

# CSIA Case Studies

Sites – Questions – Answers

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# Acronyms, Abbreviations, etc.

- ◆ CSIA: compound specific isotope analysis
- ◆  $\delta$ : del, the symbol used for the isotopic ratio as measured by CSIA
- ◆ ‰: per mil, the units that  $\delta$  is expressed in
- ◆ cis-DCE: cis-dichloroethene
- ◆ cDCE: cis-dichloroethene
- ◆ PCE: tetrachloroethene
- ◆ TCE: trichloroethene
- ◆ VC: vinyl chloride
- ◆ CO<sub>2</sub>: carbon dioxide
- ◆ MNA: Monitored Natural Attenuation, in MNA a typical contaminant fate is reductive dechlorination:  
$$\text{PCE} \rightarrow \text{TCE} \rightarrow \text{cis-DCE} \rightarrow \text{VC} \rightarrow \text{Ethene}$$
- ◆ NAPL: non-aqueous phase liquid
- ◆ ISCO: *In-situ* chemical oxidation, in which each VOC is converted to CO<sub>2</sub>.
- ◆ Ox. Oxidation (i.e. conversion to CO<sub>2</sub>)
- ◆ DNG: down-gradient
- ◆ UPG: up-gradient
- ◆ VOC: volatile organic compound

◆ Case studies demonstrate that CSIA can guide remediation decisions by:

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

◆ CSIA provides valuable insights about:

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

◆ CSIA is a powerful tool to document in-situ degradation

- Validated academic sector and regulatory agencies
- Newly available services widening the use of CSIA

◆ CSIA provides new information completely independent of concentration.

- CSIA measures the type of molecules that make up a VOC
- Concentration measures the number of those molecules.

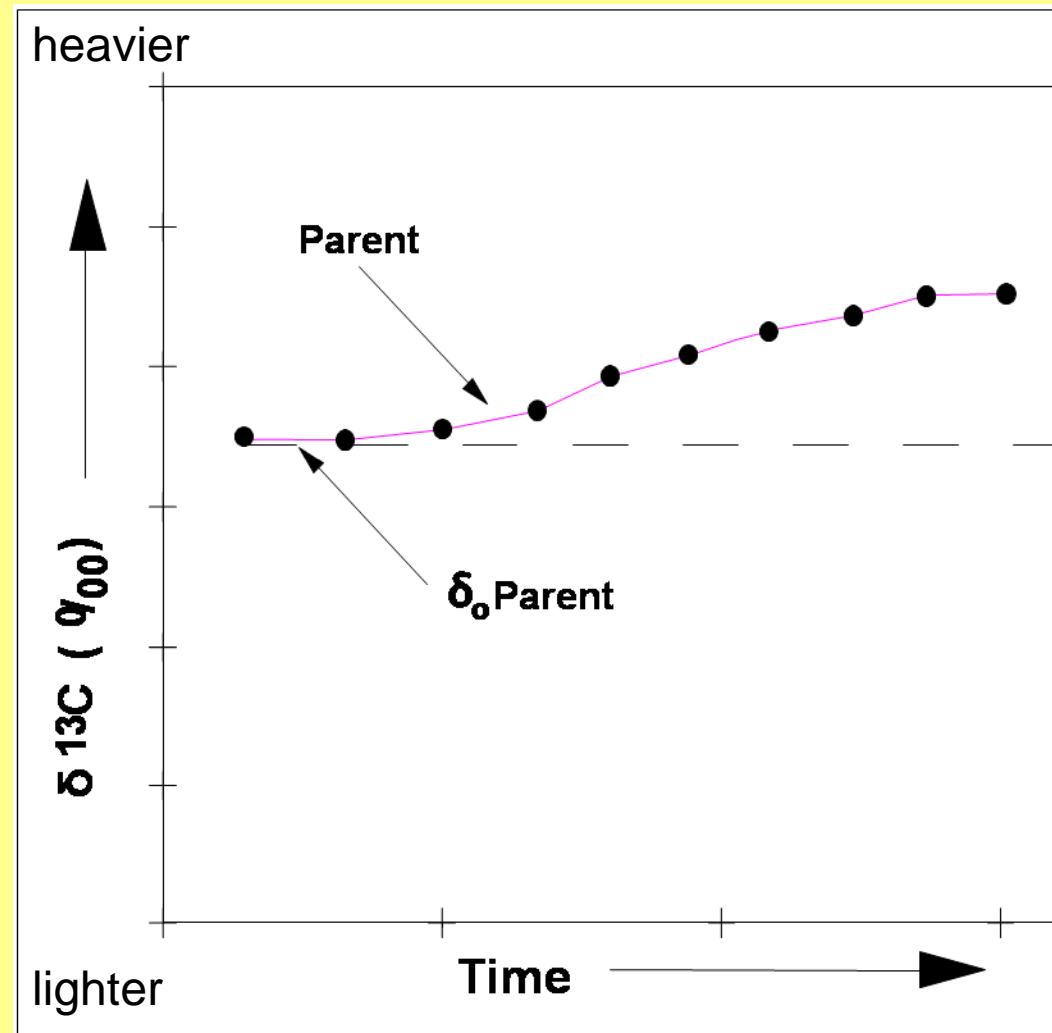
# Outline

## Five Cases – four Questions

- ◆ CSIA and degradation
  - Example is part of following case
- ◆ Case 1: Pump and treat: degradation occurring?
- ◆ Case 2: cis-DCE degrading? - Yes
- ◆ Case 3: cis-DCE degrading? – No
- ◆ Case 4: ISCO: Altered Hydrogeology or Successful Degradation?
- ◆ Case 5: BioWalls: Degraded or Lost?

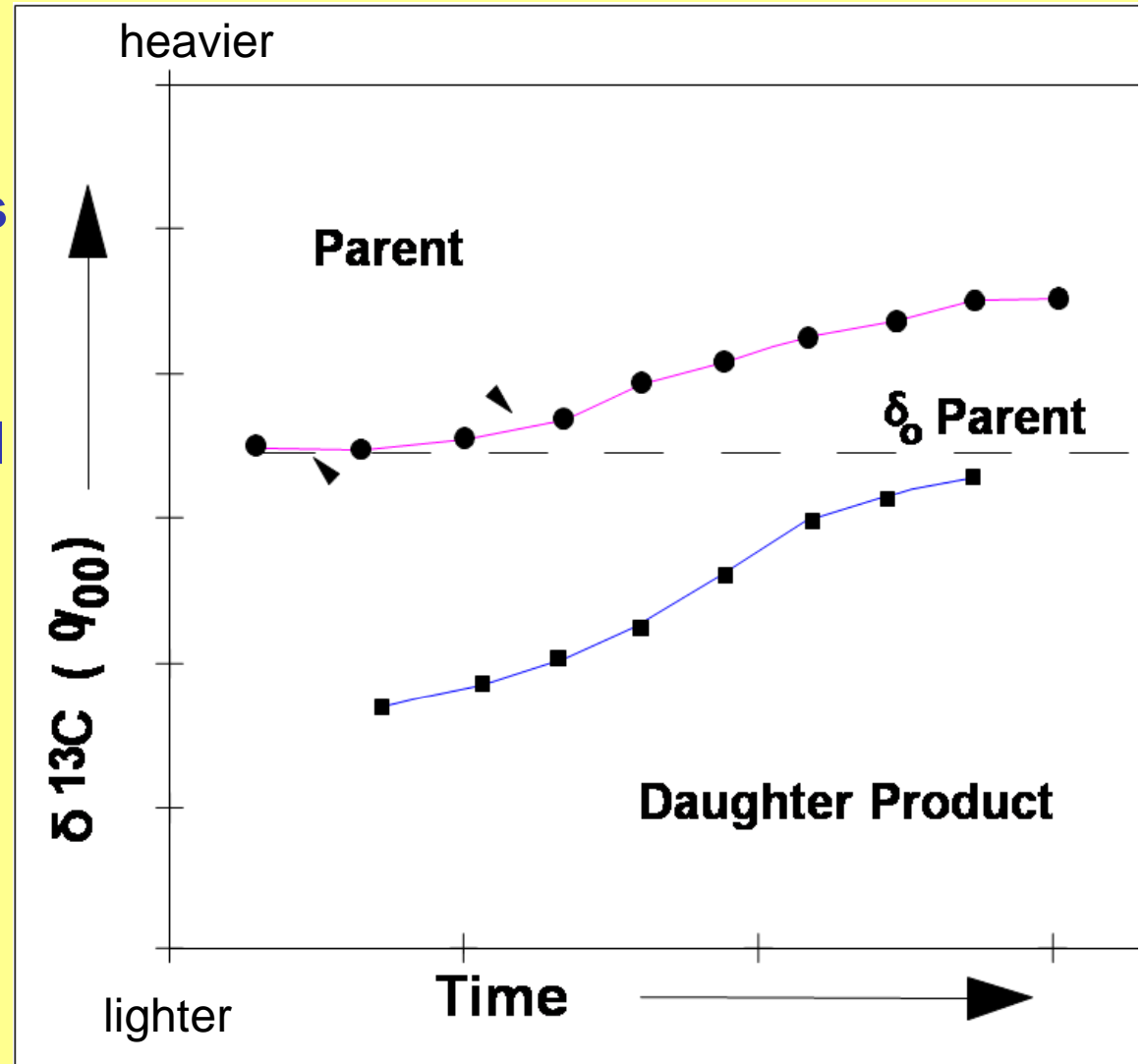
# CSIA and Degradation

- 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.



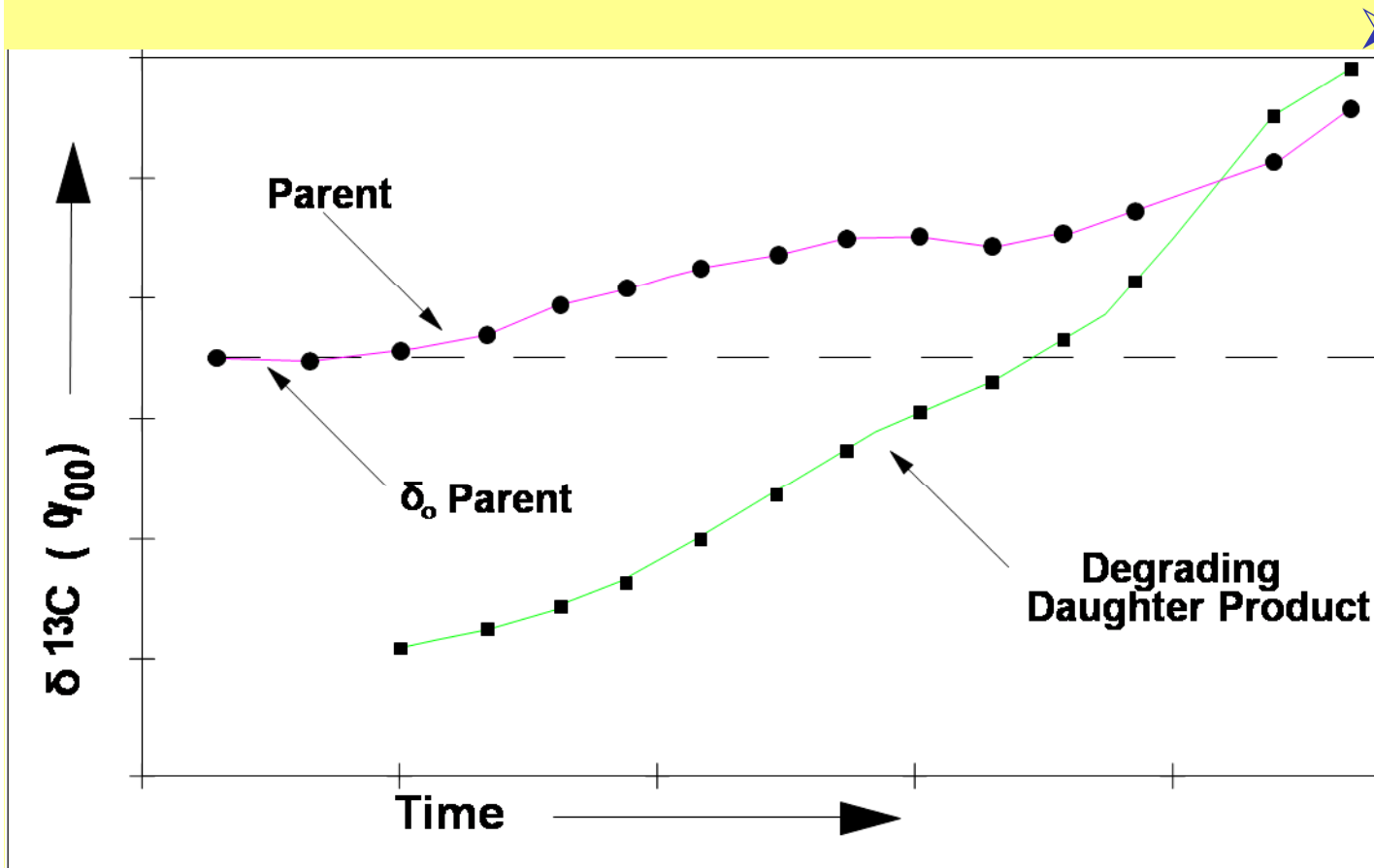
# CSIA and Degradation (cont.)

- For daughter products (not originally released but produced through degradation) fractionation alone does not prove daughter product degradation.
- If daughter product does not degrade, it still gets heavier as the parent gets heavier.
- The undegraded daughter product can get no heavier than the original (undegraded) parent product.



# CSIA and Degradation (cont.)

- If daughter product degrades, its lighter portion gets removed at all times.
- This means its isotopic ratio can get heavier than that of the parent.



➤ In chlorinated solvent daughter products, a carbon isotopic ratio heavier than the parent is evidence that the daughter product is degrading.

# CSIA and Degradation (example)

*This is part of the following case study.*

- ◆ PCE (parent), TCE (first daughter) and cis-DCE (second daughter) all present
- ◆ Question: is each VOC degrading?

# CSIA and Degradation (ex. continued)

## PCE (parent, originally released)

PCE (parent) lightest at UTZ-RW2. This is  $\delta_0$ .

Isotopic ratio ( $\delta$ , in per mil)			
	PCE	TCE	cis-DCE
UTZ-RW2	-26.91	-21.64	-4.96
UTZ-RW1	-25.95	-26.96	-1.90
LTZ-RW1	-26.43	-27.21	-29.54
LTZ-RW2	NR	NR	+1.29

PCE  $\delta$  heavier in UTZ-RW1: degrading in UTZ-RW1

# CSIA and Degradation (ex. continued)

## TCE (from PCE → TCE)

PCE (parent) lightest  
at UTZ-RW2

Isotopic ratio ( $\delta$ , in per mil)			
	PCE	TCE	cis-DCE
UTZ-RW2	-26.91	-21.64	-4.96
UTZ-RW1	-25.95	-26.96	-1.90
LTZ-RW1	-26.43	-27.21	-29.54
LTZ-RW2	NR	NR	+1.29

TCE  $\delta$  heavier than PCE in UTZ-RW2:  
degrading in UTZ-RW2

# CSIA and Degradation (ex. continued)

## cis-DCE (from TCE → cis-DCE)

PCE (parent) lightest  
at UTZ-RW2

Isotopic ratio ( $\delta$ , in per mil)			
	PCE	TCE	cis-DCE
UTZ-RW2	-26.91	-21.64	-4.96
UTZ-RW1	-25.95	-26.96	-1.90
LTZ-RW1	-26.43	-27.21	-29.54
LTZ-RW2	NR	NR	+1.29

cDCE  $\delta$  in UTZ-RW1 and UTZ-RW2 is  
heavier than the PCE  
cis-DCE degrading in UTZ-RW1 and UTZ-RW2

# CSIA and Degradation (*ex. continued*)

## cis-DCE (from TCE → cis-DCE)

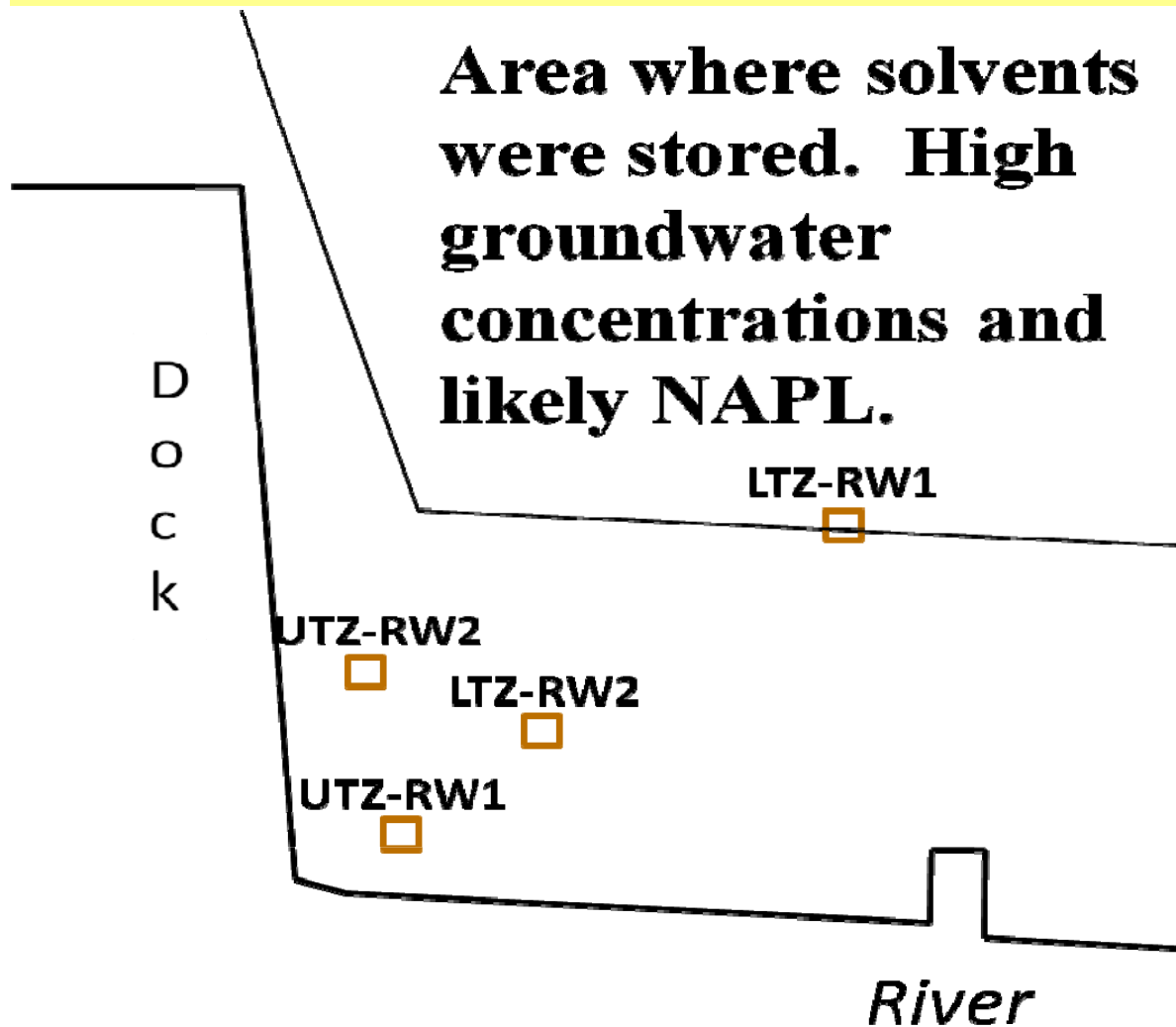
➤ Range of  $\delta^{13}\text{C}$  for manufactured chlorinated ethenes and ethanes :

**$-30 \pm 5 \text{ ‰}$**

Isotopic ratio ( $\delta$ , in per mil)			
	PCE	TCE	cis-DCE
UTZ-RW2	-26.91	-21.64	-4.96
UTZ-RW1	-25.95	-26.96	-1.90
LTZ-RW1	-26.43	-27.21	-29.54
LTZ-RW2	NR	NR	+1.29

cis-DCE in LTZ-RW2 is heavier than any reported literature value for undegraded PCE  
cis-DCE degrading in LTZ-RW2

# Case 1: Pump and treat: degradation occurring?



- ◆ Two transmissive zones being pumped
- ◆ Concentrations are declining, but is this partly due to degradation?

# Case 1 (cont.)

	PCE	TCE	cDCE	VC
Concentration (ug/L)				
LTZ-RW1	9000	20,000	40,000	9000
LTZ-RW2	<5	<5	8	20
UTZ-RW1	20	20	100	500
UTZ-RW2	<5	<5	6	80
Isotopic ratio (del, in per mil)				
LTZ-RW1	-26.43	-27.21	-29.54	-33.89
LTZ-RW2	NR	NR	+1.29	-1.48
UTZ-RW1	-25.95	-26.96	-1.90	-18.10
UTZ-RW2	-26.91	-21.64	-4.96	-19.80

◆ PCE, TCE and cis-DCE already discussed in example

◆ Isotopic Ratios of VC are heavier (more positive) than parent PCE, indicating degradation

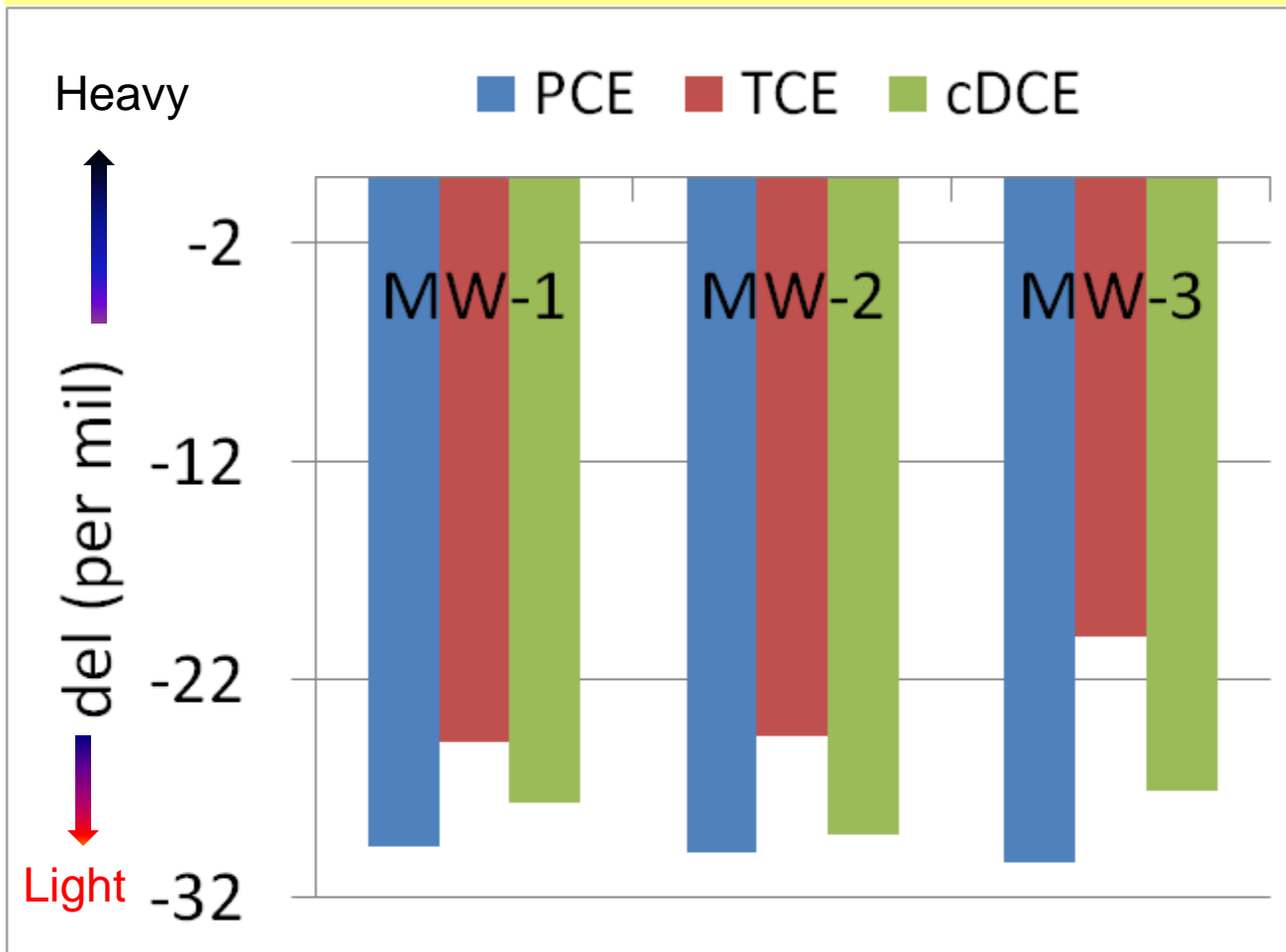
◆ Degradation of cis-DCE and VC is extensive

CSIA demonstrated potential viability of MNA solution to replace pump and treat.

## Case 2: cis-DCE degrading? - Yes

- ◆ Site was predominated by cis-DCE
  - Some TCE, PCE
- ◆ Plume crossed a geologic fault, eliminating applicability of standard “concentration vs. distance” analyses.
- ◆ VC could not be observed
- ◆ Was the cis-DCE degrading?

## Case 2 (cont.)



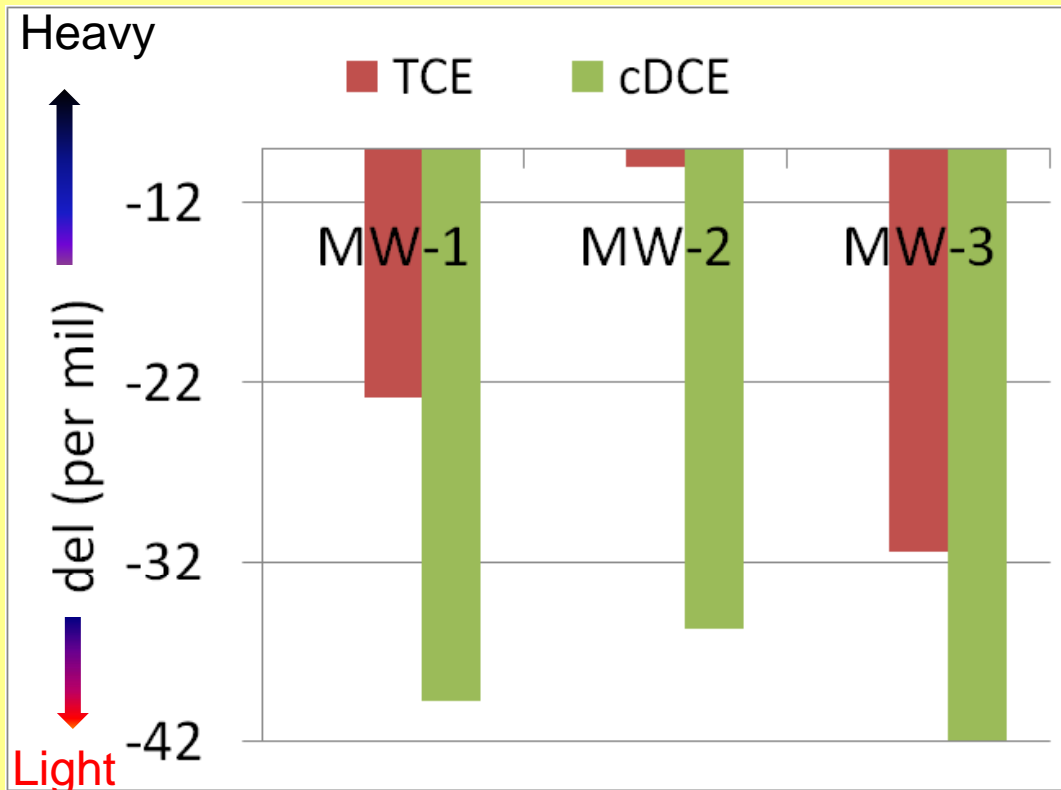
- ◆ cis-DCE is heavier than PCE it came from (PCE ≡ “parent”)
- ◆ cis-DCE gets heavier than parent **ONLY** if the cis-DCE is degrading

CSIA confirmed that cis-DCE is degrading and the remediation is effective.

## Case 3: cis-DCE degrading? - No

- ◆ Site was predominated by TCE
  - Some cis-DCE.
- ◆ Site was predominantly oxic.
- ◆ VC could not be observed
- ◆ Was the cis-DCE degrading?

## Case 3 (cont.)



- ◆ cis-DCE lighter than TCE
- ◆ cis-DCE < -30 per mil
- ◆ CSIA indicates degradation, if present, is slow compared to TCE degradation.

CSIA confirmed what other analyses could only suggest:  
MNA ineffective - alternate remediation strategy  
required.

## Case 4: ISCO: Altered Hydrogeology or Successful Degradation?

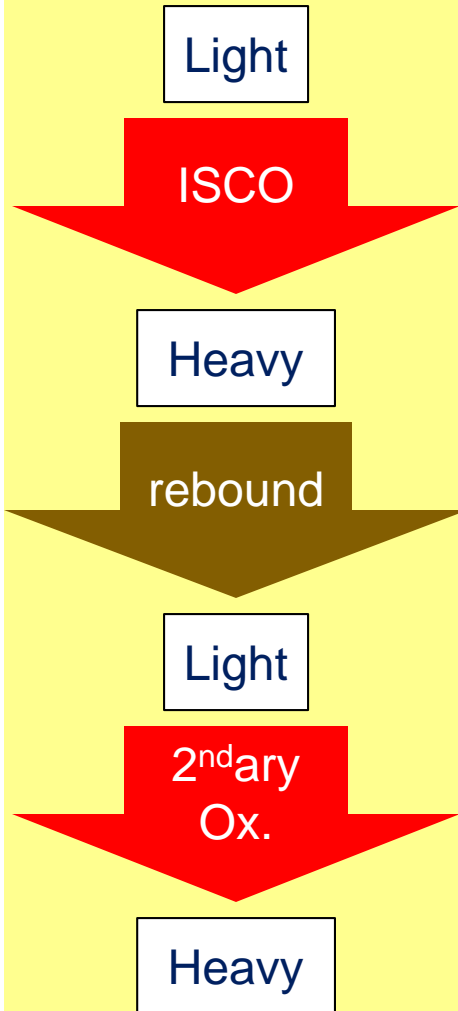
- ◆ Site contaminated with PCE and all daughter products.
- ◆ Very tight formation
- ◆ ISCO with fracturing was the planned remediation.
- ◆ Was there degradation?

# Case 4

- ◆ Concentration decrease coupled with isotopic shift (change in del) shows strong degradation at MW-A (and probably MW-23)
- ◆ ISCO effect unclear in MW-D, but CSIA shows degradation in MW-D.
- ◆ CSIA proved degradation
- ◆ but did the rebound undo any progress?

	MW-A		MW-23		MW-D	
<b>TCE</b>						
	del	conc.	del	conc.	del	conc.
Dec-07	-29.6	3000	-34.4	400	-32.3	7000
<b>ISCO</b>						
Jul-08	-3.7	80			-30.5	1000
Dec-08	-27.0	1000	-25.7	500	-31.0	5000
Mar-09	-25.0	1000 J	-30.1	600 J		
<b>cis-DCE</b>						
Dec-07	-29.8	20000	-30.7	200	-31.3	7000
<b>ISCO</b>						
Jul-08	-7.4	2000			-29.4	20000
Dec-08	-30.5	30000	-23.1	400	-31.3	10000
Mar-09	-26.3	30000	-30.4	600 J		
<b>Vinyl Chloride</b>						
Dec-07	-38.4	600	-29.4	90	-33.8	500
<b>ISCO</b>						
Jul-08	-	2 (J)			-34.2	1000
Dec-08	-35.8	900	-	<5	-36.9	500 J
Mar-09	-33.2	40	-	<1000		

# Case 4 (cont.)



CSIA Shows  
Light>Heavy>Light>Heavy  
pattern, indicating secondary  
oxidation in MW-A

This implies that the rebound  
is inevitable, but the ISCO  
dosage accounted for that  
rebound

Without CSIA, this secondary  
effect, though careful planned  
for and important, would have  
been undocumented.

		MW-A	
<b>TCE</b>		del	conc.
Dec-07		-29.6	3000
<b>ISCO</b>			
Jul-08		-3.7	80
Dec-08		-27.0	1000
Mar-09		-25.0	1000 J
<b>cis-DCE</b>			
Dec-07		-29.8	20000
<b>ISCO</b>			
Jul-08		-7.4	2000
Dec-08		-30.5	30000
Mar-09		-26.3	30000
<b>Vinyl Chloride</b>			
Dec-07		-38.4	600
<b>ISCO</b>			
Jul-08		-	2 (J)
Dec-08		-35.8	900
Mar-09		-33.2	40

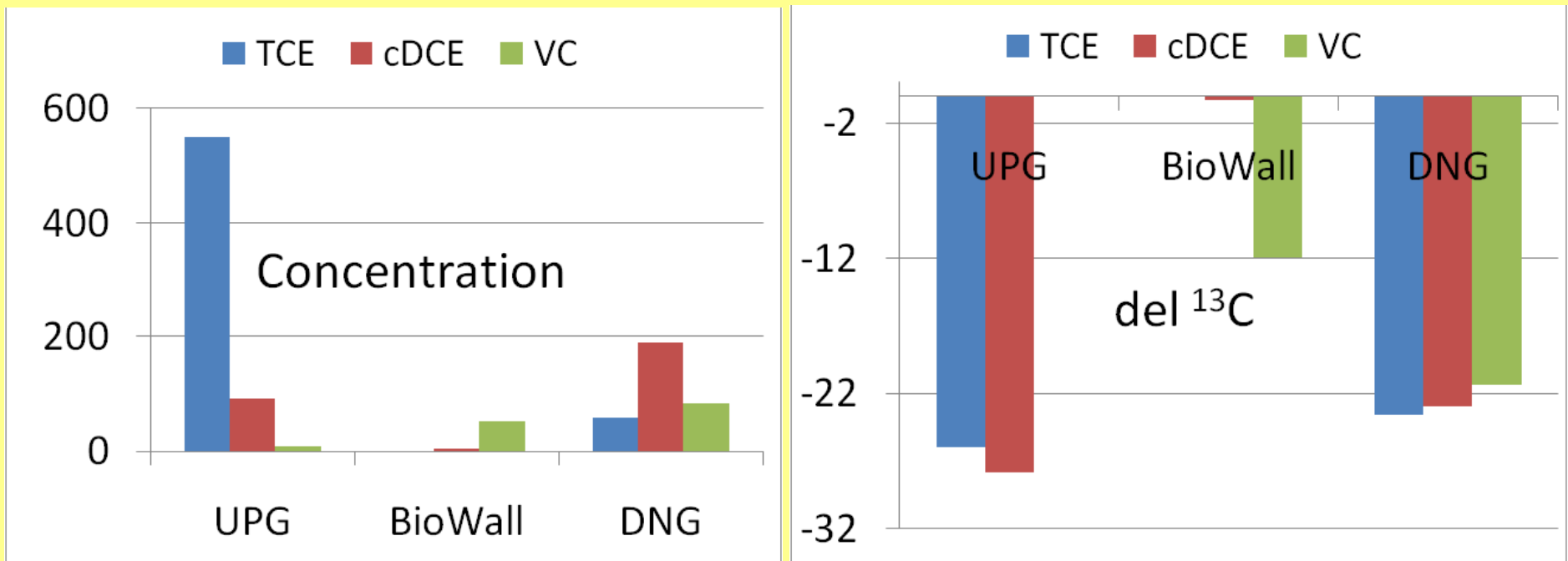
## Case 5: BioWalls: Degraded or Lost?

- ◆ Organic Mulch trenched in place (BioWall) to provide continued source of organic substrate.
- ◆ Organic substrate drives conditions conducive to chlorinated solvent degradation.
- ◆ BioWall intercepted a TCE/daughter product plume.
- ◆ Concentration shows a rebound down-gradient (DNG). Is further remediation needed?

# Case 5 (cont.)

CSIA Shows:

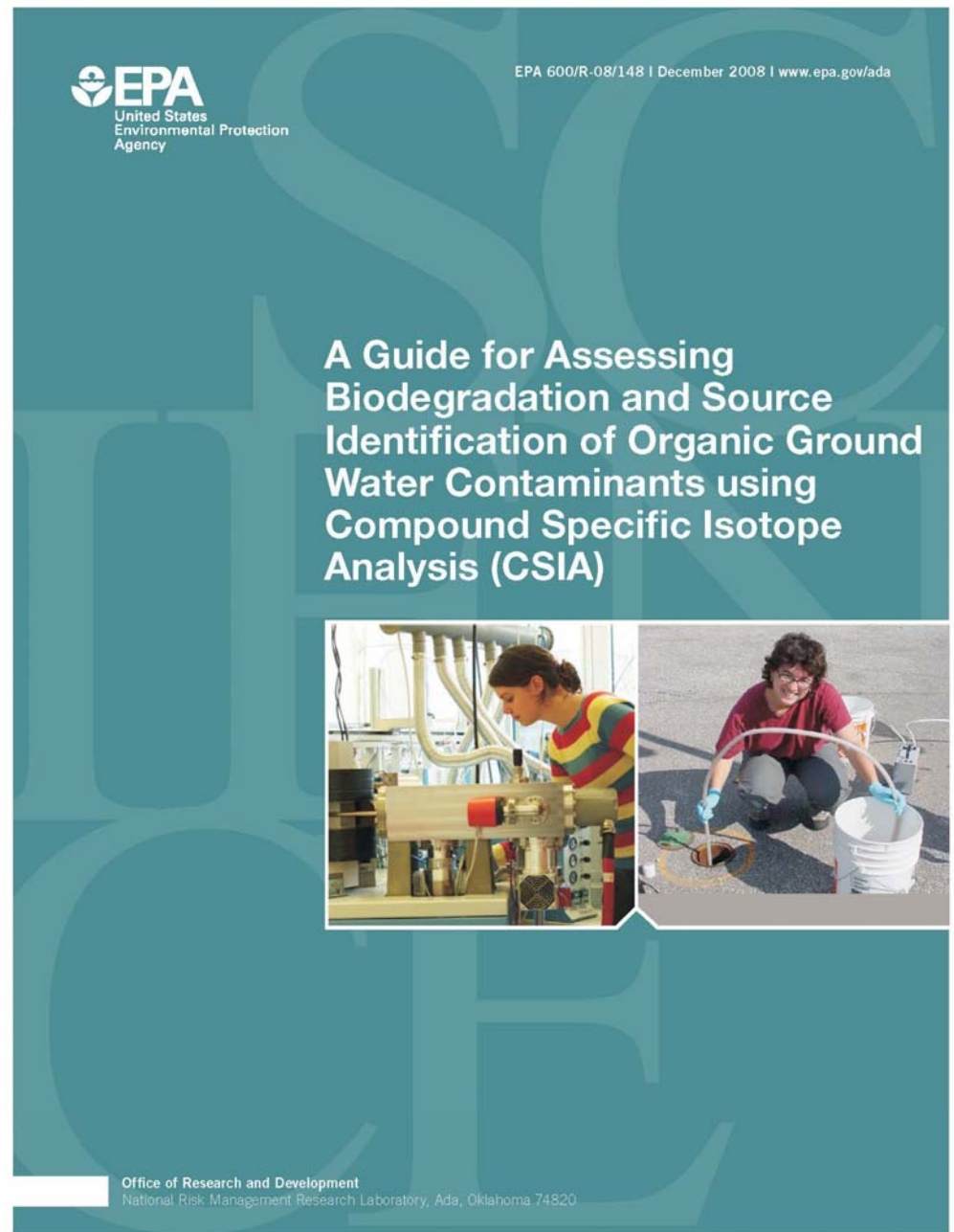
- ◆ Degradation in the BioWall
- ◆ BioWall changes degradation mechanism DNG.
- ◆ Evidence of complete degradation down-gradient of BioWall
  - DNG is located ~25ft from BioWall
  - Total plume length >3000ft.



CSIA suggests BioWall may be sufficient.

# USEPA Guidance document for CSIA emphasizes regulatory

- ◆ Acceptance
- ◆ Support
- ◆ Available through  
[www.Microseeps.com](http://www.Microseeps.com)  
> Resources >  
Technical Articles



# Summary

## ◆ Is the cis-DCE degrading?

- CSIA confirmed that cis-DCE is degrading and the remediation is effective.

*or*

- CSIA confirmed what other analyses could only suggest: MNA ineffective - alternate remediation strategy required.

## ◆ Pump and treat shutoff: is degradation occurring?

- CSIA demonstrated potential viability of MNA solution to replace pump and treat.

## ◆ ISCO: Altered Hydrogeology or Successful Degradation?

- CSIA proved degradation
- Without CSIA, this secondary effect, though carefully planned for and important, would have been undocumented.

## ◆ BioWalls: Degraded or Lost?

- CSIA suggests BioWall may be sufficient.