Pilot scale *in situ* treatment of chlorinated solvent source zone – use of compound-specific isotope analysis (CSIA) to assess treatment performance and injection design

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Remtech East
Niagara Falls, Ont
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Context

Remediation technologies aim at stimulating a specific contaminant removal process:

i. Destructive (chemical and biological processes)

ii. non-destructive (physical process)

How do we know if the intended removal process is actually occurring ?

i. Presence of co-occurring processes decreasing contaminant concentrations:
   - Dilution vs destruction
   - Dilution vs non-destructive removal
   - Destruction vs non-destructive removal

Context

What is your monitoring program?

i. Targeted VOC
   a. Concentration
   b. Mass flux

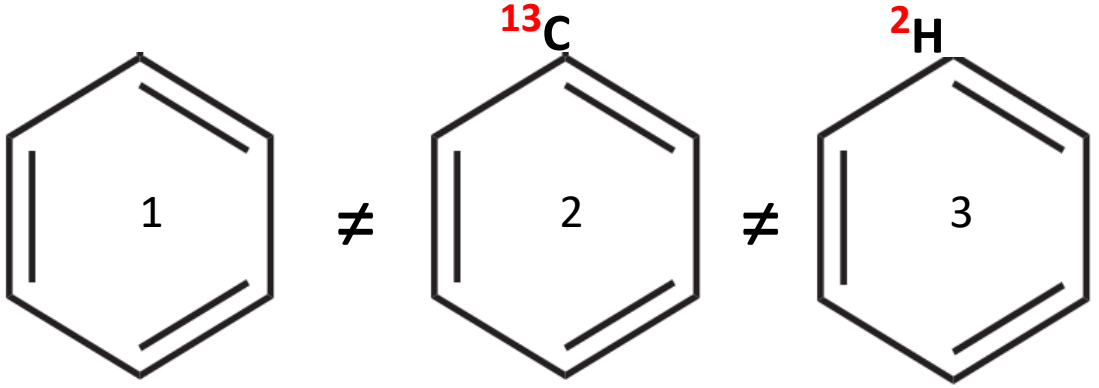
ii. Hydrogeochemical parameters:
   a. DO, ORP, pH
   b. NO_3, Fe, SO_4,
   c. H_2S, ethene/ethane/methane

iii. Microbial population
   a. Change over time
   b. Right population present

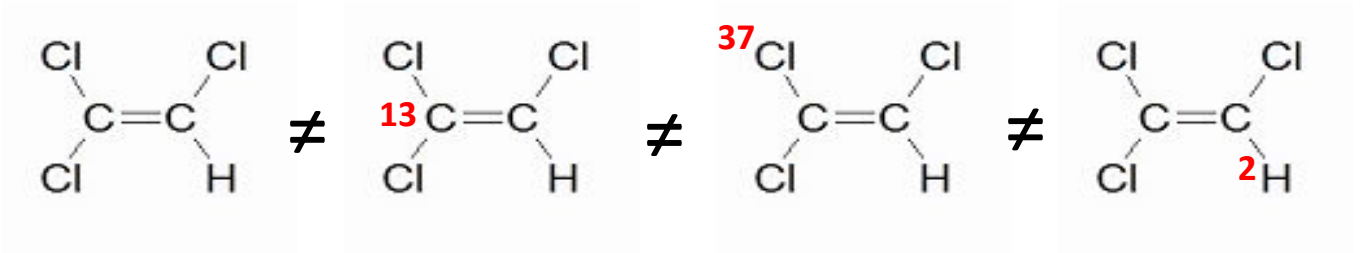
iv. Are the compounds of concern degraded ?
   a. Compound-specific isotope analysis (CSIA)

Implication of heavy isotopes

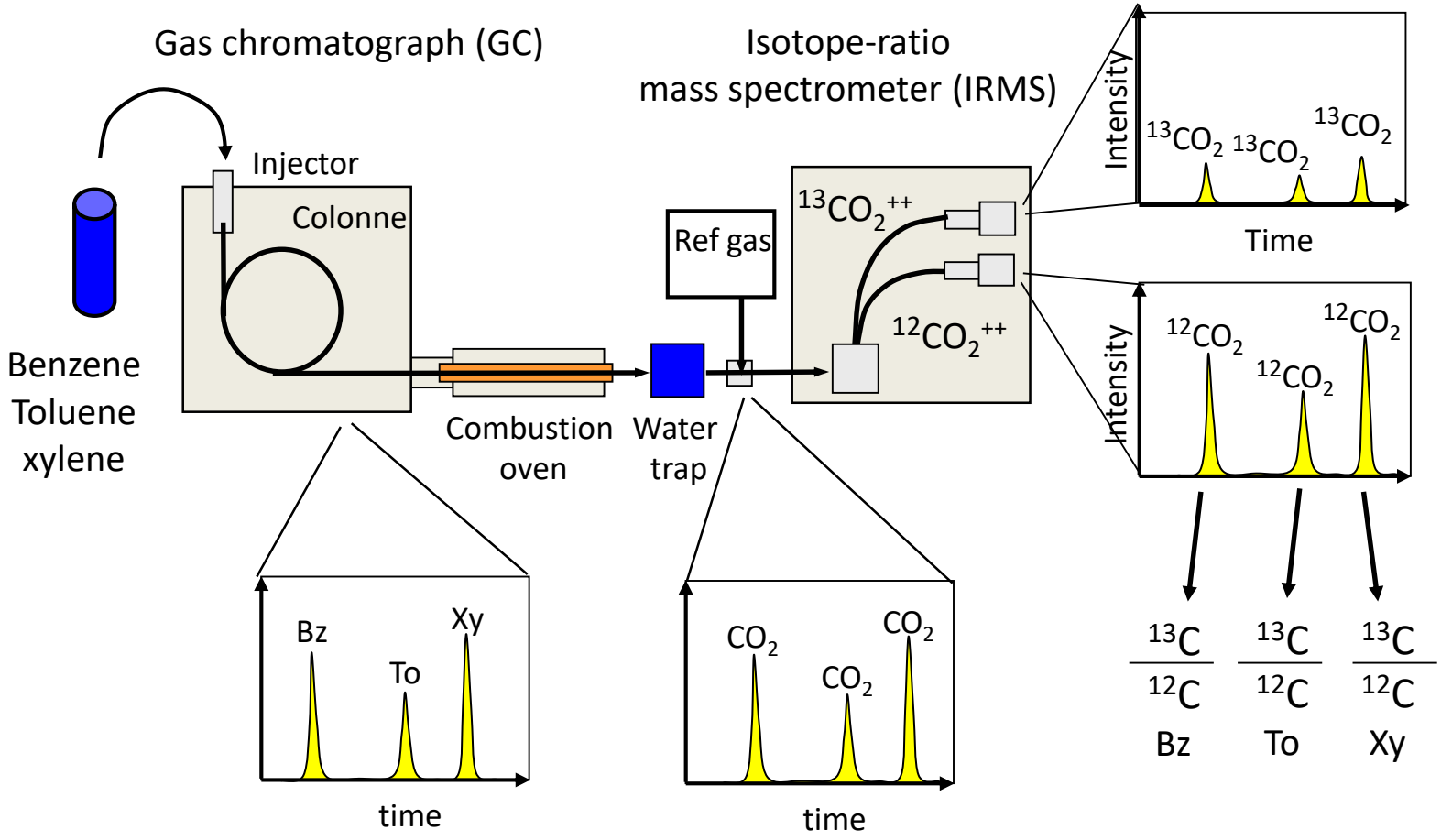
benzene



TCE



Sample analysis



Delta (δ) notation

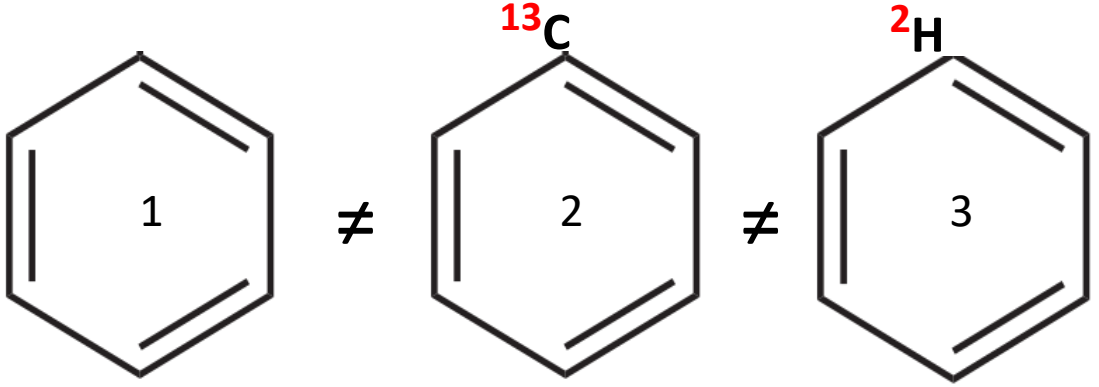
$$\delta^{13}C\ (‰) = \frac{{}^{13}C/{}^{12}C_{sample} - {}^{13}C/{}^{12}C_{standard}}{{}^{13}C/{}^{12}C_{standard}} \times 1000$$

International standard

- Carbon: V-PDB
- Hydrogen: V-SMOW
- Chlorine : V-SMOC

Implication of heavy isotopes

benzene



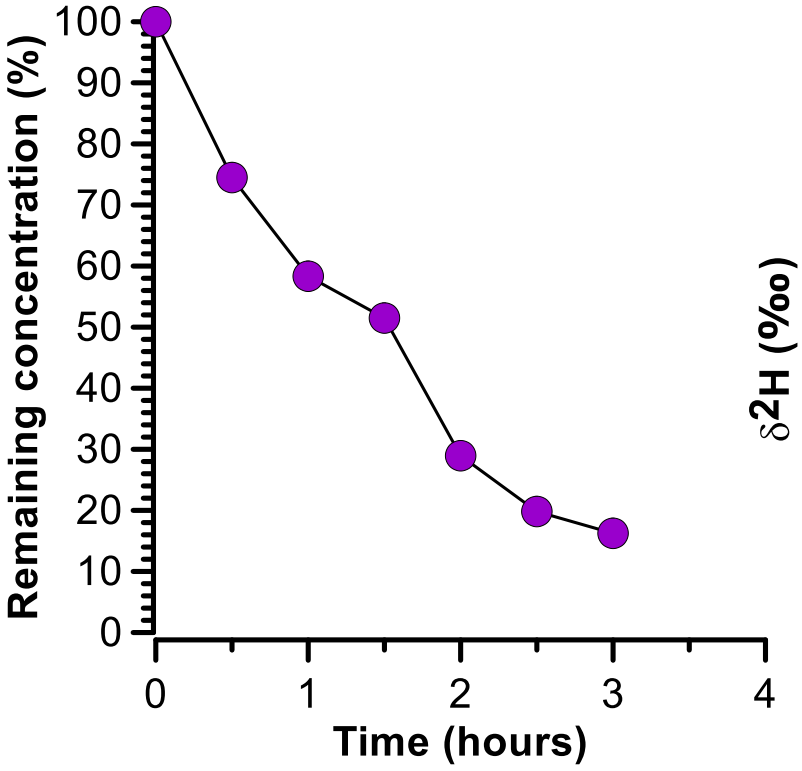
Degradation rate	normal	slower	slower

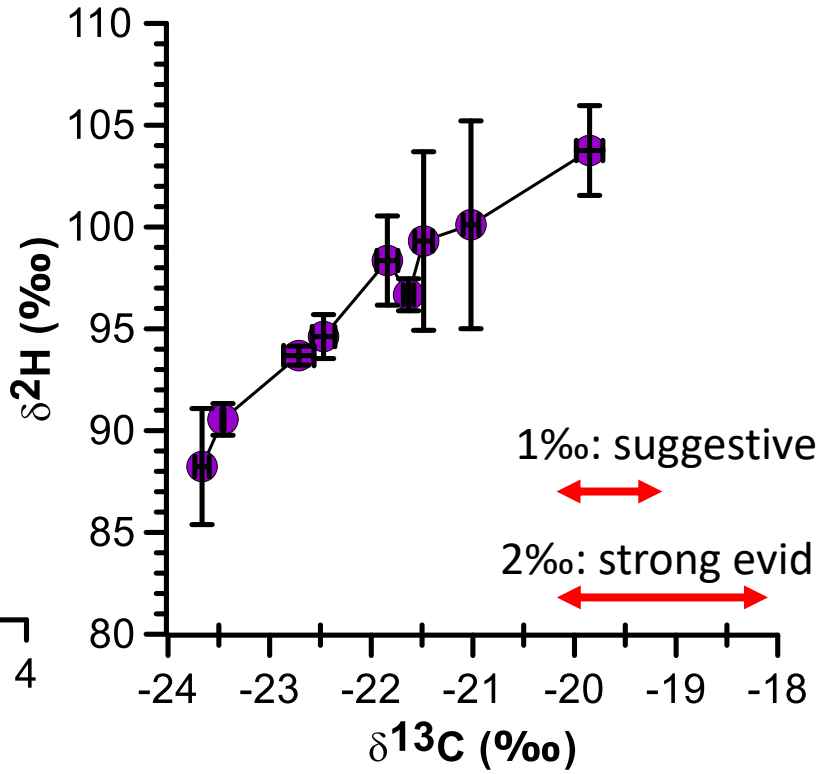
Method aim:

tracking the $^{13}C/^{12}C$ ratio evolution over time

Implication of heavy isotopes

- Biodegradation of benzene

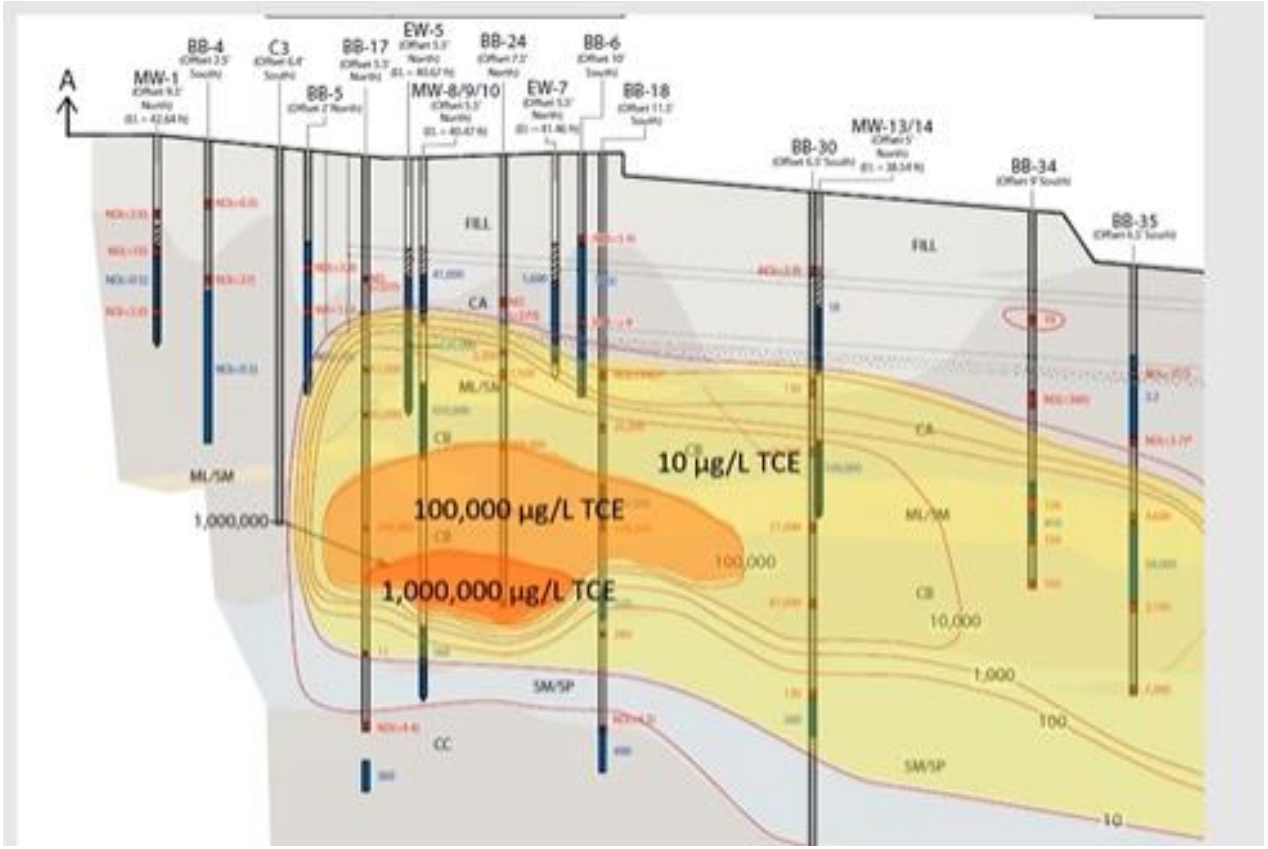




CSIA Application during In situ Remediation Treatment

Site Description

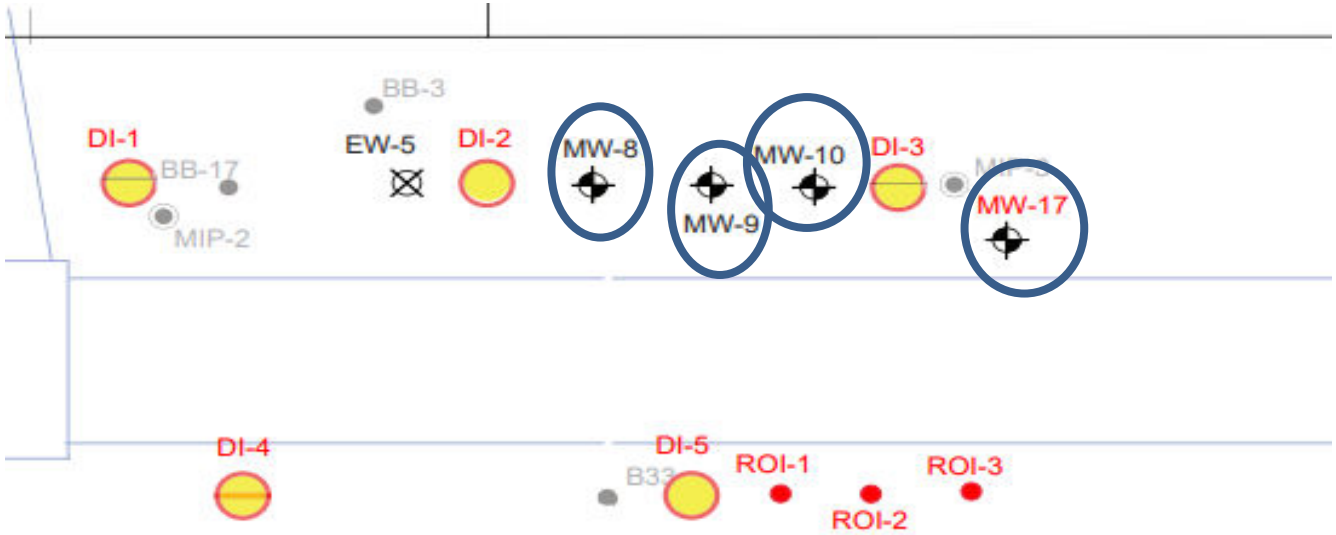
- Contaminant: TCE (source zone)
- Sandy silt layer above a sandy layer



CSIA Application during In situ Remediation Treatment

Site Description

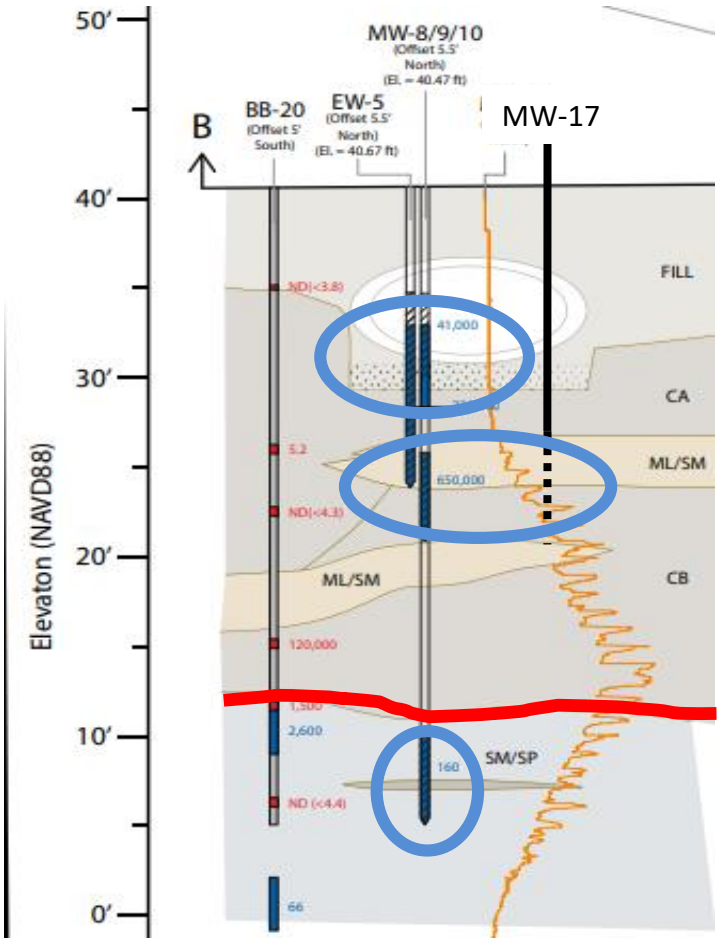
- Enhanced anaerobic biodegradation
  - EVO (EDS-ER™) + dhc (KB-1™) + ZVI
- in situ bioremediation - pilot test
  - 5 injection points
  - 2500 gallons (500 gal / point)
  - larger volume at the bottom of silt layer
  - performance monitoring
    - 4 MWs
    - baseline + 3 post injection sampling events



CSIA Application during In situ Remediation Treatment

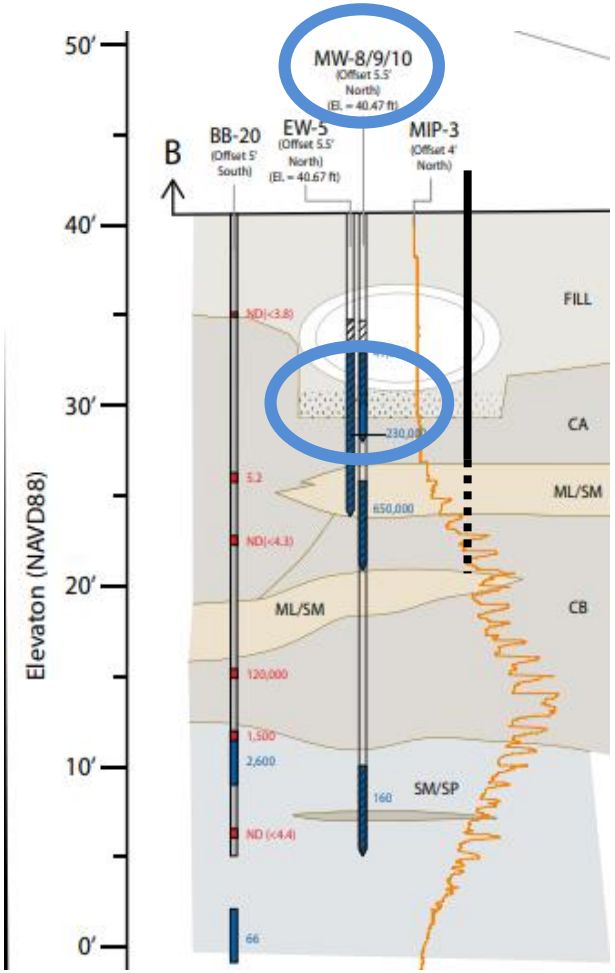
Site Description

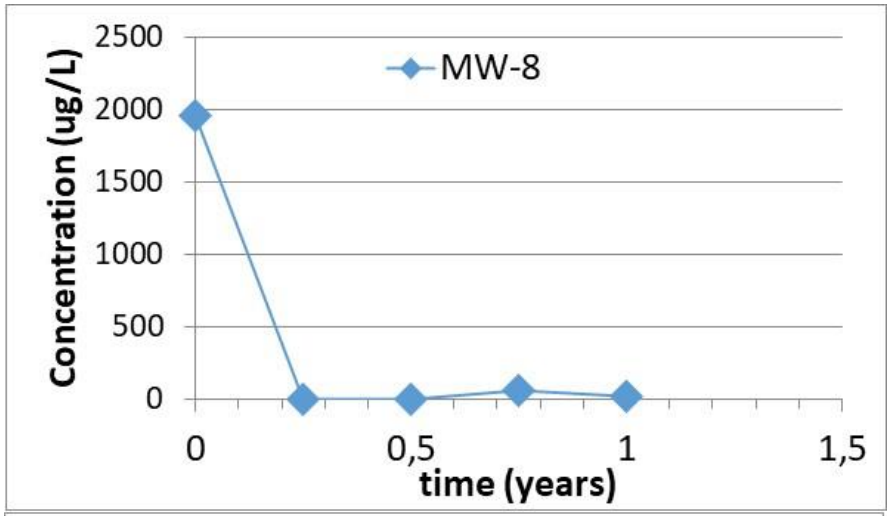
- Questions for CSIA:
  - Is the treatment occurring as intended ?
  - Dilution or degradation?
  - Was TCE pushed downward, into the sandy layer ?

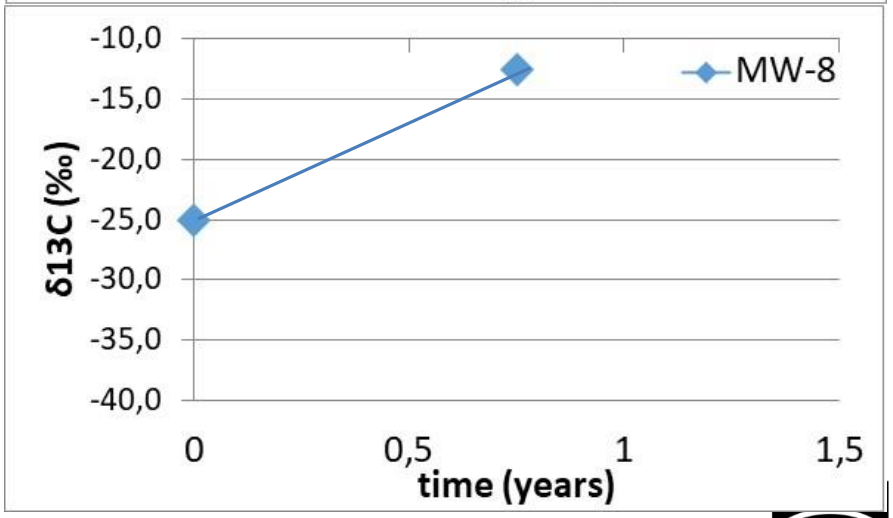


Results

CSIA Application during In situ Remediation Treatment







Results

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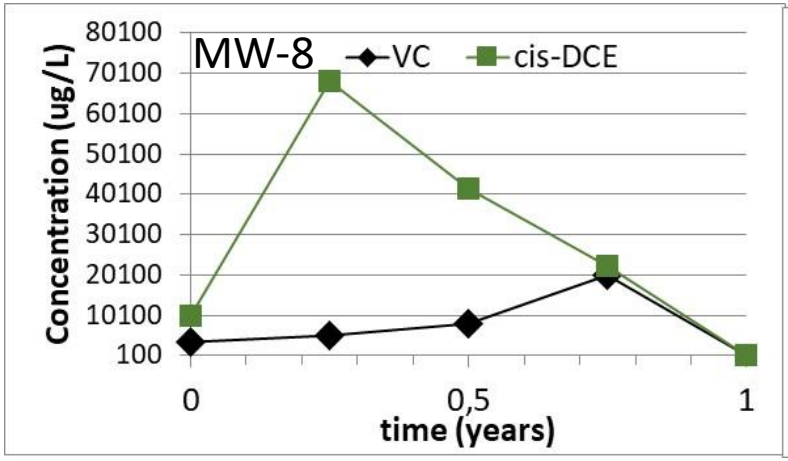

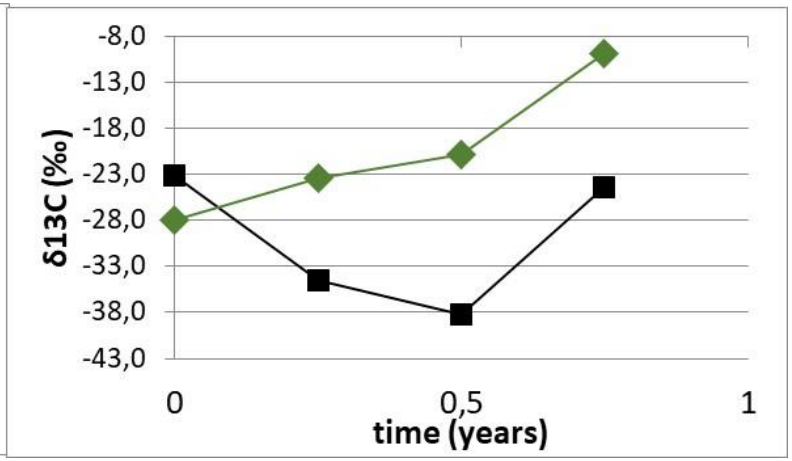

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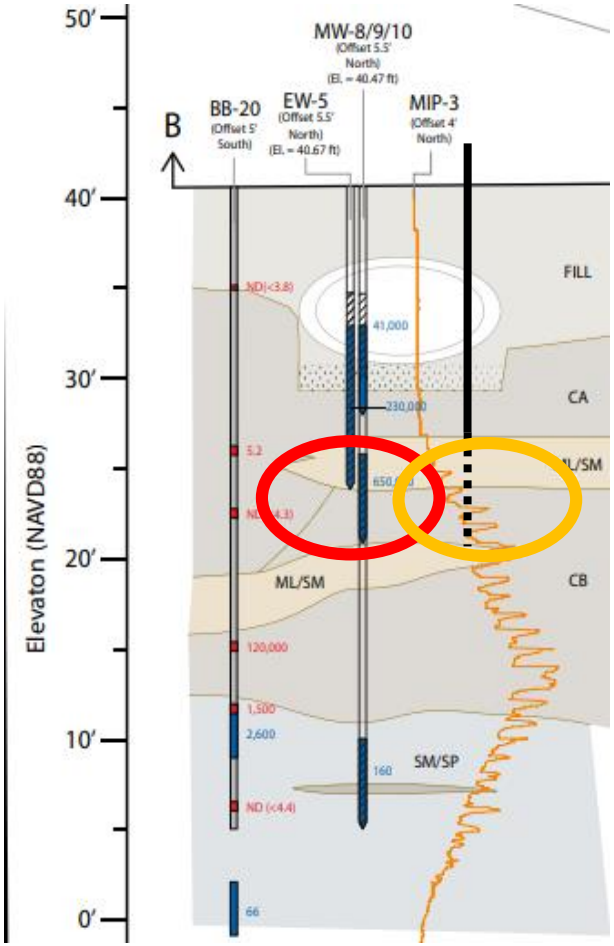
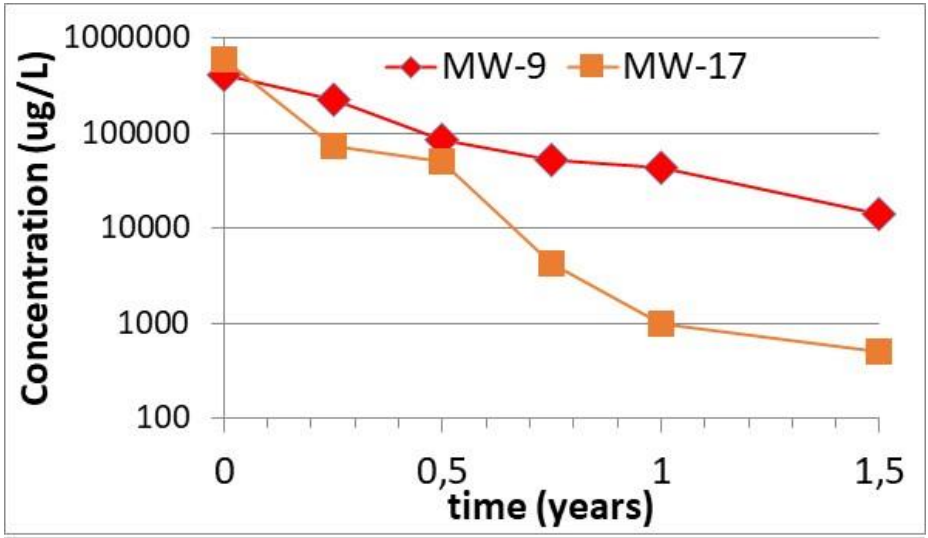
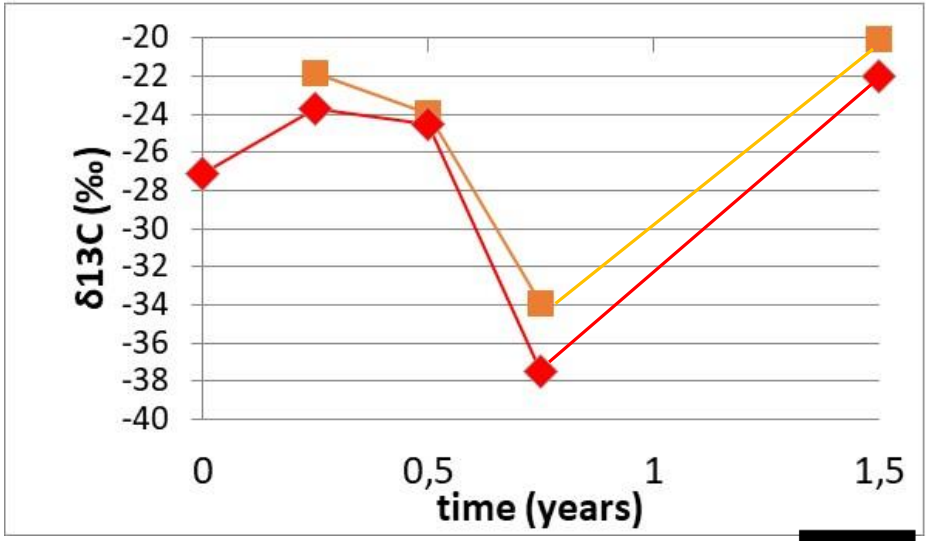


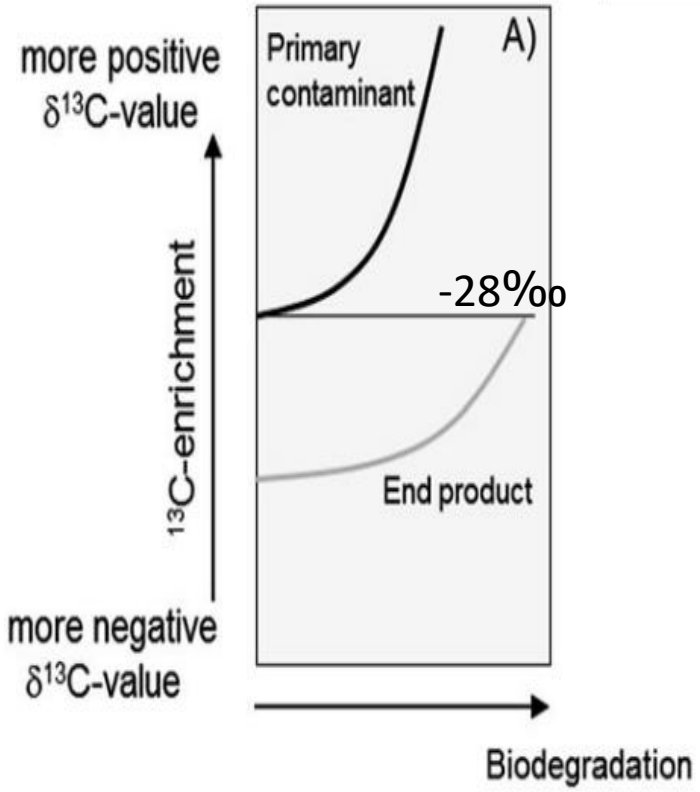




CSIA Application during In situ Remediation Treatment

Results - Isotopic balance

MW	event	TCE		cis-DCE		VC		Total $\delta^{13}C$ (‰)
		Conc (ug/L)	$\delta^{13}C$ (‰) mean	Conc (ug/L)	$\delta^{13}C$ (‰) mean	Conc (ug/L)	$\delta^{13}C$ (‰) mean	
MW-8	Baseline	1960	-25,0	10100	-28,0	3580	-23,1	-26,1
	Q 1	<1000	BDL	68200	-23,5	5210	-34,6	-24,7
	Q 2	<250	BDL	41400	-20,8	7870	-38,2	-24,8
	Q 3	57	-12,5	22200	-9,9	19900	-24,5	-18,4
	Q 4	24,5	--	118	--	19,9	--	--



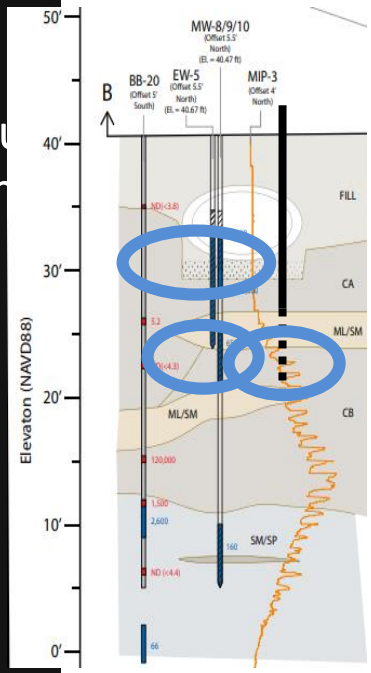
Isotopic balance : $\delta^{13}C_{sum} = x_{PCE} \cdot \delta^{13}C_{PCE} + x_{TCE} \cdot \delta^{13}C_{TCE} + x_{DCE} \cdot \delta^{13}C_{DCE} + x_{VC} \cdot \delta^{13}C_{VC}$

= > -28‰ **full dechlor**

= -28‰ **No full dechlor**

Results - Isotopic balance

CSIA Application during In situ Remediation



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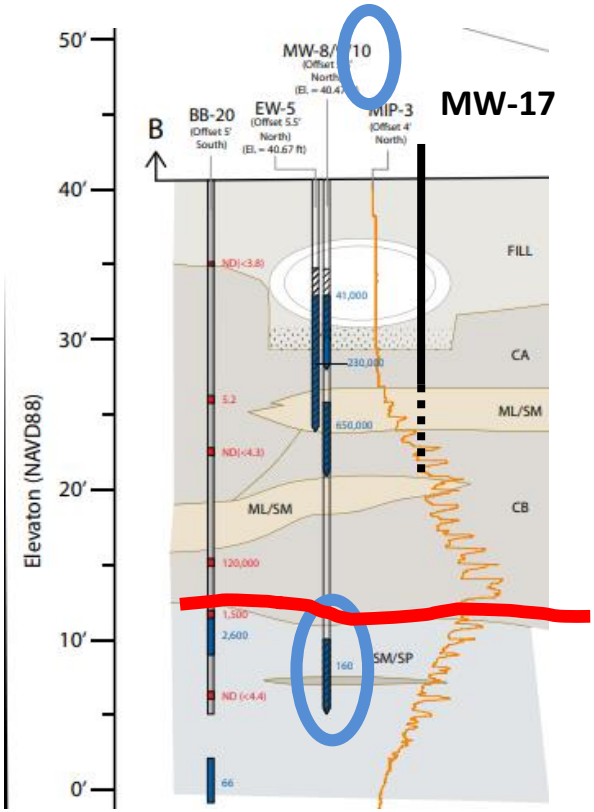
	Q 4	24,5	--	118	--	19,9	--	--
MW-9	Baseline	409000	-27,1	42700	-32,0	<5000	-26,3	-27,7
	Q 1	229000	-23,7	307000	-29,9	<2500	-16,4	-27,6
	Q 2	86700	-24,5	357000	-24,7	<5000	-37,2	-24,9
	Q 3	52100	-37,5	420000	-31,2	2690	-30,0	-31,7
	Q 4	44100	--	430000	--	7850	--	--
	Q-5	13900	-22,0	619000	-23,7	47800	-39,8	-25,4
MW-17	Baseline	598000	na	48900	na	<1000	na	--
	Q 1	74000	-21,8	561000	-25,8	2170	-27,7	-25,4
	Q 2	50500	-24,0	258000	-28,2	3660	BDL	-27,1
	Q 3	4230	-34,0	557000	-23,6	68700	-35,3	-25,5
	Q 4	<10000	--	321000	--	80800	--	--
	Q-5	<5000	-20,1	290000	-21,8	55100	-26,1	-22,8

Site 4 –Results

CSIA Application during In situ Remediation Treatment



MW	event	TCE	
		Conc (ug/L)	$\delta^{13}C$ (‰) mean
MW-10	Baseline	100	-21,4
	Q 1	14,4	-16,0
	Q 2	3,71	na
	Q 3	2,74	-11,8
	Q 4	8,74	--

Summary & conclusion

Benefits of CSIA

1. Confirms COC degradation has occurred as intended (large shift)
2. No DCE stall, but periodic VC stall
3. Supports full dechlorination occurrence (due to abiotic and biotic processes)
4. Supports the selected dosage
5. Direct push did not displace TCE downward
6. Mass degraded:
    I. Rayleigh equation – not fully respected
    II. Enrichment factor – mixt of biotic and abiotic process

Summary & conclusion

CSIA is a reliable tool to assess performance of remediation treatments

i. Gain information independently from concentration data

ii. For various in situ approaches (biological, chemical, physical)

CSIA application possibilities

i. Using 1 isotope:
   - destruction versus dilution

ii. Using 2 isotopes – to target a specific mass removal process among co-occurring mass removal process
   - Aerobic vs anaerobic biodegradation
   - Chemical oxidation vs biodegradation
   - Biodegradation vs volatilization

Summary & conclusion

To document treatment efficiency

i. Pilot scale
   i. Proof of concept
   ii. Dimensioning full scale

ii. Full scale
   i. Document the progress
   ii. Support decision to pursuit, to optimize the treatment
   iii. Provide evidences of treatment limitations have been reached
   iv. Support transitioning to next phase

Acknowledments

- Field work
  - Tyson Fulmer – CE solution
  - David Alden - Tersus Environmental
- CSIA
  - Isotope Tracer Technologies - Orfan Shouakar Stash

Thank You

ghd.com

CSIA Application during In situ Remediation Treatment

Site 4 –Results

MW	event	TCE		cis-DCE		VC		Total $\delta^{13}C$ (‰)
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	Q 1	14,4	-16,0	413	-24,6	23,7	BDL	-22,4
	Q 2	3,71	na	272	na	225	na	--
	Q 3	2,74	-11,8	118	-21,3	164	-20,8	-20,9
	Q 4	8,74	--	133	--	137	--	--

Fully dechlorination is occuring, thanks to abiotic process

Field deployment

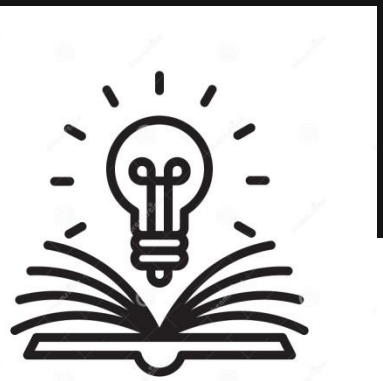
Sampling procedures

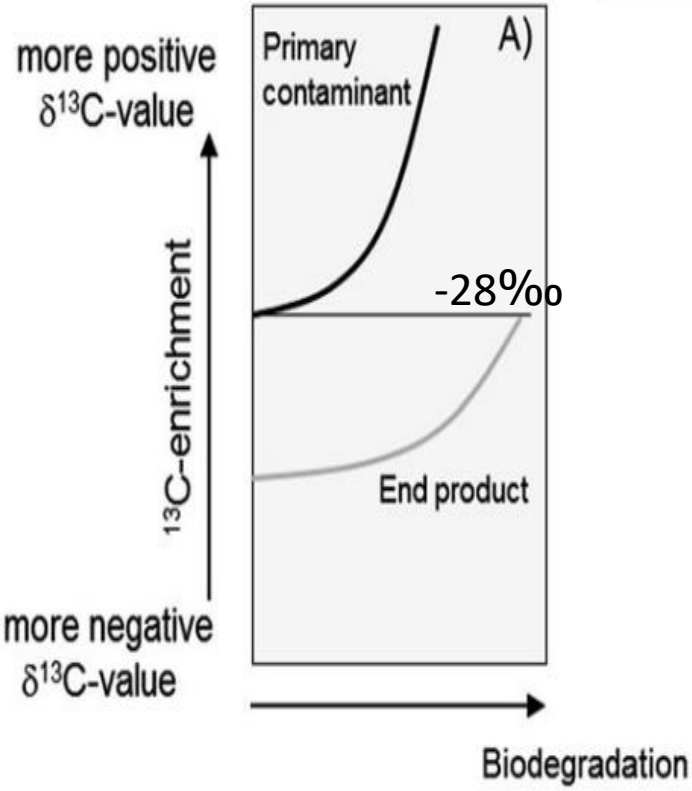
i. Groundwater Sampling
   - Similar field procedure as for VOC concentrations
   - Additional 40 ml vials
   - Preservative, shipping and storage conditions
   - Longer holding time (1-3 months)
   - Detection limits (BTEX)
     - For $\delta^{13}C$: 5-25 ug/L
     - For $\delta^{2}H$: 50-100 ug/L

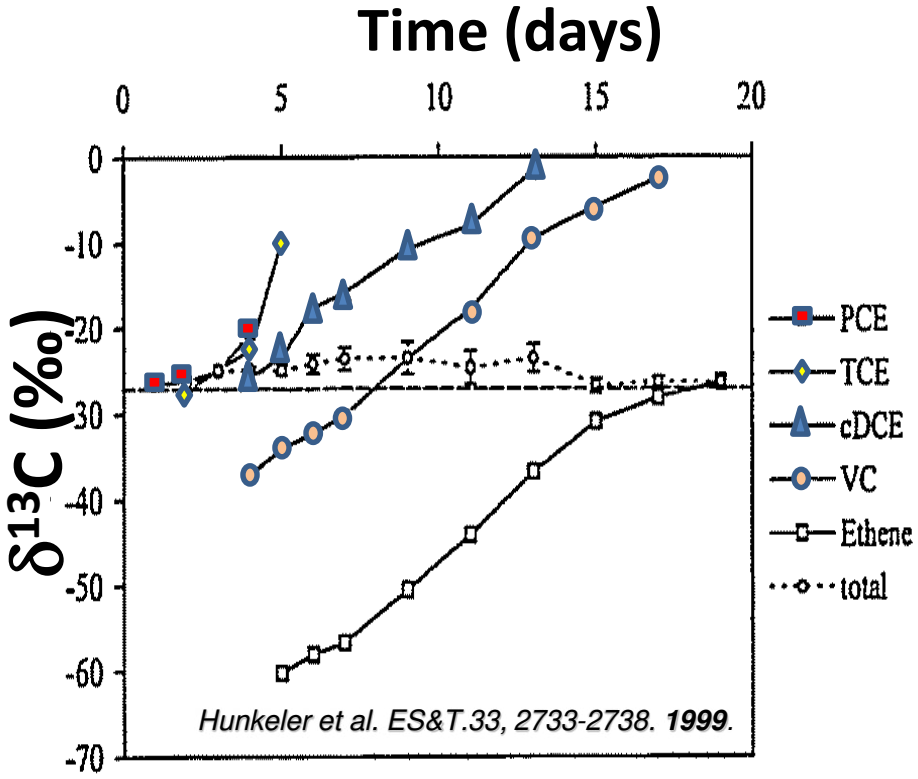
ii. Gas-phase sampling
   - Sorbant tubes
   - Solvent-based method

Costs (approx.)

- $\delta^{13}C$: 140 $ / compound
- $\delta^{2}H$: 150 $ / compound
- $\delta^{37}Cl$: 450 $ first cVOC, then 200 $ (PCE + TCE = 650$/sample)







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= > -28‰ **full dechlor**

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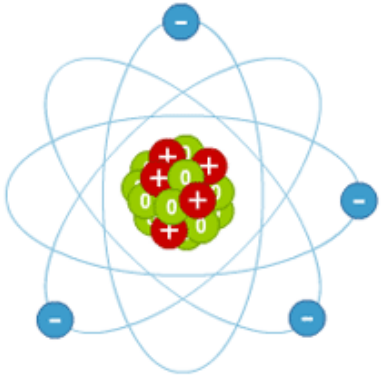
Carbon atom



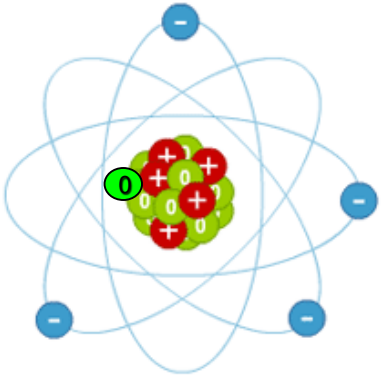
Carbone 12

Atome stable

6 neutron

6 proton

electron



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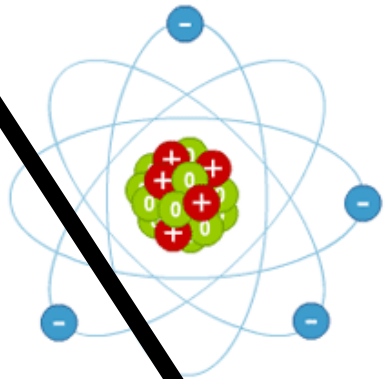

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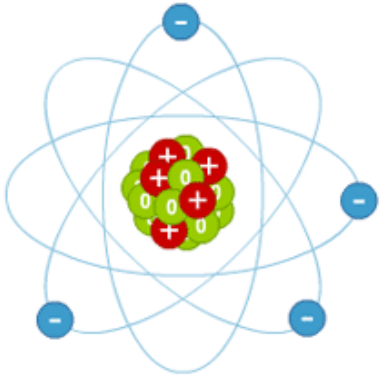

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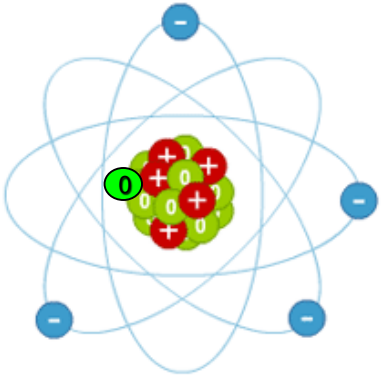

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electron

Abondance naturelle

1 : 88

^{12}C : 98,89 %

^{13}C : 1,11 %

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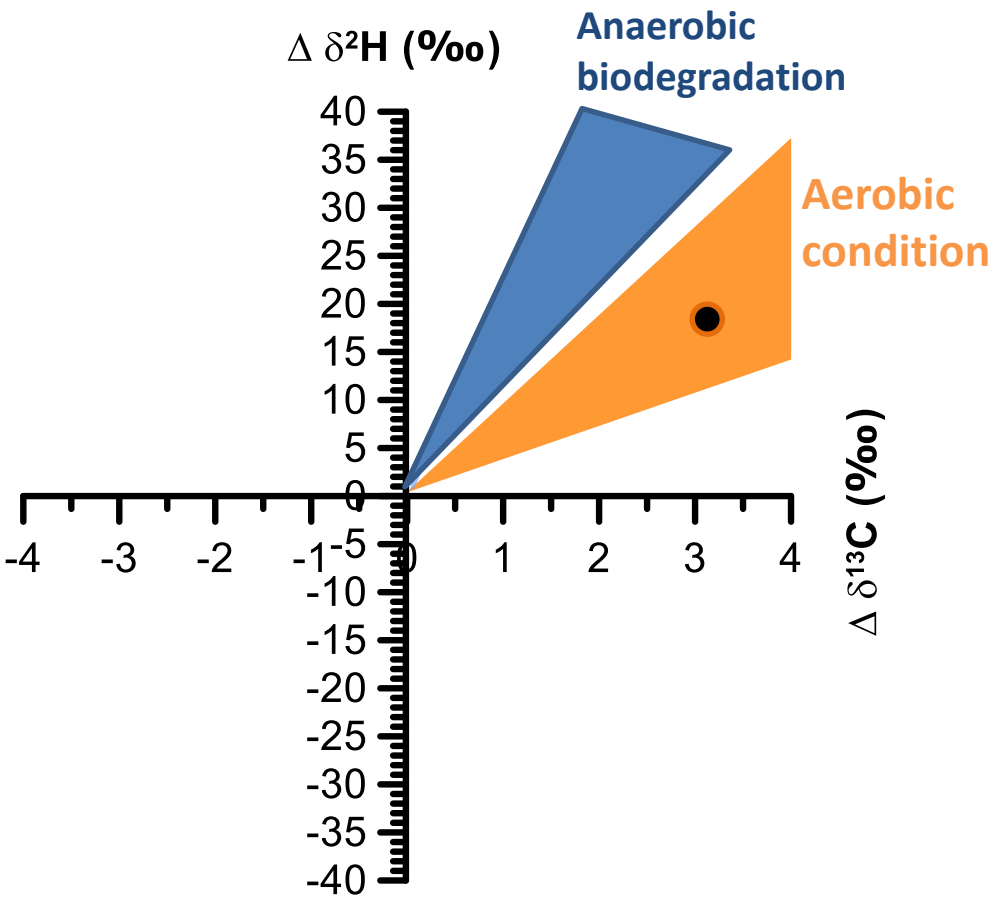
^{1}H: 99,985 % **^{35}Cl: 75,7 %**

^{2}H : 0,0155 % **^{37}Cl : 24,3 %**

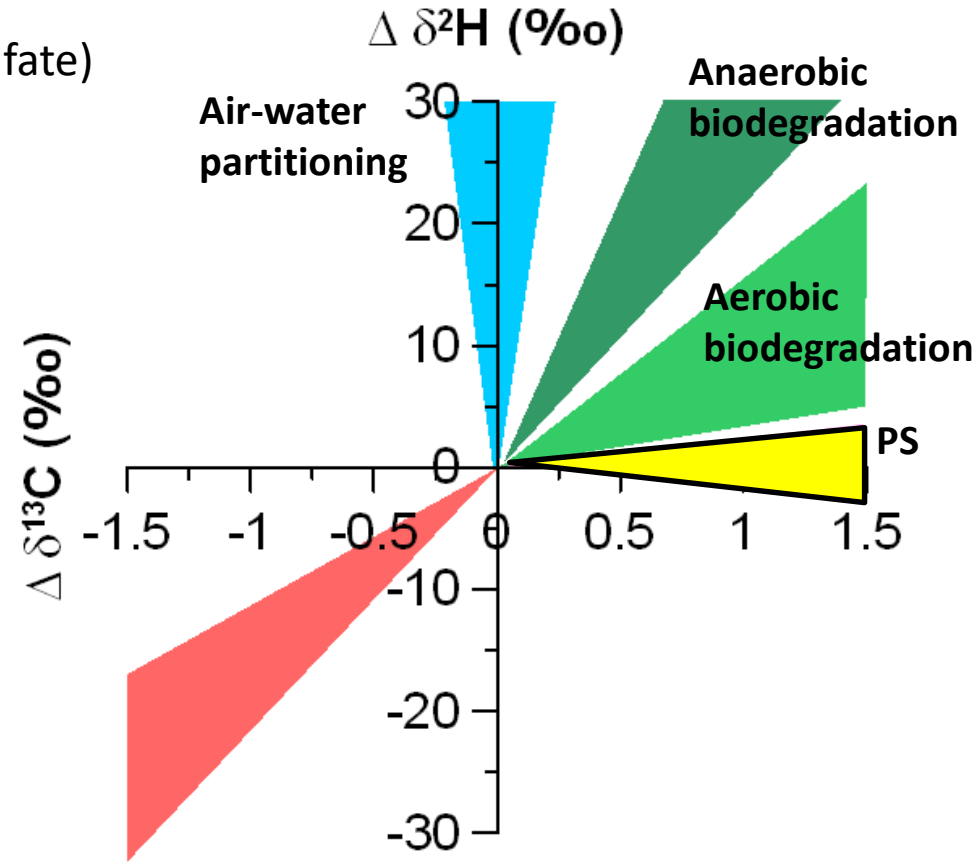
Implication of heavy isotopes

- Biodegradation of benzene
- Different enrichment pattern
  - Aerobic
  - Anaerobic



Implication of heavy isotopes

- Biodegradation of benzene
- Different enrichment pattern
  - Aerobic
  - Anaerobic
  - ISCO (unact Persulfate)
  - Air-NAPL parti
  - Air-Water parti



Introduction

Concept

Dual isotope plot concept: to distinguish destructive and non-destructive processes

How to plot field results:

- Calculate Δ (‰) for C and H
- δ Sample - $\delta^{13}C$ Source
- $(\Delta\ \delta^{13}C, \Delta\ \delta^{2}H) = (1.5\ ,\ 20\ )$