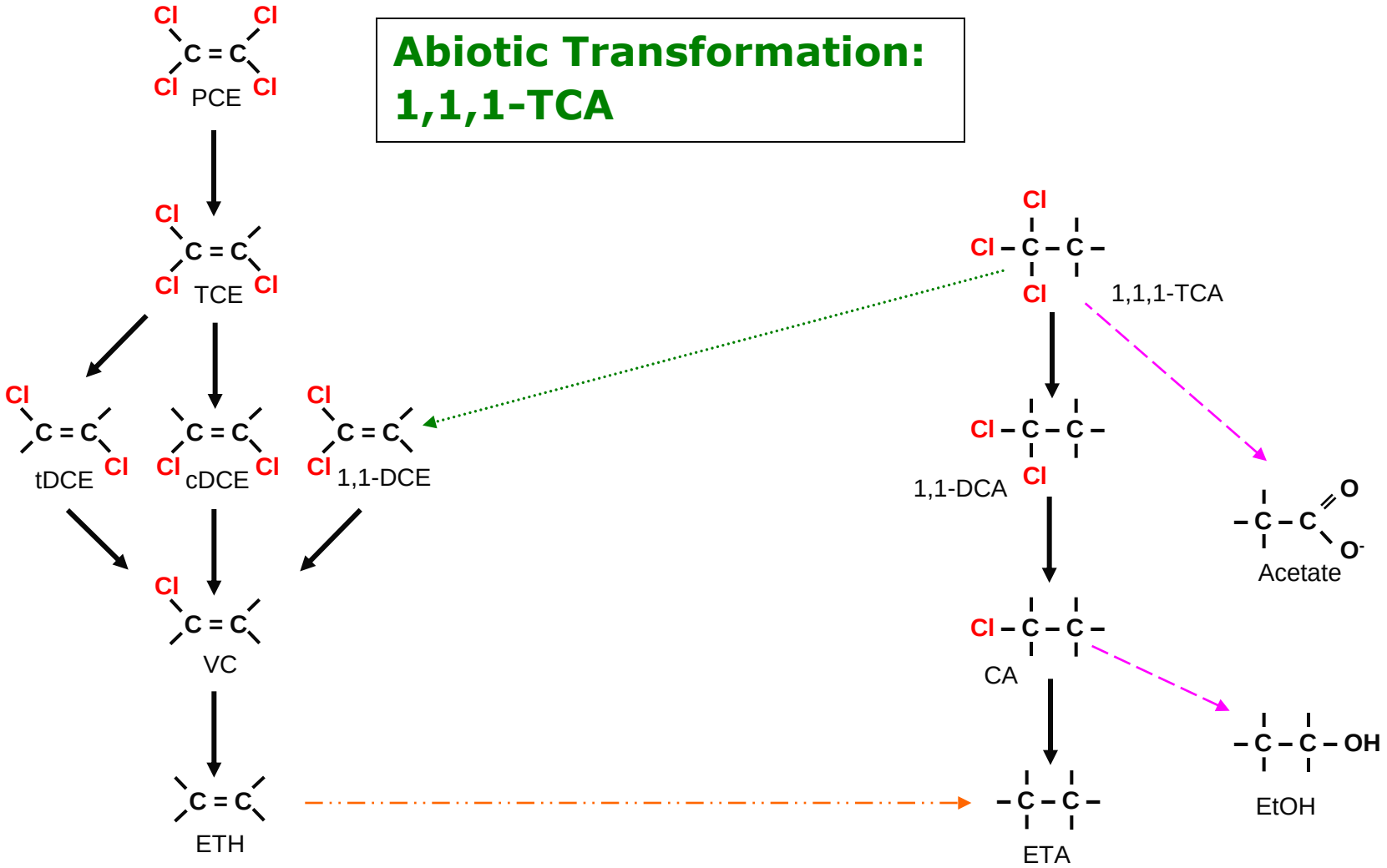
Abiotic hydrolysis of 1,1,1-TCA can produce acetate



Abiotic hydrolysis of CA can produce ethanol (EtOH)



Transformation Pathways



Case Study
Site Description

- Parent compounds are PCE, TCE, and 1,1,1-TCA; petroleum hydrocarbons are also present.
- Transformation products include cis-DCE, 1,1-DCE, 1,1-DCA, vinyl chloride (VC), chloroethane (CA), ethene (ETH) and ethane (ETA).
- CSIA was selected to:
  - verify transformation of all chlorinated compounds
  - understand the degradation pathways responsible for VC production
- Geochemical parameters demonstrate strongly reducing, anaerobic conditions.

Collaboration with the University of Oklahoma

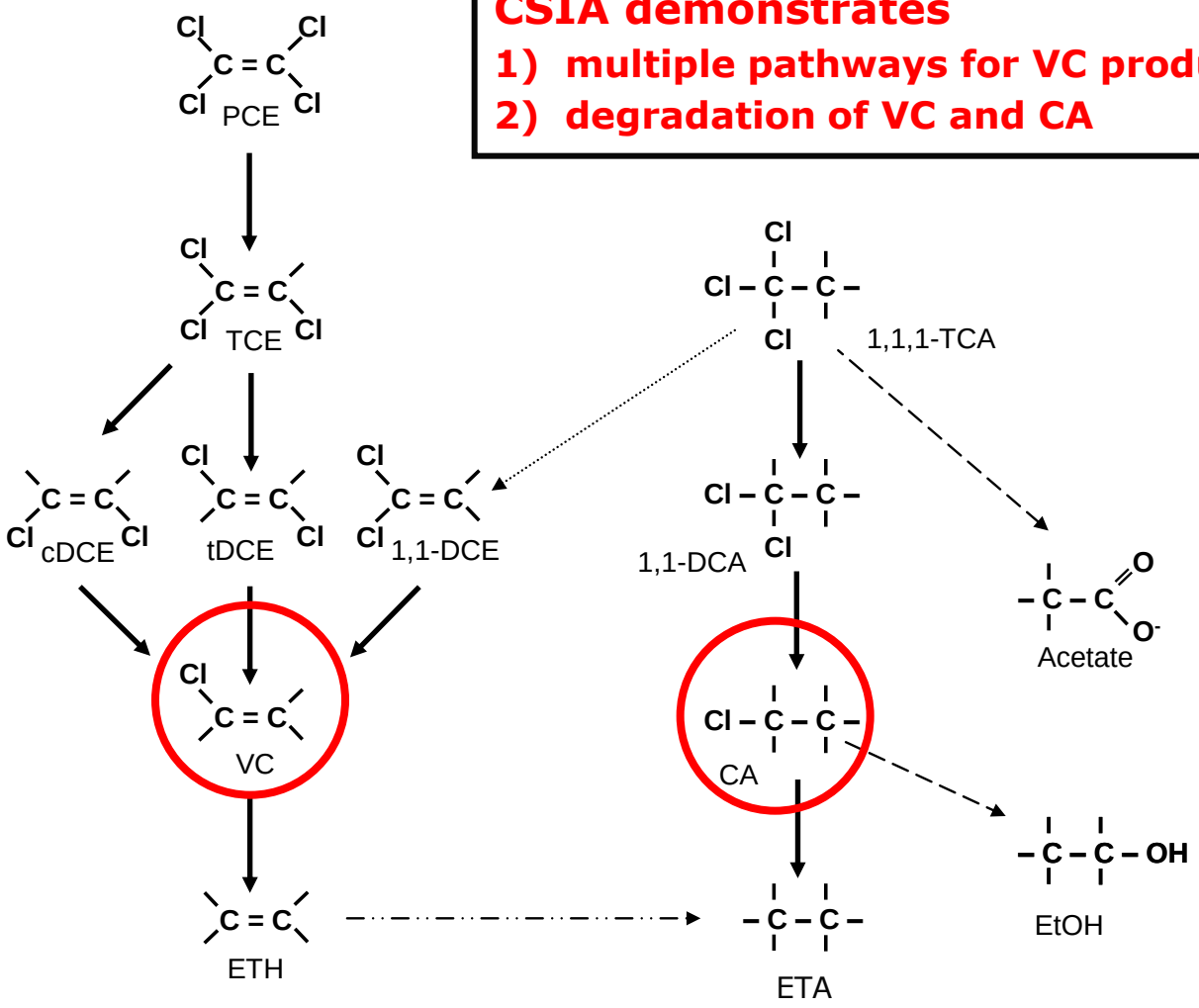
Case Study
Hydrogeology

- The depth of shallow fill material varies from a few feet to over 10 feet.
- The underlying fluvial channel sequence consists of coarse sands/gravels in the base, grading to finer sands with silts and clays toward the top layer.
- Shallow groundwater occurs unconfined in fill material, perched on native clay and till (three of the CSIA monitoring wells are screened in this shallow zone).
- The second, intermediate water-bearing zone occurs in the upper fluvial channel sequence (most of the CSIA monitoring wells are screened across the more permeable coarse-grained materials).
- There is limited hydraulic communication between the shallow and intermediate water-bearing zones and an upward hydraulic gradient between these zones.
- The intermediate zone groundwater seepage velocity is approximately 20 ft/yr.

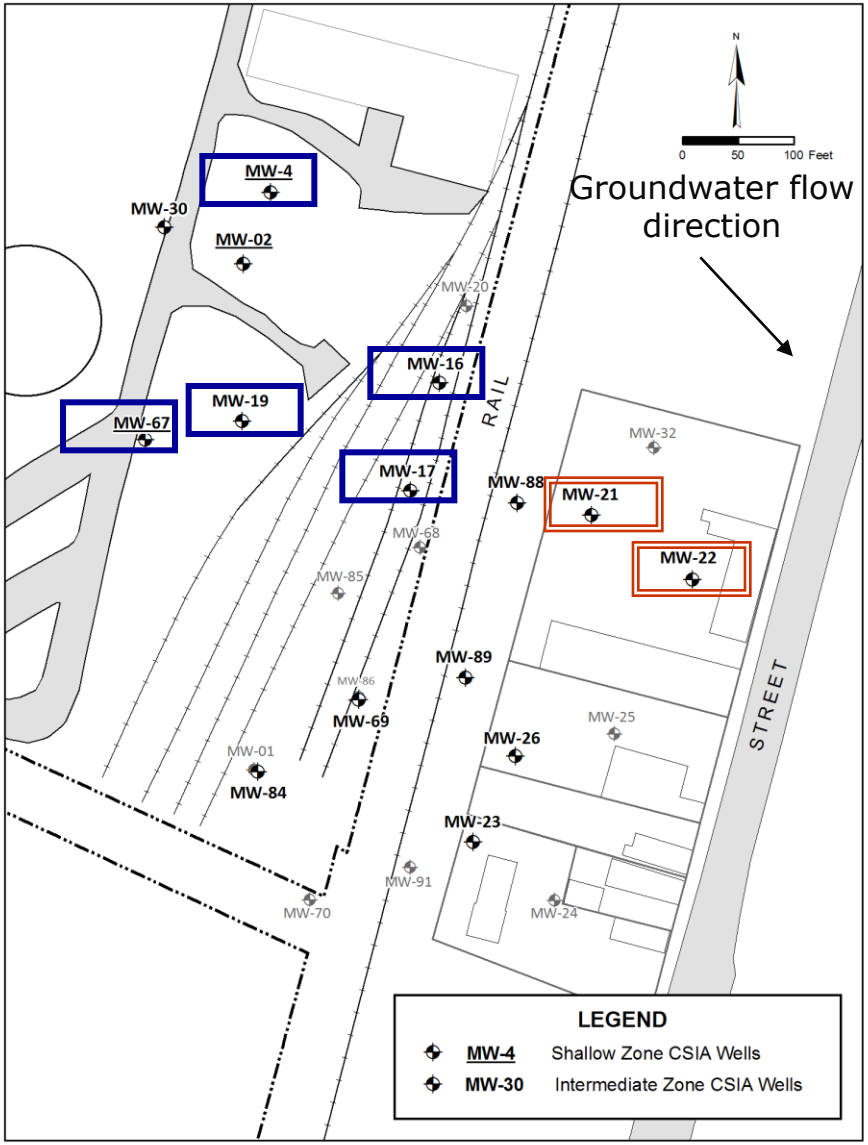
Potential Transformation Pathways

CSIA demonstrates

1) **multiple pathways for VC production**
2) **degradation of VC and CA**



CSIA Monitoring Wells: On-Site and Offsite
2006 to 2009

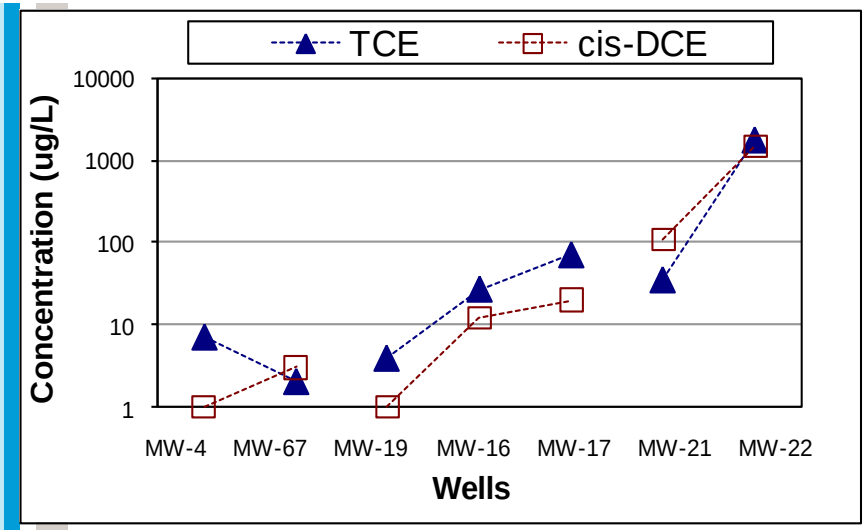


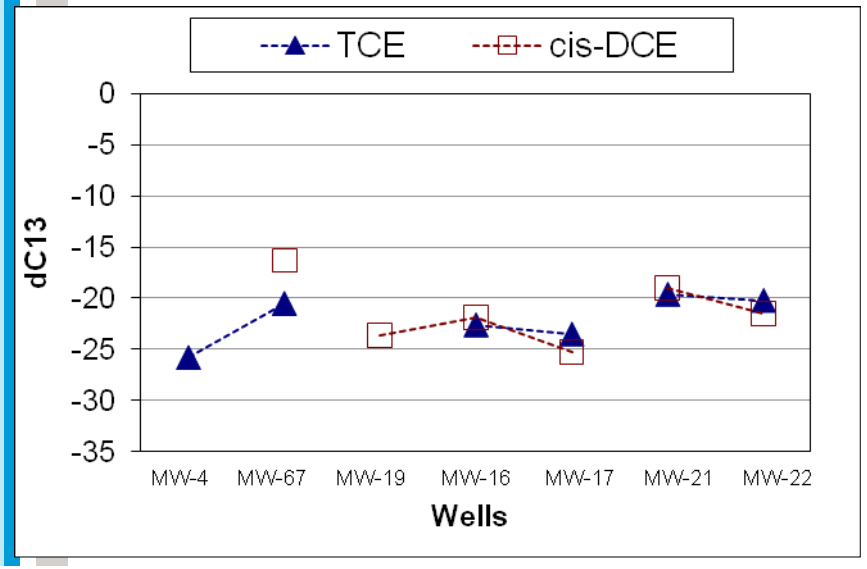
Wells used to demonstrate reductive dechlorination of TCE and abiotic transformation of 1,1,1-TCA

On-site wells
MW-4, 67, 19, 16, and 17

Offsite wells
MW-21 and 22

Reductive Dechlorination of TCE
1st Quarter 2006



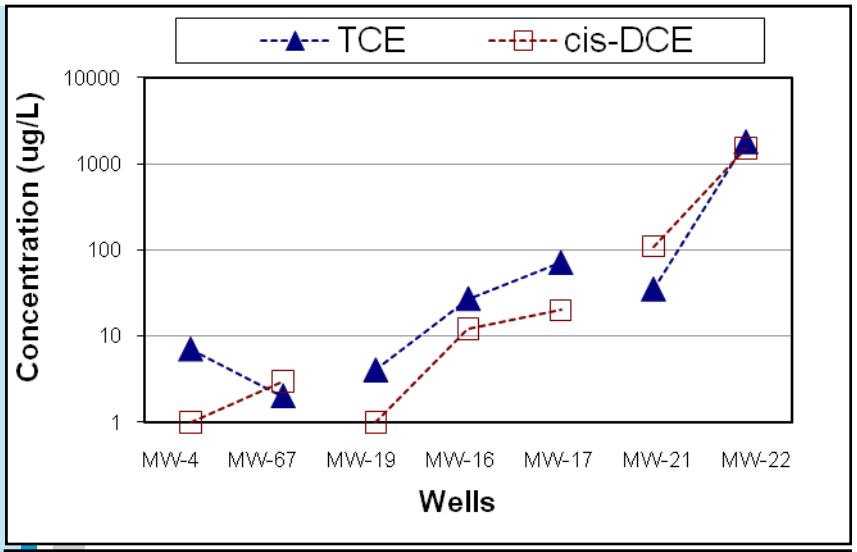


- Concentrations increase to the east and south in offsite wells
- Elevated TCE in MW-22 suggests a potential offsite source
- Transformation of TCE to cis-DCE

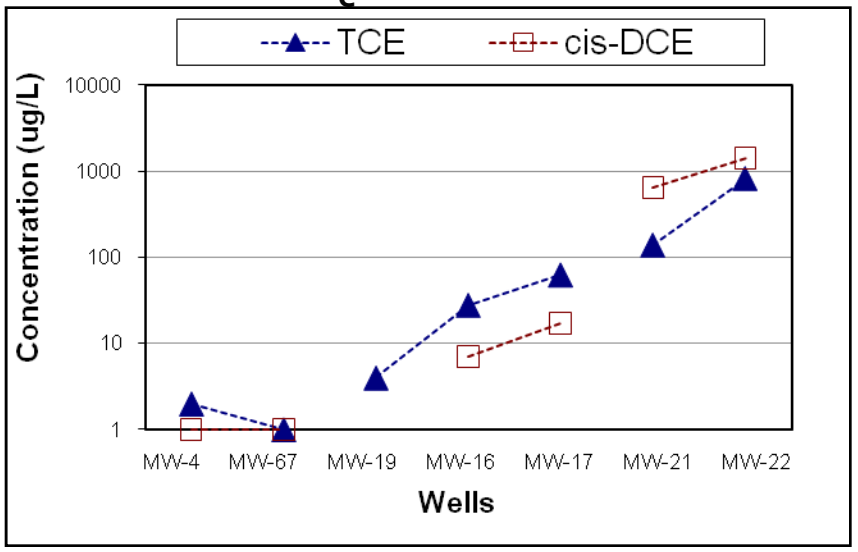
- Some enrichment in $\delta^{13}C$ for TCE and cis-DCE

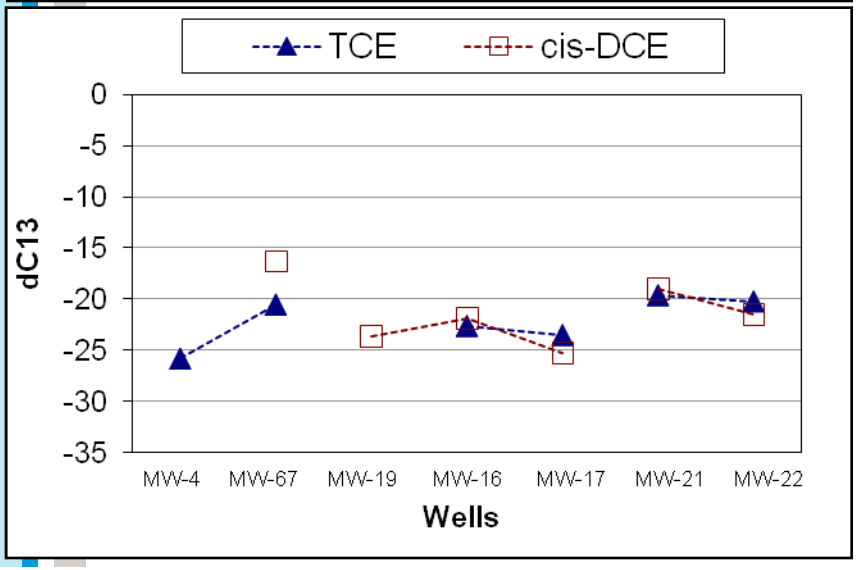
Reductive Dechlorination of TCE

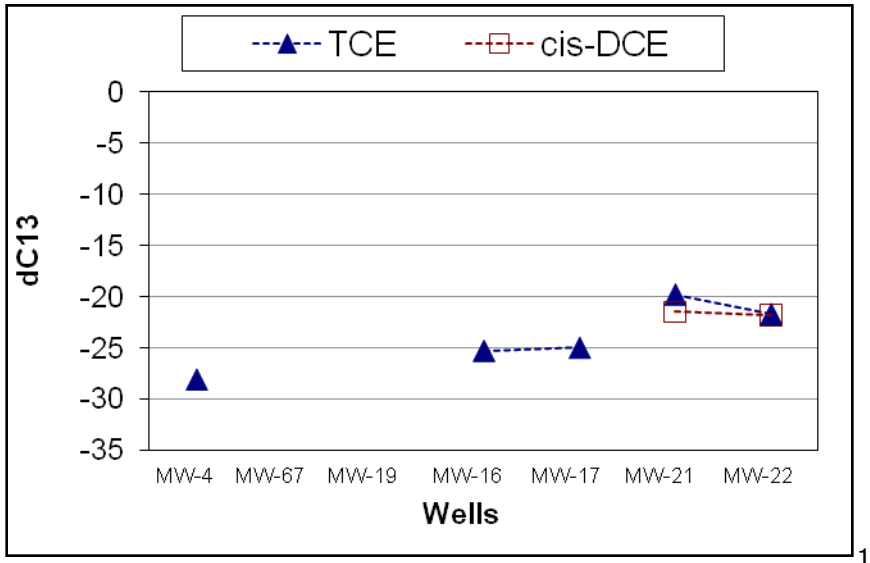
1st Quarter 2006



3rd Quarter 2009

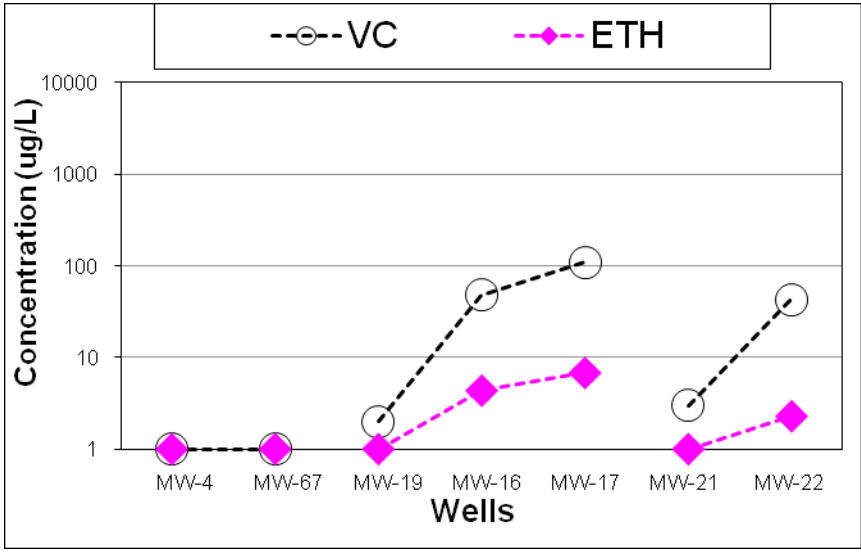




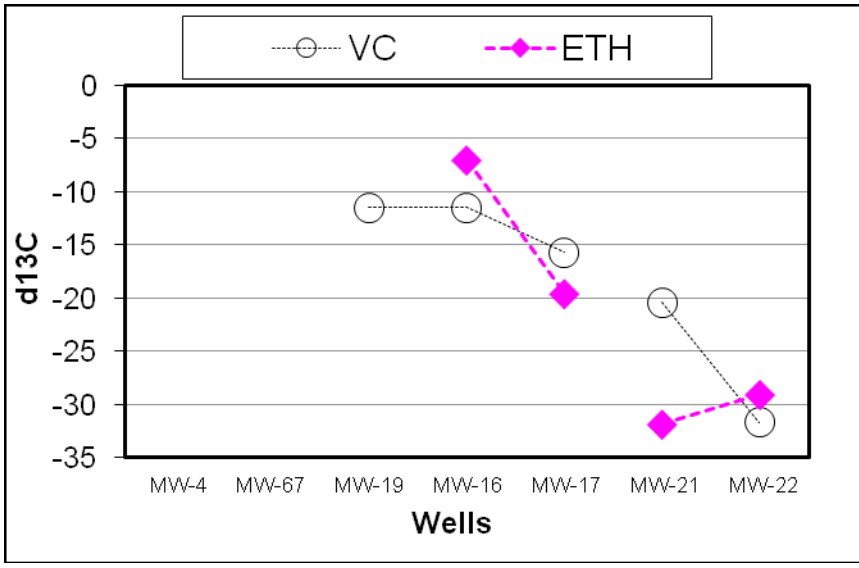


Reductive Dechlorination of TCE
1st Quarter 2006

- VC can be produced through multiple pathways

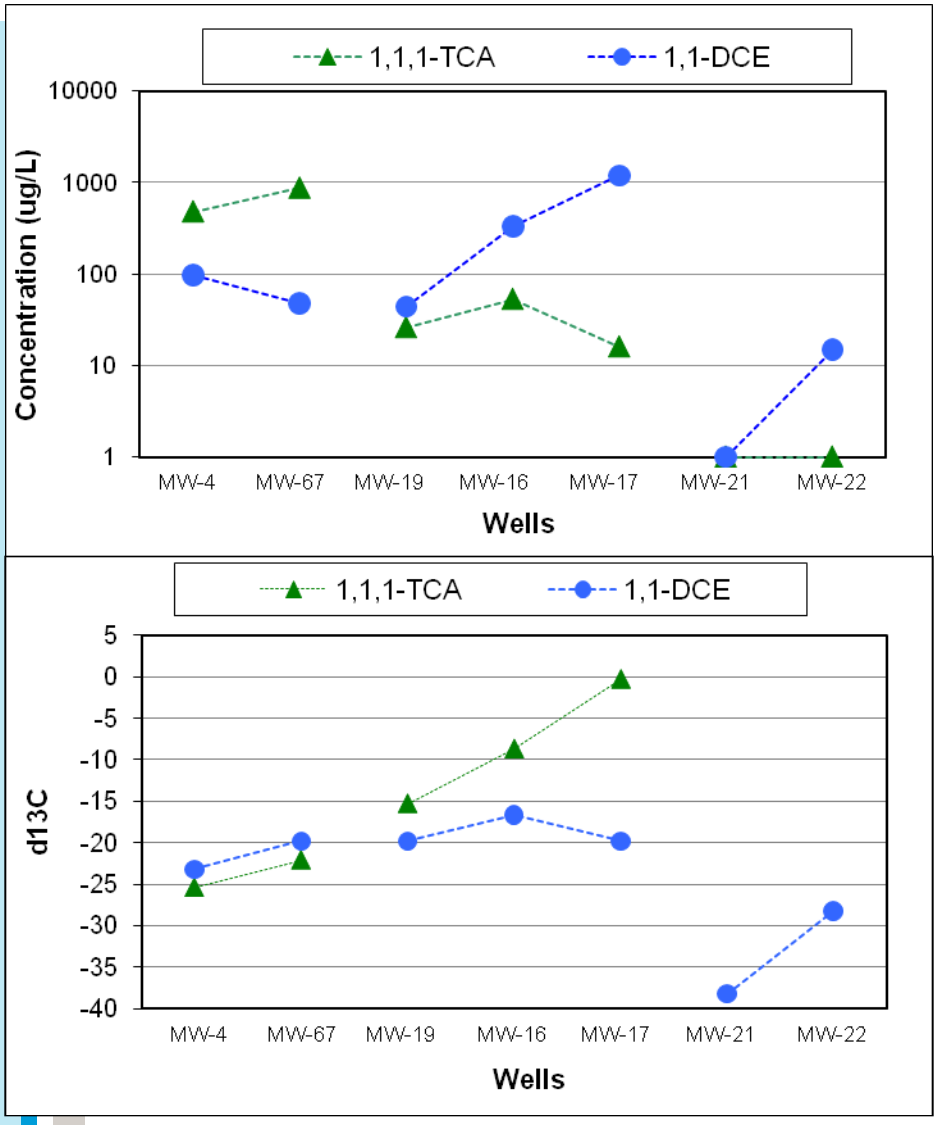


- Transformation of VC and ethene is more significant on-site than offsite
- Strongly negative $\delta^{13}C$ ethene in offsite wells suggests this product may be more recently generated



Abiotic Transformation of 1,1,1-TCA and Formation of 1,1-DCE

1st Quarter 2006

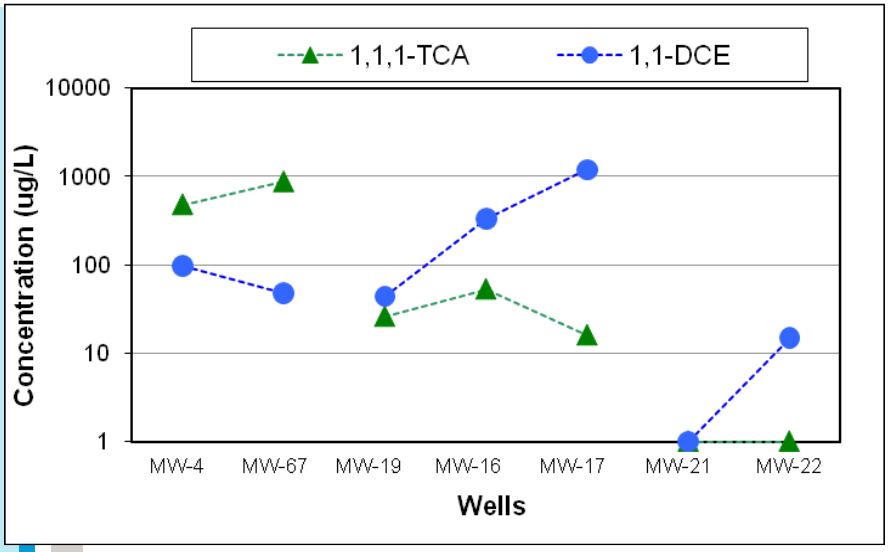


- Transformation of 1,1,1-TCA produces 1,1-DCE (abiotic) and 1,1-DCA
- 1,1,1-TCA not detected in offsite wells

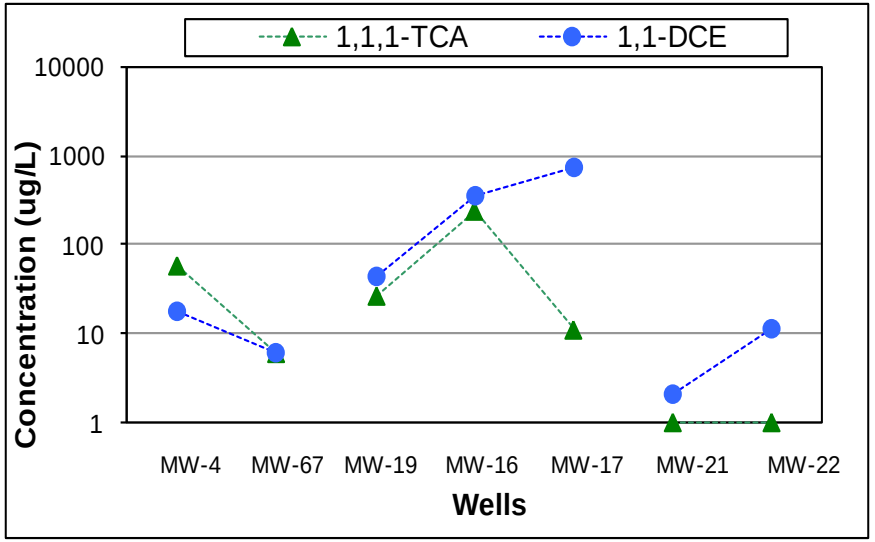
- 1,1,1-TCA $\delta^{13}C$ is strongly enriched in on-site wells
- 1,1-DCE $\delta^{13}C$ is enriched in on-site wells, but not in offsite wells
- $\delta^{13}C$ enrichment is more significant for 1,1-DCE than for cis-DCE

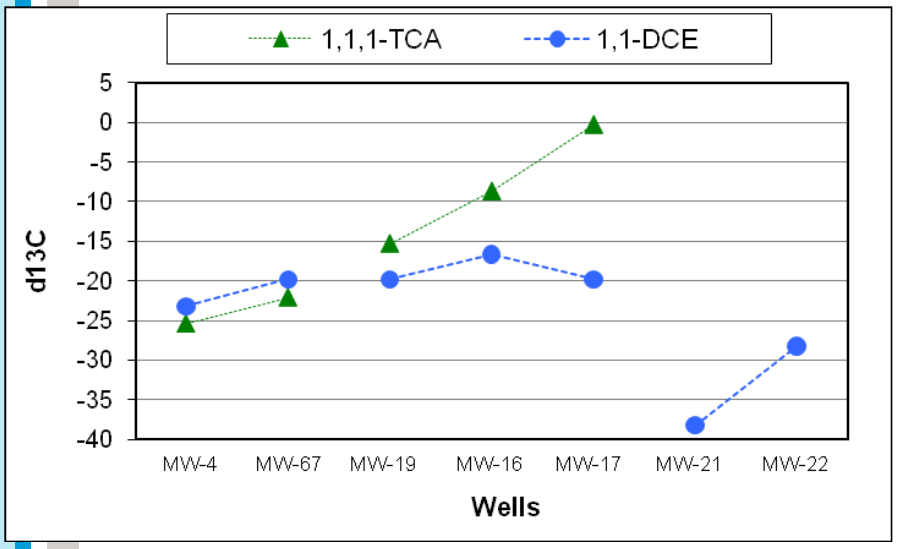
Abiotic Transformation of 1,1,1-TCA and Formation of 1,1-DCE

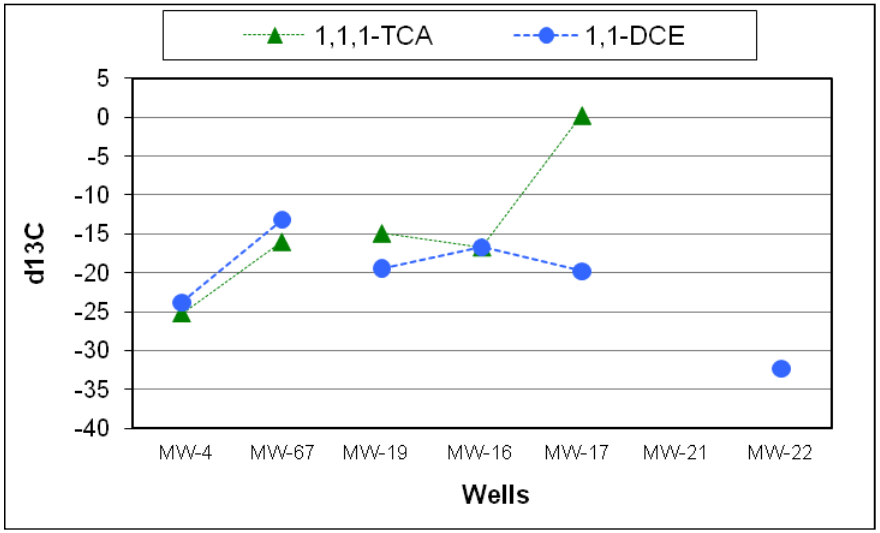
1st Quarter 2006



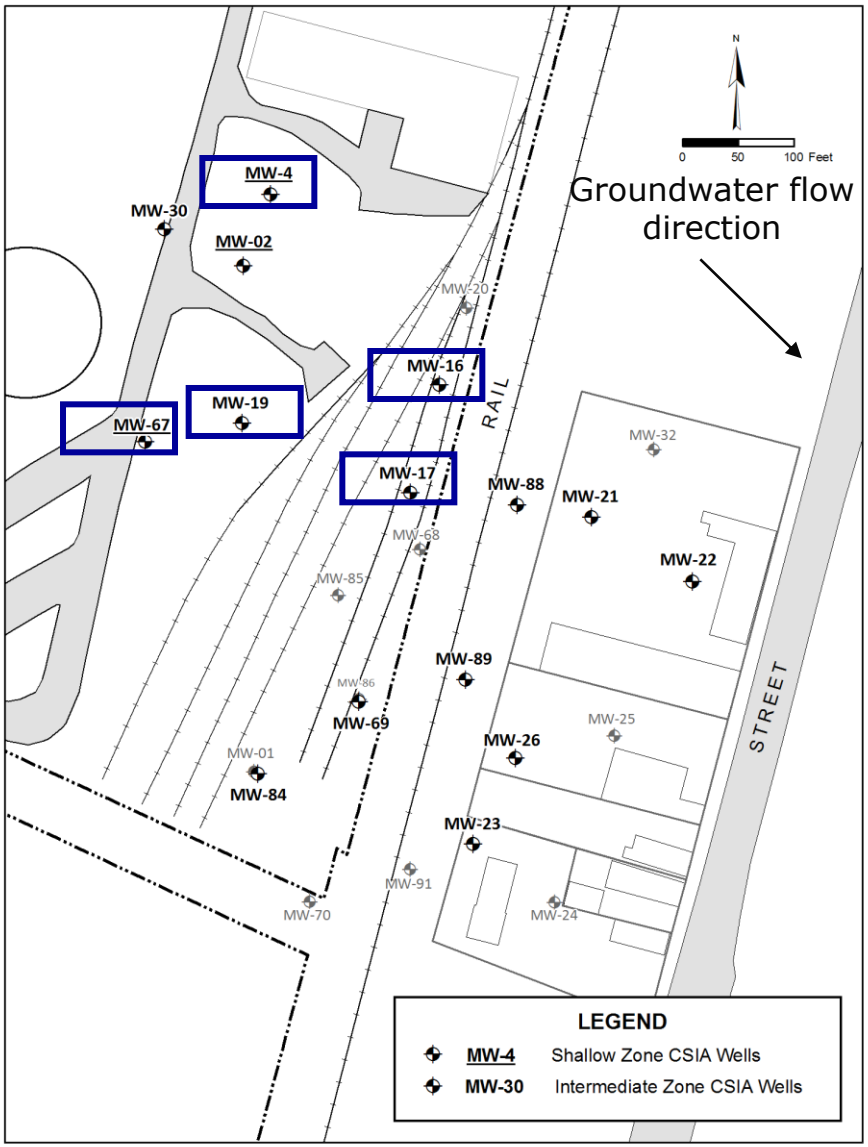
3rd Quarter 2009







Reductive Dechlorination of 1,1,1-TCA

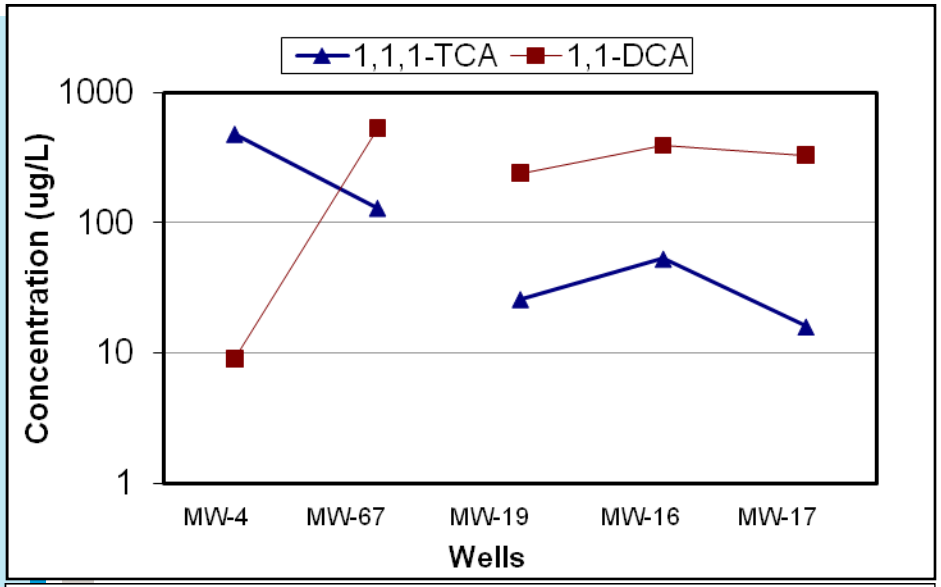


Wells used to demonstrate reductive dechlorination of 1,1,1-TCA

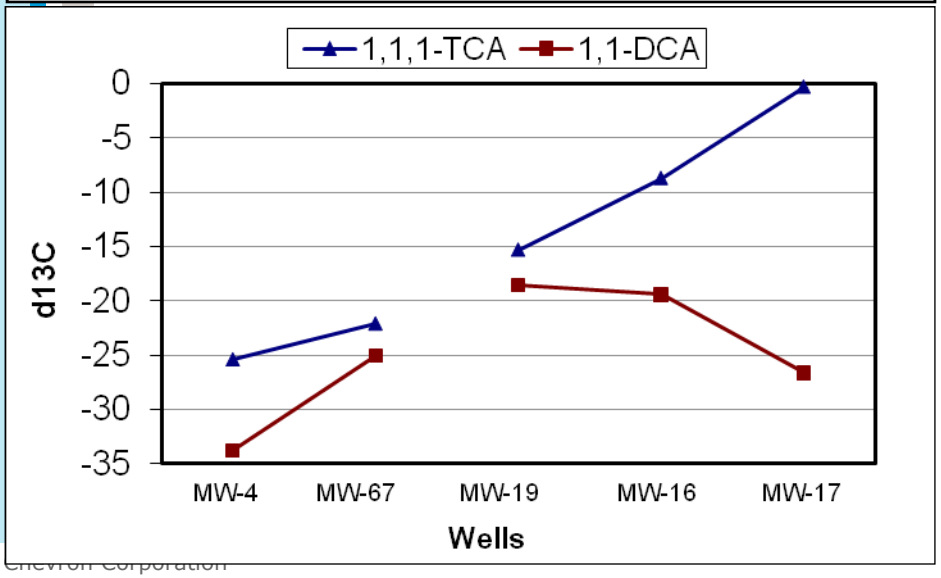
On-site wells
MW-4, 67, 19, 16, and 17

The chlorinated ethanes are not detected in the offsite wells

Reductive Dechlorination of 1,1,1-TCA
1st Quarter 2006



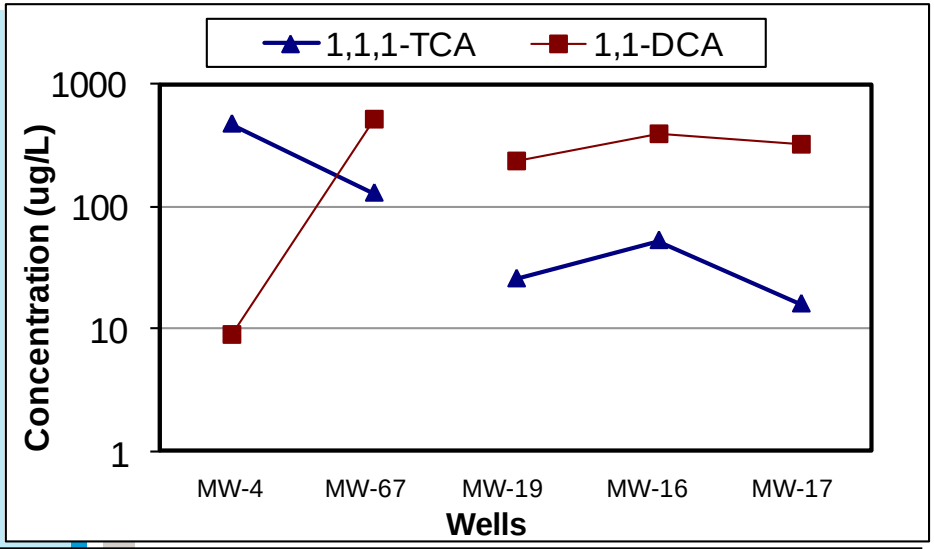
- Declining 1,1,1-TCA concentrations
- 1,1-DCA exceeds the parent concentrations in the four downgradient wells, consistent with reductive dechlorination of the parent compound



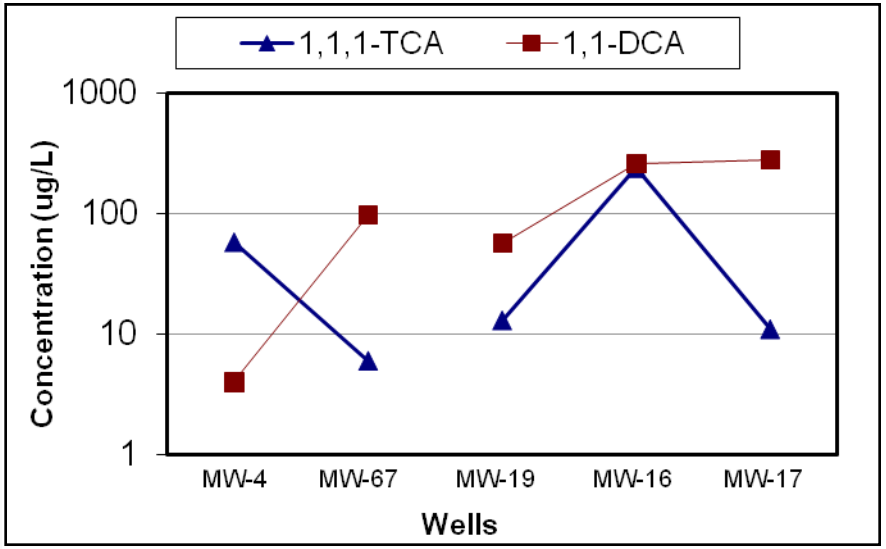
- Strongly enriched 1,1,1-TCA $\delta^{13}C$ indicates reductive dechlorination and/or abiotic transformation of the parent compound
- 1,1-DCA $\delta^{13}C$ enrichment is consistent with the formation of CA

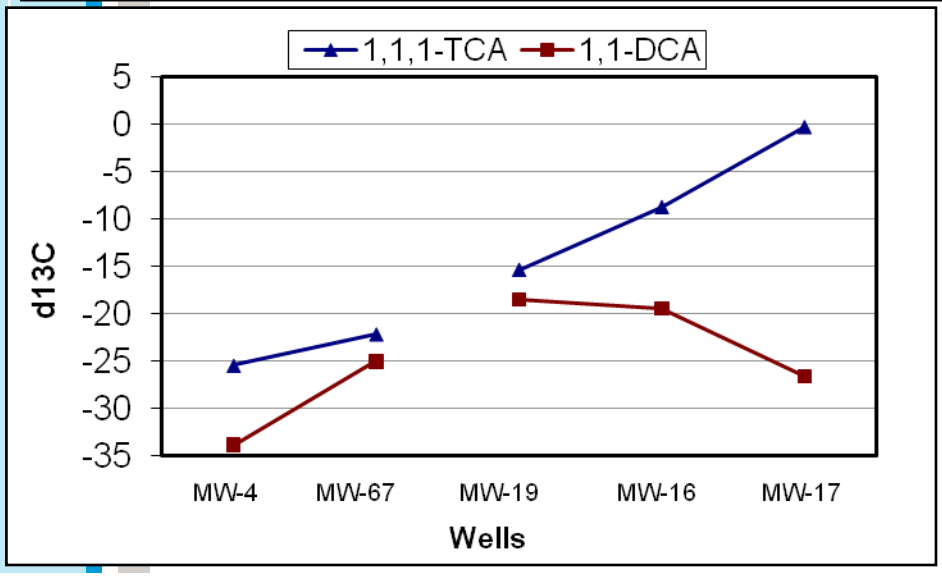
Reductive Dechlorination of 1,1,1-TCA

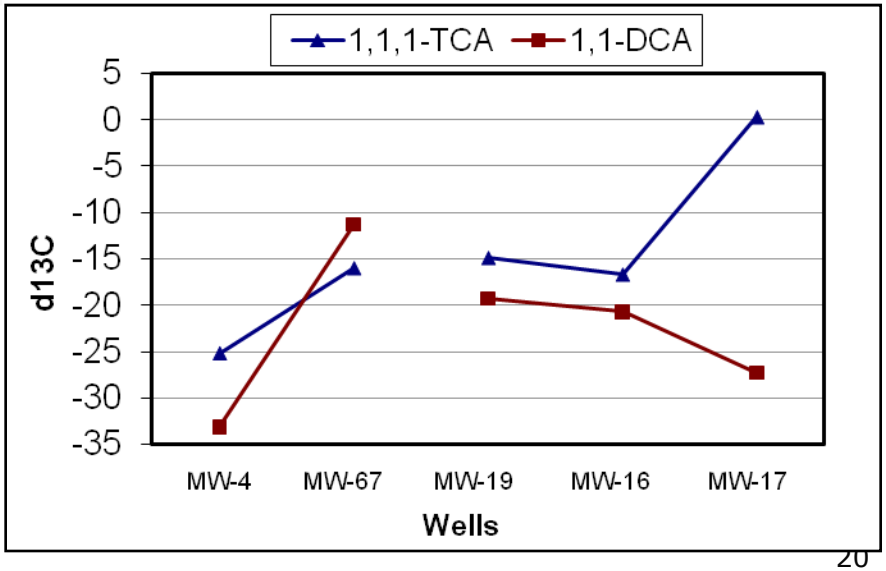
1st Quarter 2006



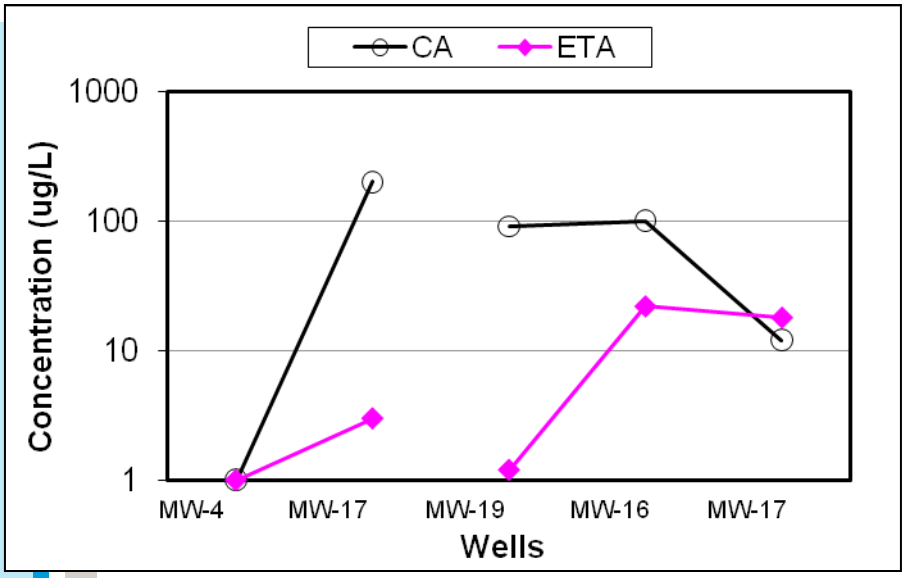
3rd Quarter 2009



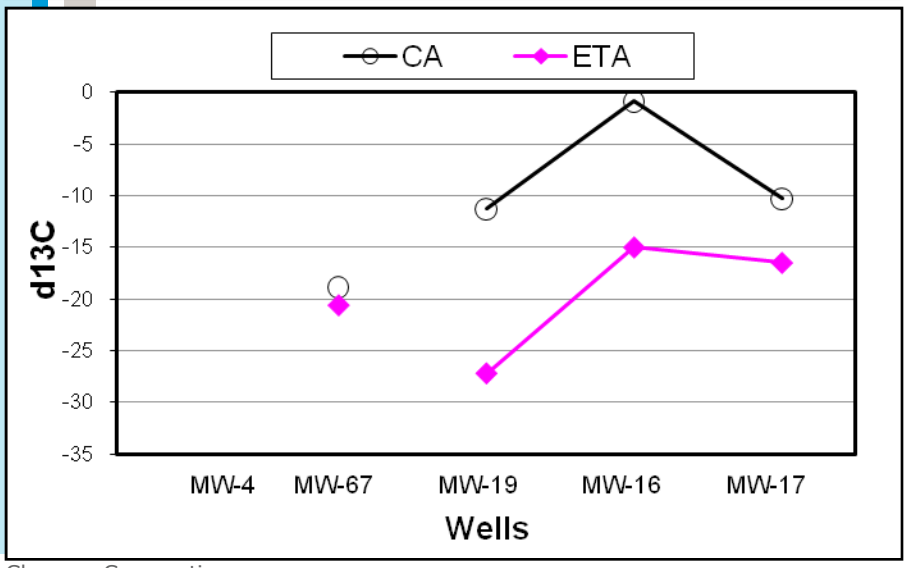




Reductive Dechlorination of 1,1,1-TCA
1st Quarter 2006



- CA concentrations exceed ethane (ETA) in three of four downgradient wells
- Abiotic hydrolysis of CA can also produce ethanol



- Significantly enriched $\delta^{13}C$ values indicate an enhanced state of degradation for CA and ethane
- The isotopic signature confirms complete reductive dechlorination of 1,1,1-TCA to CA and further degradation of CA

Conclusions

Contaminant concentrations and CSIA results demonstrate the chlorinated compounds are being degraded by the following pathways:

- Reductive dechlorination of PCE and TCE to ethene
- Reductive dechlorination of 1,1,1-TCA to ethane
- Abiotic transformation of 1,1,1-TCA to 1,1-DCE followed by reductive dechlorination to ethene
  - This is an important pathway contributing to the occurrence of VC and would not be easily identified without CSIA

Conclusions (continued)

- The isotopic signature suggests a potential offsite source
  - Transformation of VC and ethene is more significant on-site than offsite
  - Strongly negative $\delta^{13}C$ ethene in offsite wells suggests this product may be more recently generated

References

- Buscheck, T.E., T.P. Hoelen, and T. Kuder, 2006. Stable Carbon Isotope Fractionation in a Mixed Plume with Chlorinated Ethenes and Ethanes. In Proceedings of the Battelle International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, CA, May 22-25.
- Sherwood Lollar, B., G.F. Slater, J. Ahad, B. Sleep, J. Spivack, M. Brennan, and P. MacKenzie. 1999. "Contrasting Carbon Isotope Fractionation during Biodegradation of Trichloroethylene and Toluene: Implications for Intrinsic Bioremediation." Organic Geochemistry 30: 813-820.