New Application of CSIA in Organic Contaminant Studies in Groundwater

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Talk Outline

- Introduction to environmental isotopes

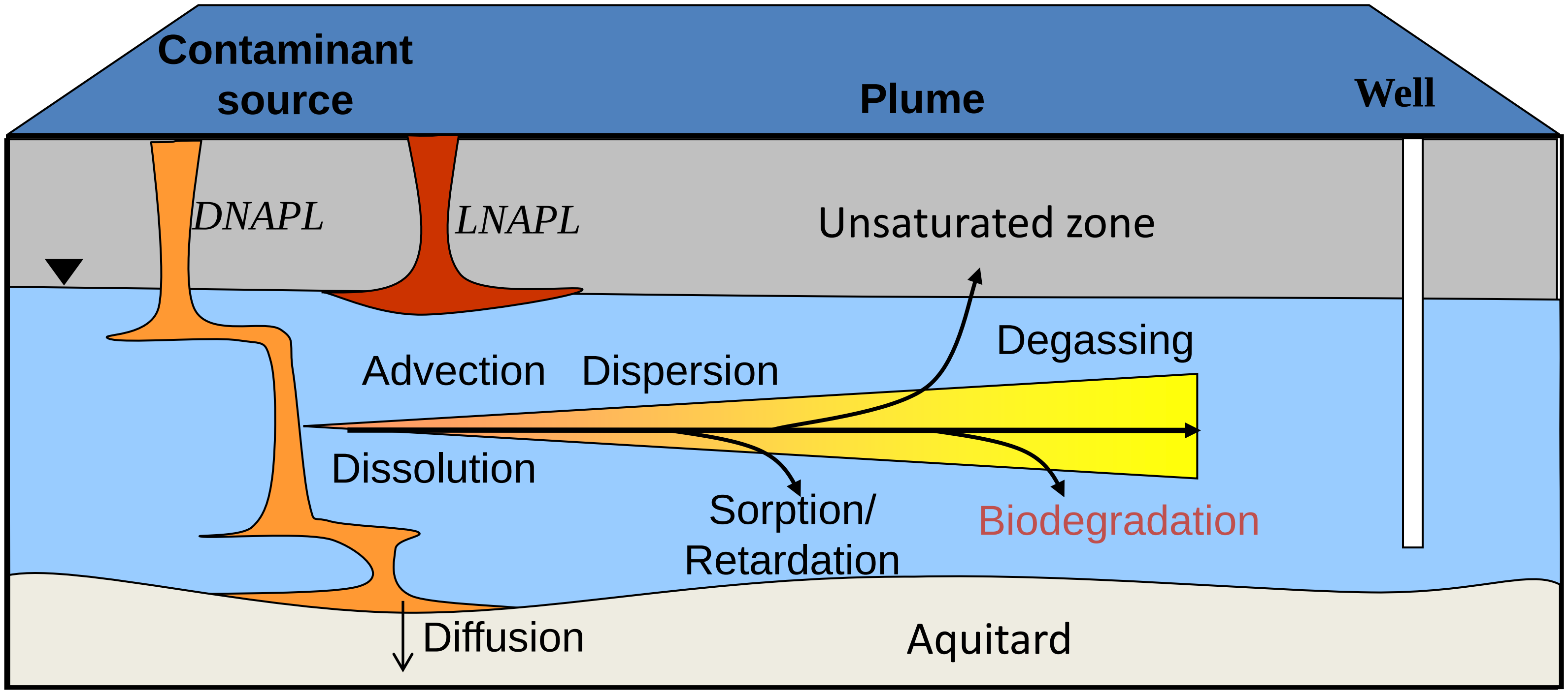
- Application of CSIA in unsaturated studies

  - implications for vapor intrusion studies

- Application of CSIA in studies of low permeability sediments

  - implications for long term persistence of contaminants plumes on sites where the source has been remediated

Processes that Control Contaminant Concentration in Groundwater



Natural Abundance of Stable Isotopes

Isotope	*Ratio*	*% natural abundance*	*Reference*
^{2}H	$^{2}H/^{1}H$	**0.015**	VSMOW
^{3}He	$^{3}He/^{4}He$	**0.000138**	Atmospheric He
^{13}C	$^{13}C/^{12}C$	**1.11**	VPDB
^{15}N	$^{15}N/^{14}N$	**0.366**	AIR N_2
^{18}O	$^{18}O/^{16}O$	**0.204**	VSMOW
^{34}S	$^{34}S/^{32}S$	**4.21**	CDT
^{37}Cl	$^{37}Cl/^{35}Cl$	**24.23**	SMOC

Reporting isotope ratios
The δ-notation

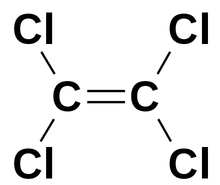
$$\delta^{13}\mathbf{C} = \left(\frac{^{13}\mathbf{C}/^{12}\mathbf{C}_{\mathbf{Sample}}}{^{13}\mathbf{C}/^{12}\mathbf{C}_{\mathbf{Standard}}} - 1 \right) \cdot 1000 \quad \textbf{(‰ VPDB)}$$

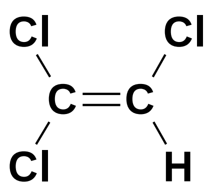
Example: Average carbon isotope ratio of natural compounds

	$^{13}C/^{12}C$	$\delta^{13}C$	
Carbonates	**0.01124**	**0**	
CO_2 of atmosphere	**0.01116**	**-7**	**more**
Biomass	**0.01096**	**-25**	**^{13}C**
Biogenic methane	**0.01045**	**-70**	

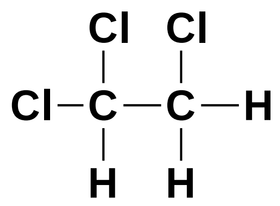
Main Organic Contaminants found in Groundwater

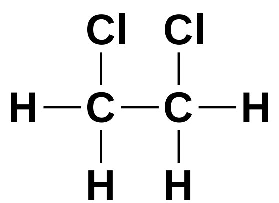
Chlorinated Ethene



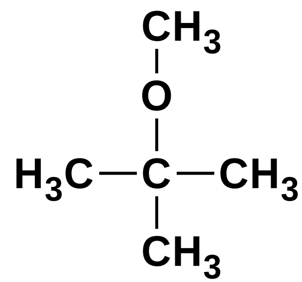


Chlorinated Ethane

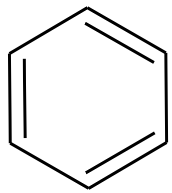


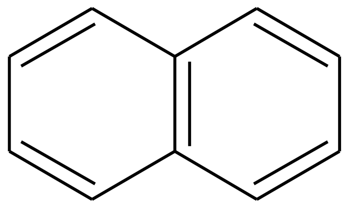


MTBE



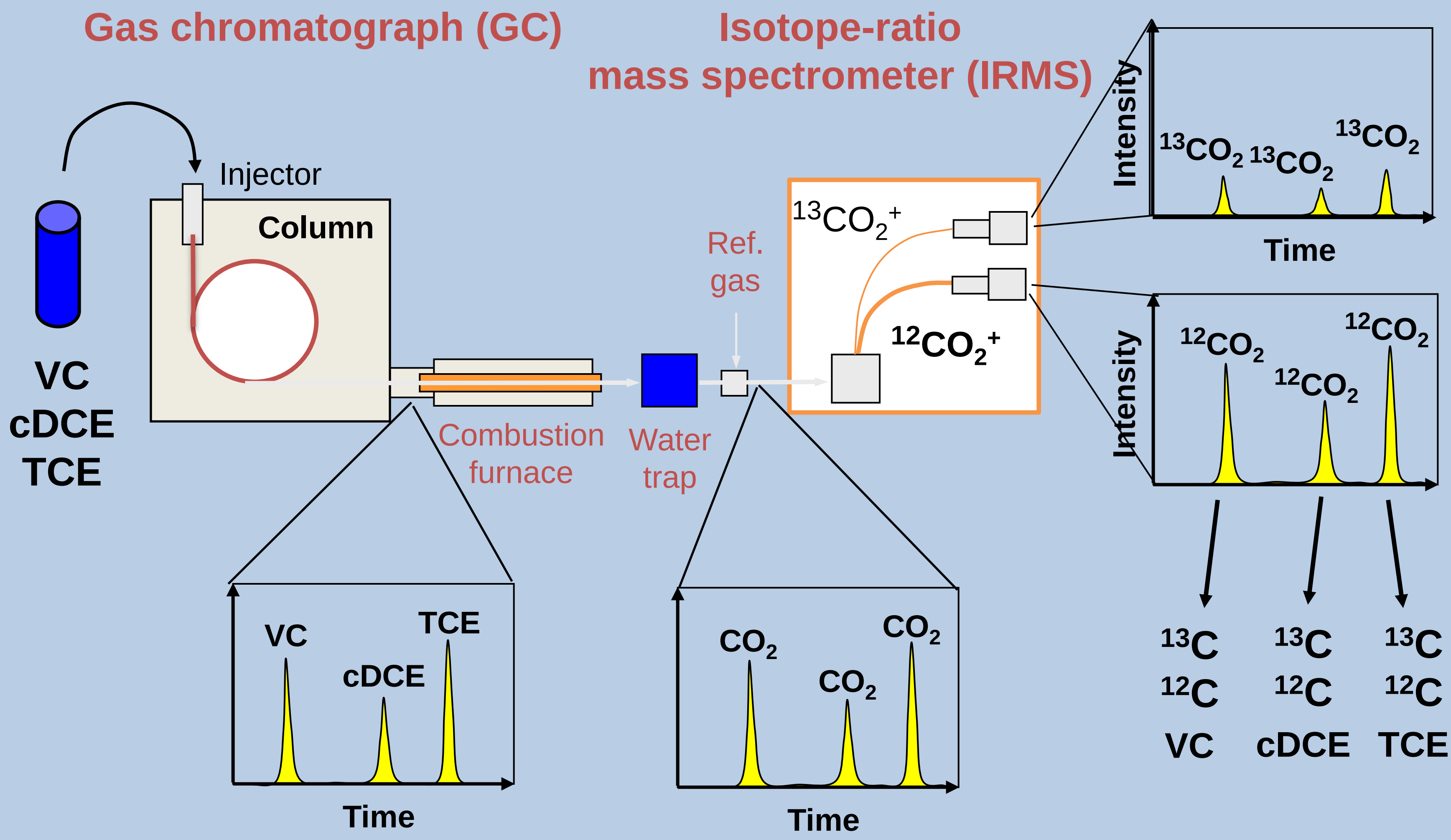
Benzene and Naphthalene



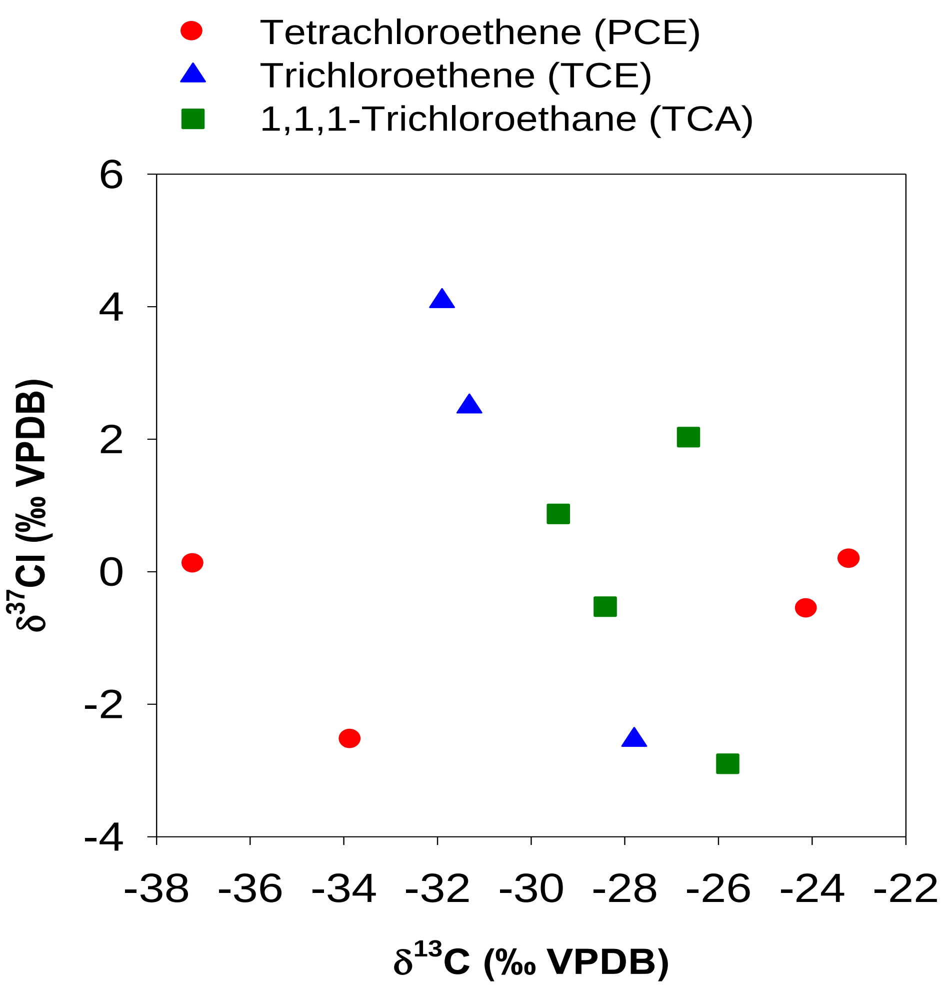


Isotope: $^{13}C/^{12}C$, D/H, $^{37}Cl/^{35}Cl$

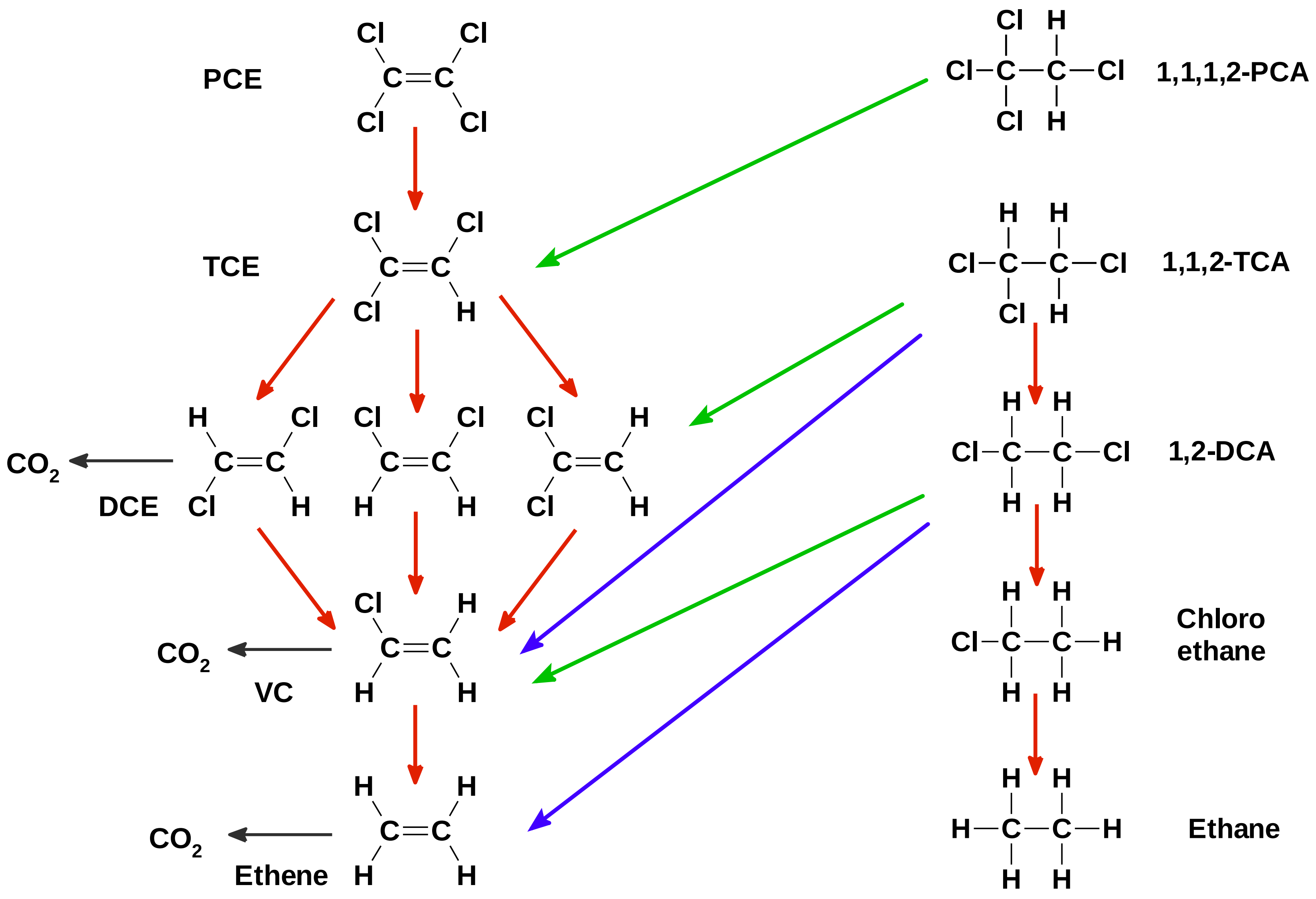
Determination of compound-specific isotope ratios by GC-IRMS Example: Carbon isotopes $^{13}C/^{12}C$



Chlorinated Solvents from Different Manufacturers



Degradation of chlorinated hydrocarbons under anaerobic conditions

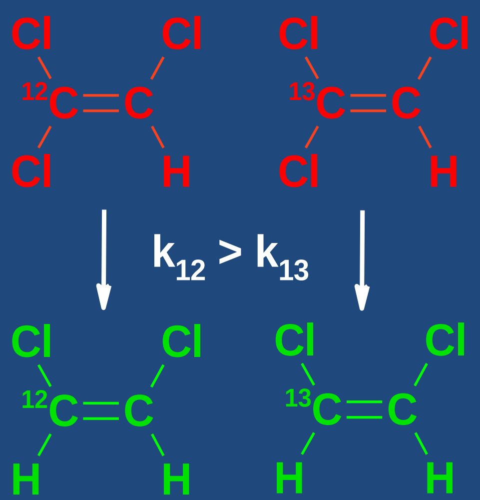


Use of isotopes to evaluate biodegradation of organic contaminants

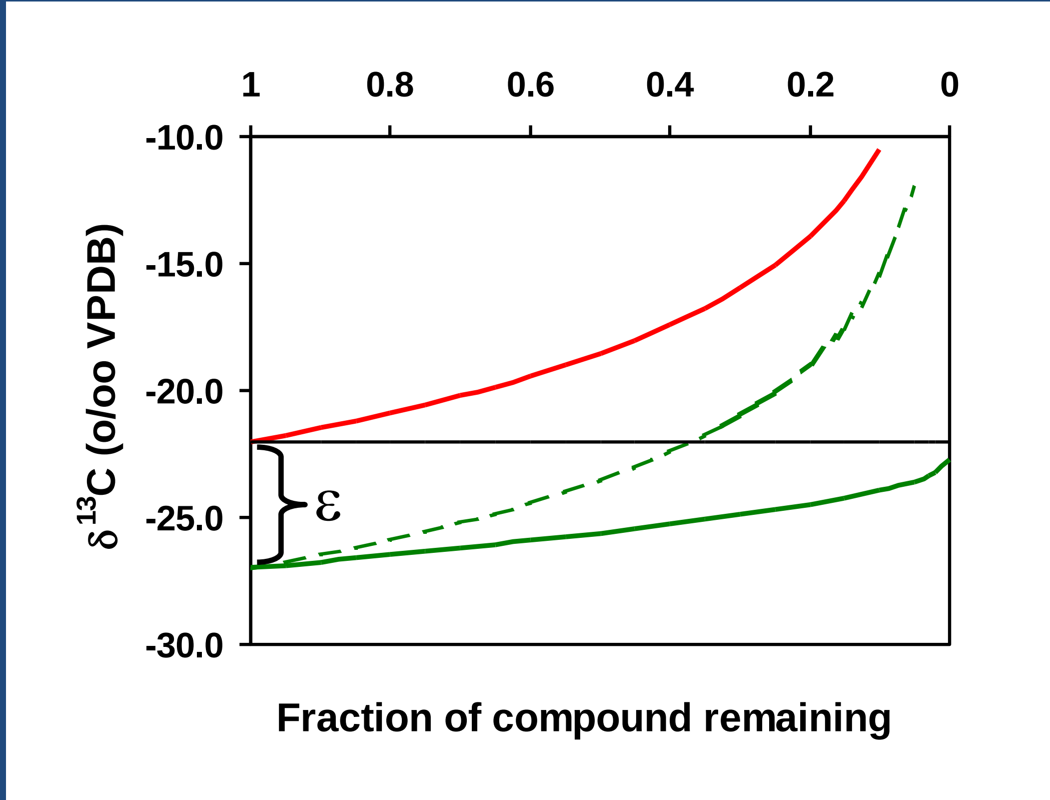
- Laboratory studies
  - Isotope pattern of substrate and product during biodegradation
  - Quantification of magnitude of isotope fractionation
  - Isotope fractionation during biodegradation of BTEX, MTBE and other petroleum hydrocarbons
  - Isotope fractionation during biodegradation of chlorinated hydrocarbons
- Field studies
  - Evaluation of biodegradation at sites contaminated with petroleum hydrocarbons and chlorinated hydrocarbons
- Approaches to evaluate isotope data

Isotope fractionation: Occurrence and magnitude

TCE



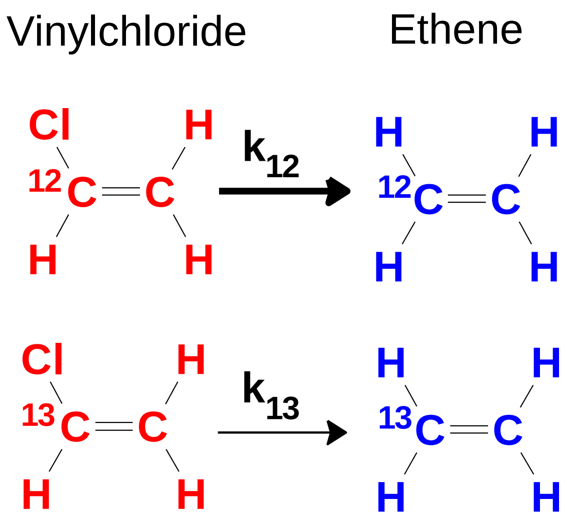
cis-1,2-DCE

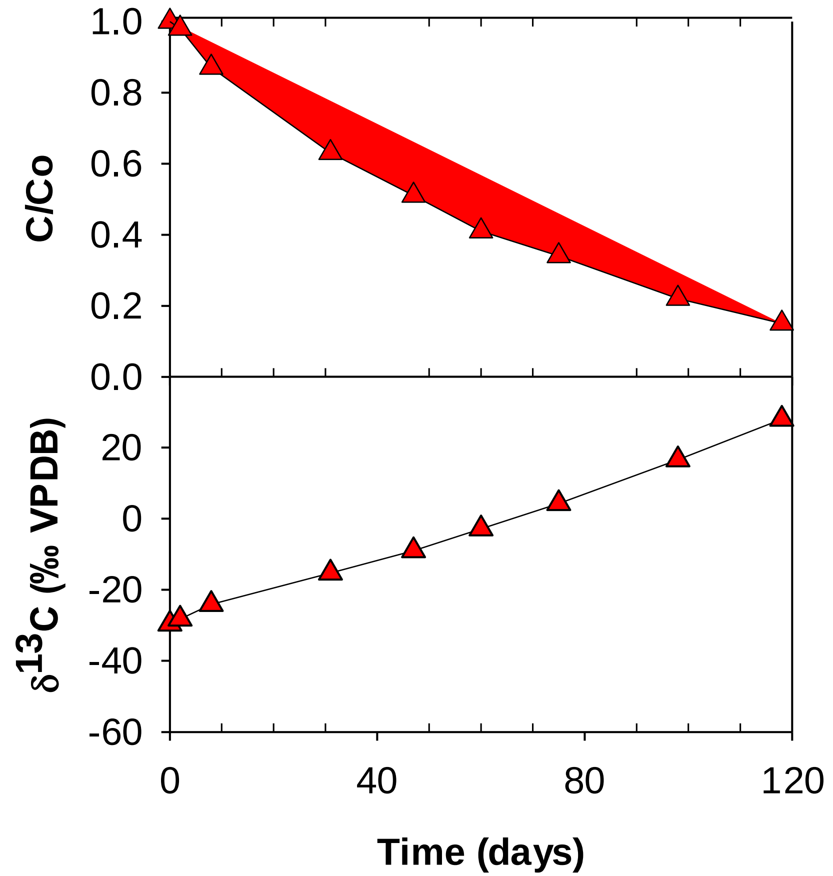


$$\delta - \delta_o \cong 10^3\,(\alpha - 1) \cdot \ln f$$

$$\text{or}\quad \delta - \delta_o \cong \varepsilon \cdot \ln f$$

Carbon isotope fractionation during reductive dechlorination of VC to ethene

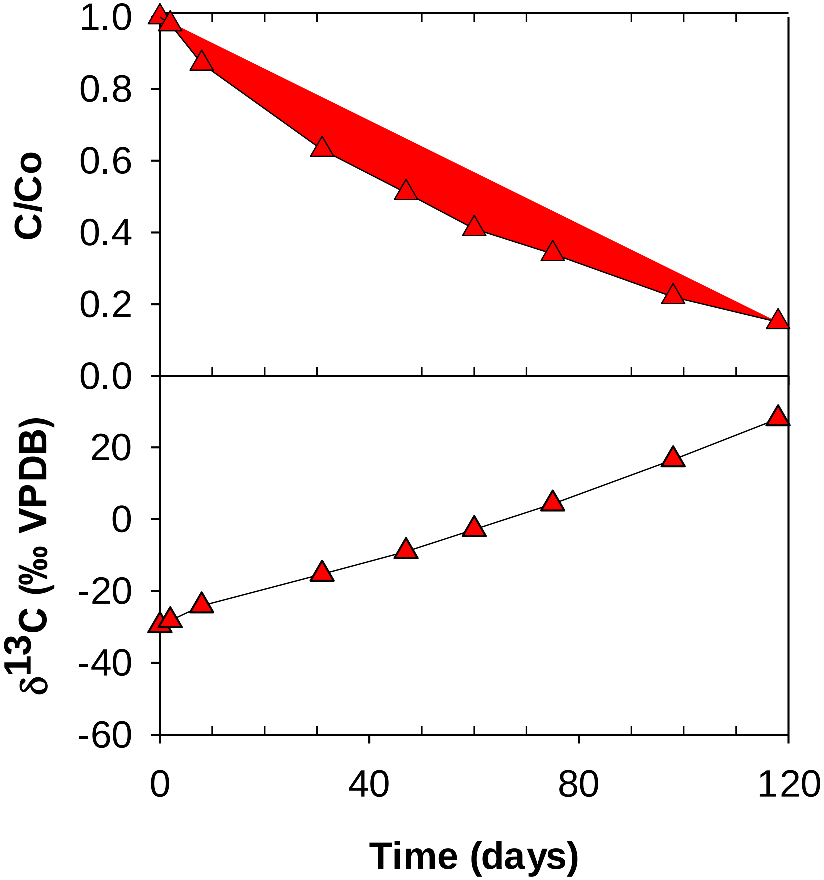


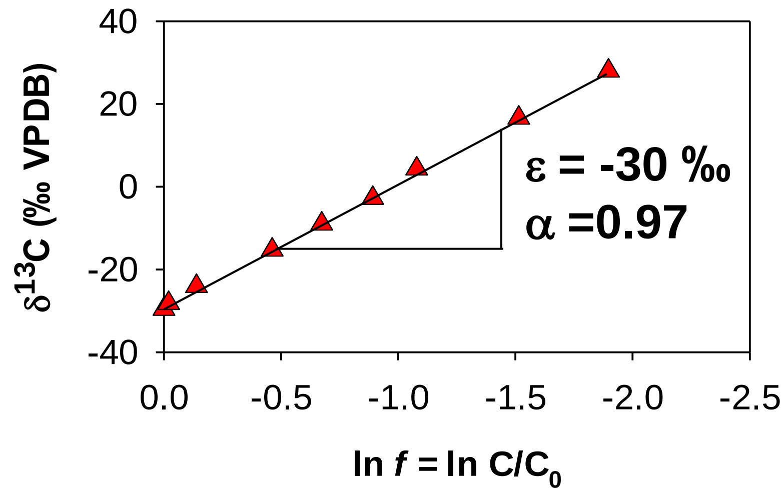


Bonds to light isotopes are weaker and thus break faster
-> Difference in reaction rates
= Kinetic isotope effect (KIE)

Ref: Hunkeler, D., Aravena, R., Cox. E., 2002.
Environmental Science and Technology, 36, 3378-3384.

Quantification of isotope fractionation



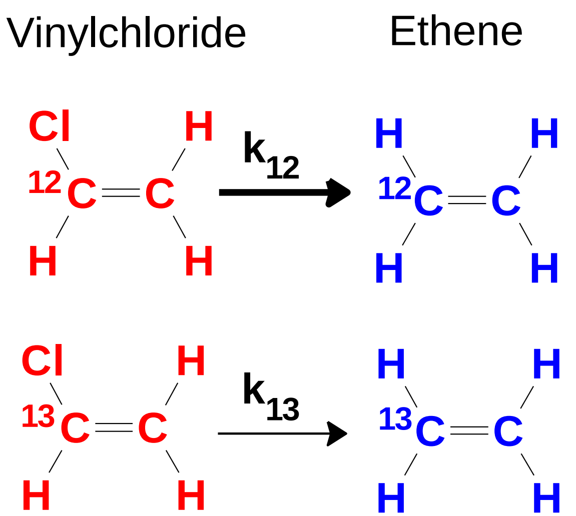


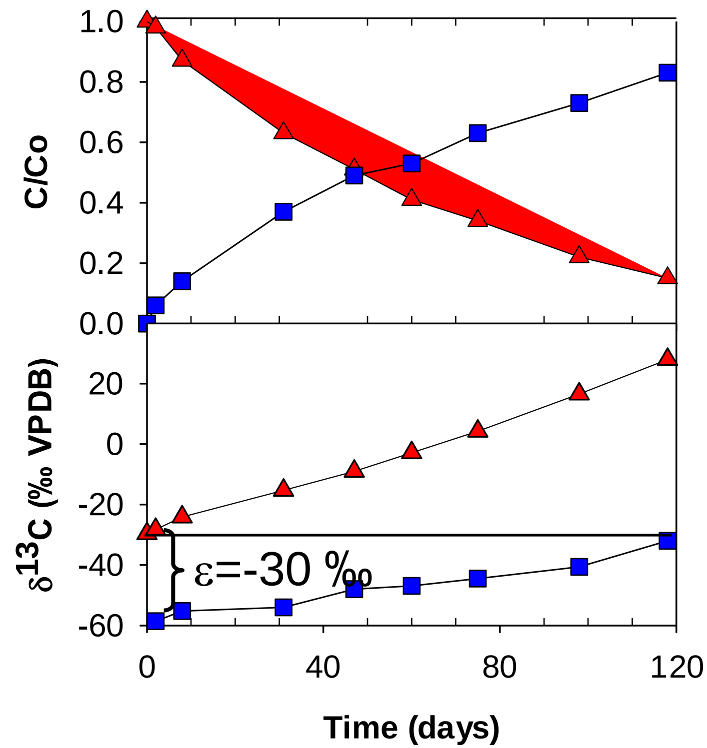
Rayleigh equation:
simplified and in ‰-notation

$$\delta^{13}C = \delta^{13}C_0 + \varepsilon \cdot \ln\frac{C}{C_0}$$

$\delta^{13}C$	isotope ratio of compound (‰)
$\delta^{13}C_0$	initial isotope ratio of compound (‰)
ε	**isotopic enrichment factor (‰)** (measure of strength of isotope fractionation)

Isotope evolution of product





Ref: Hunkeler, D., Aravena, R., Cox. E., 2002.
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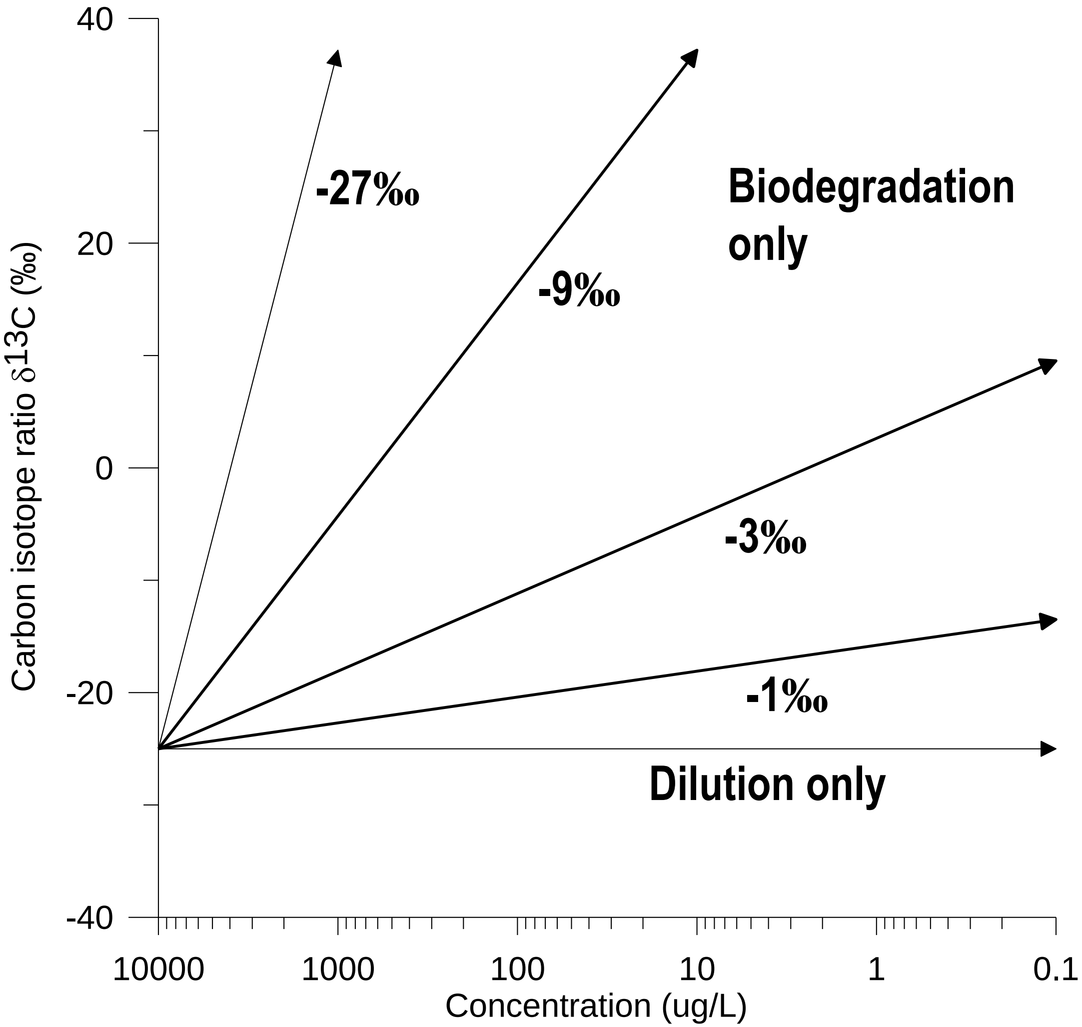
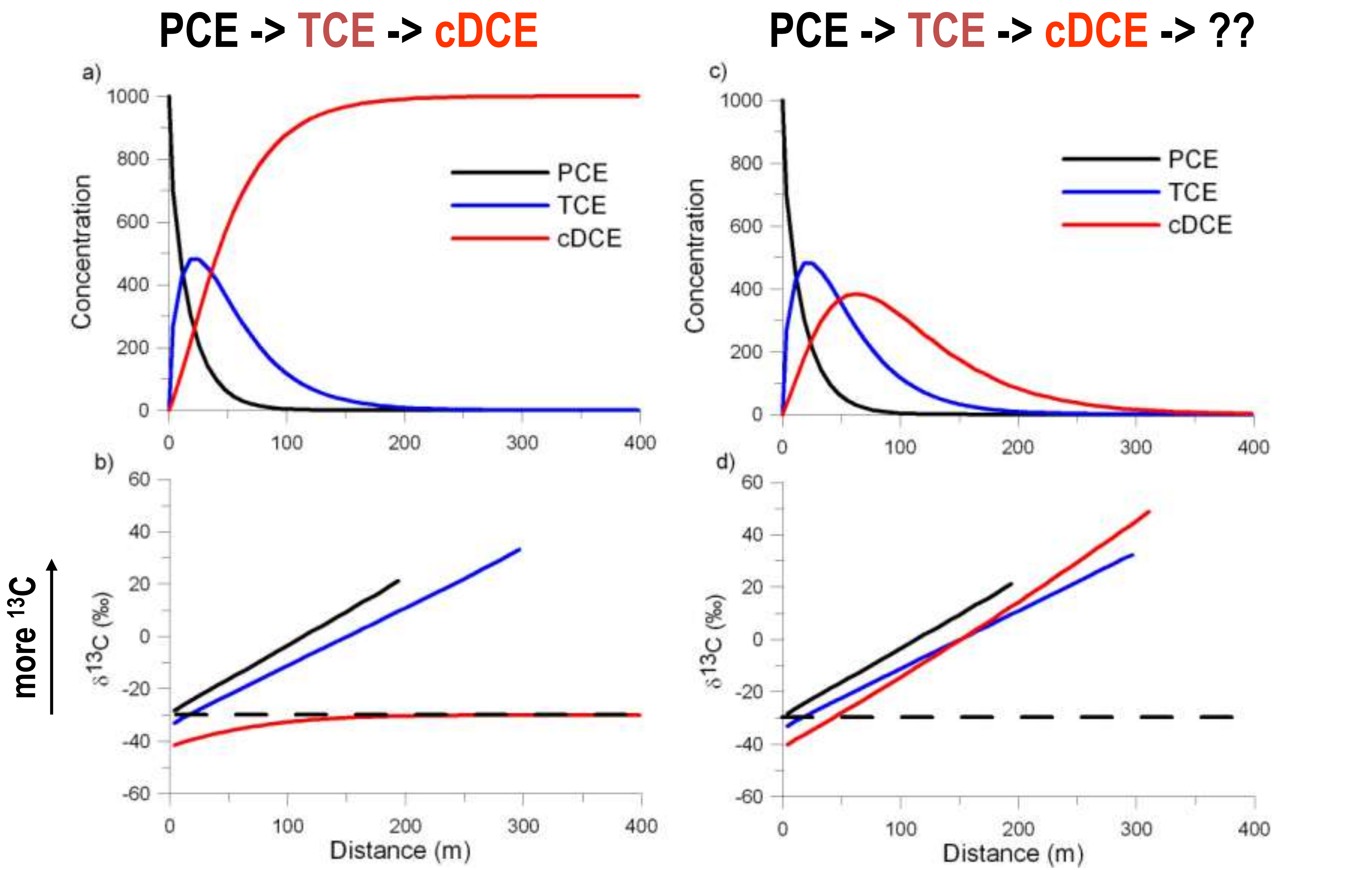
Expected isotope evolution



$$\Delta\delta^{13}C = \varepsilon \cdot \ln f$$
$$= 2.3 \cdot \varepsilon \cdot \ln f$$

Expected isotope evolution



Basic premises in saturated zone applications

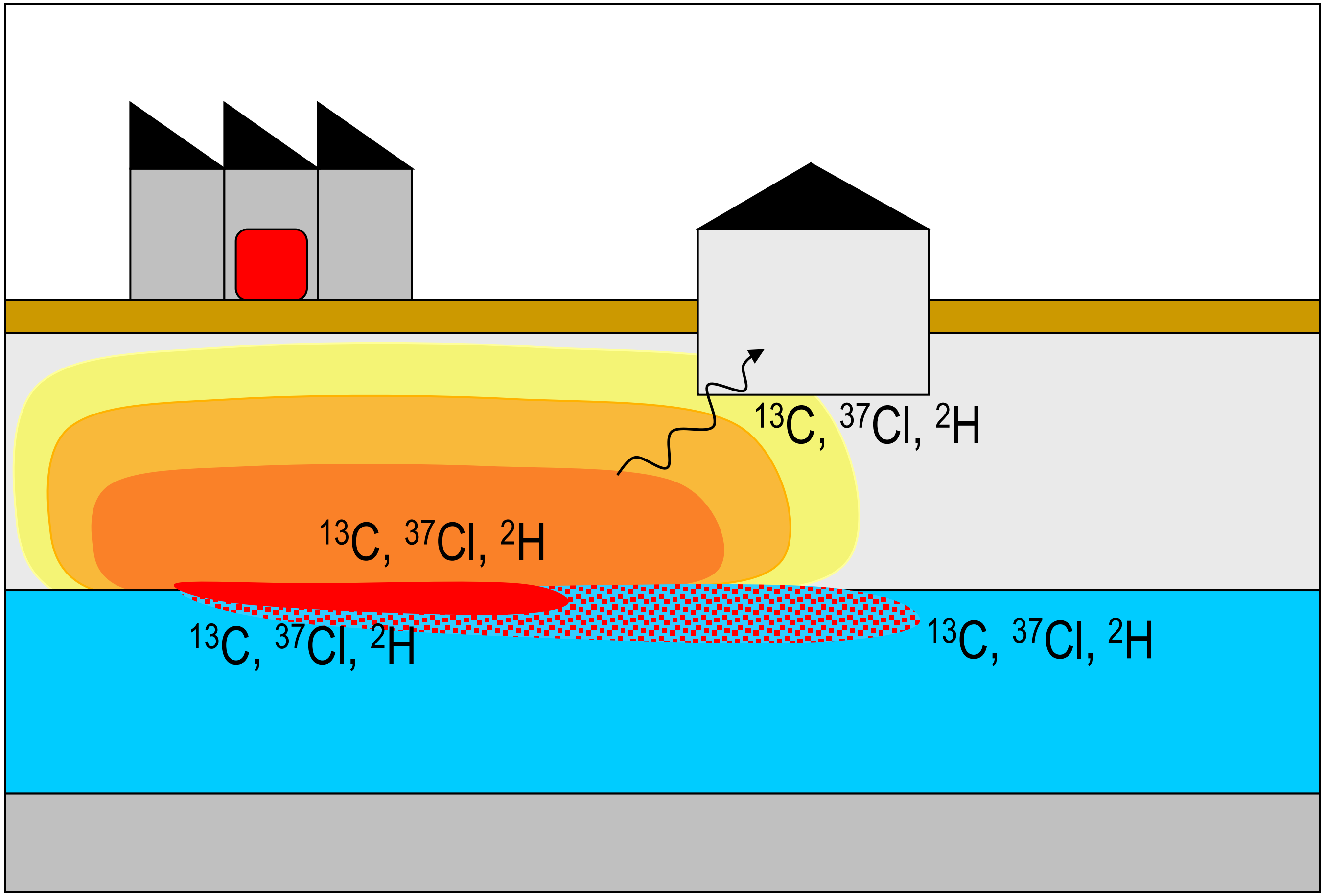
- Physical processes (dissolution, advective-dispersive transport, sorption) do not significantly alter stable isotope ratios

- Reactive processes are associated with detectable and reproducible isotope fractionation

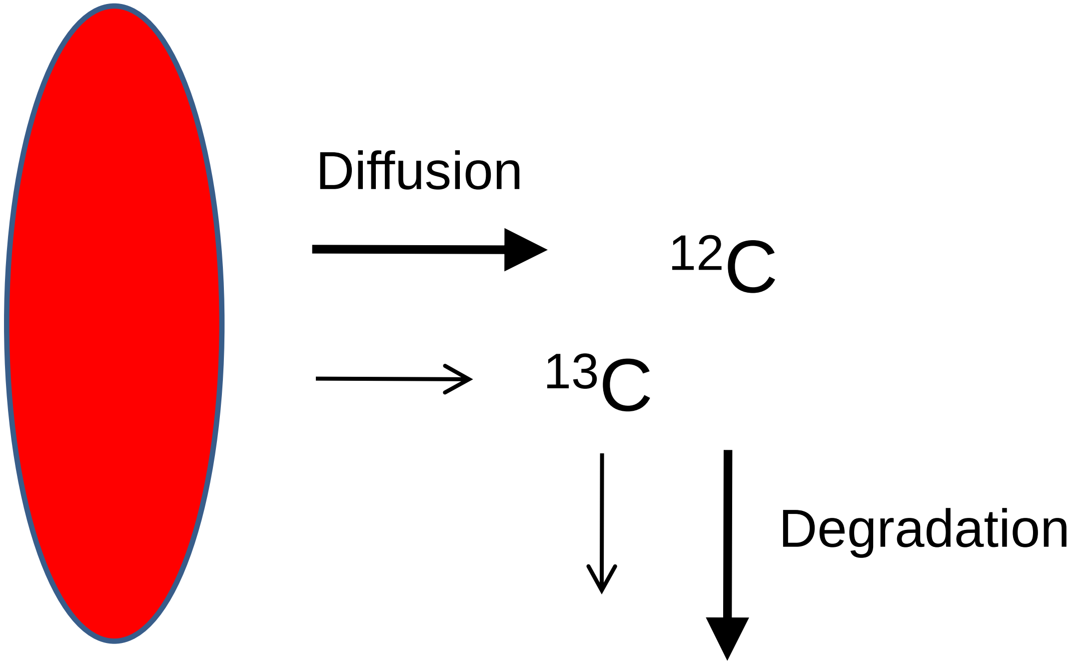
-> Application for source fingerprinting and tracking biodegradation

Do these conclusions also apply in unsaturated zone studies when considering vapor migration?

CSIA in Unsaturated Zone Studies

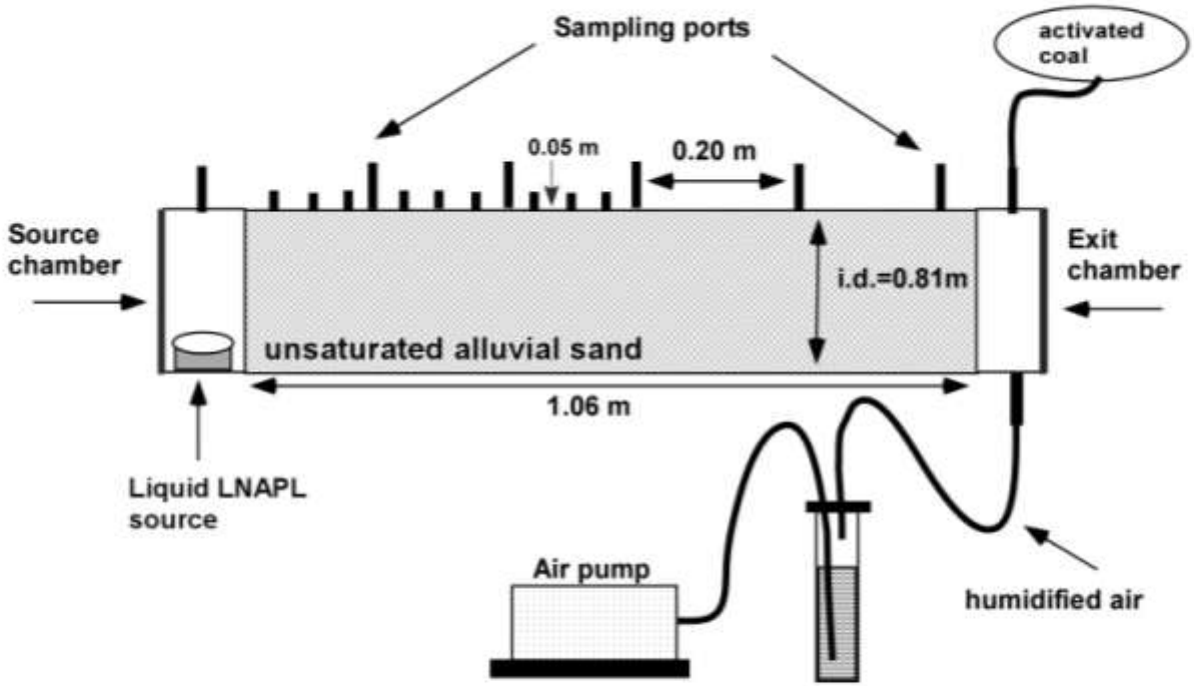


Interaction biodegradation and diffusion

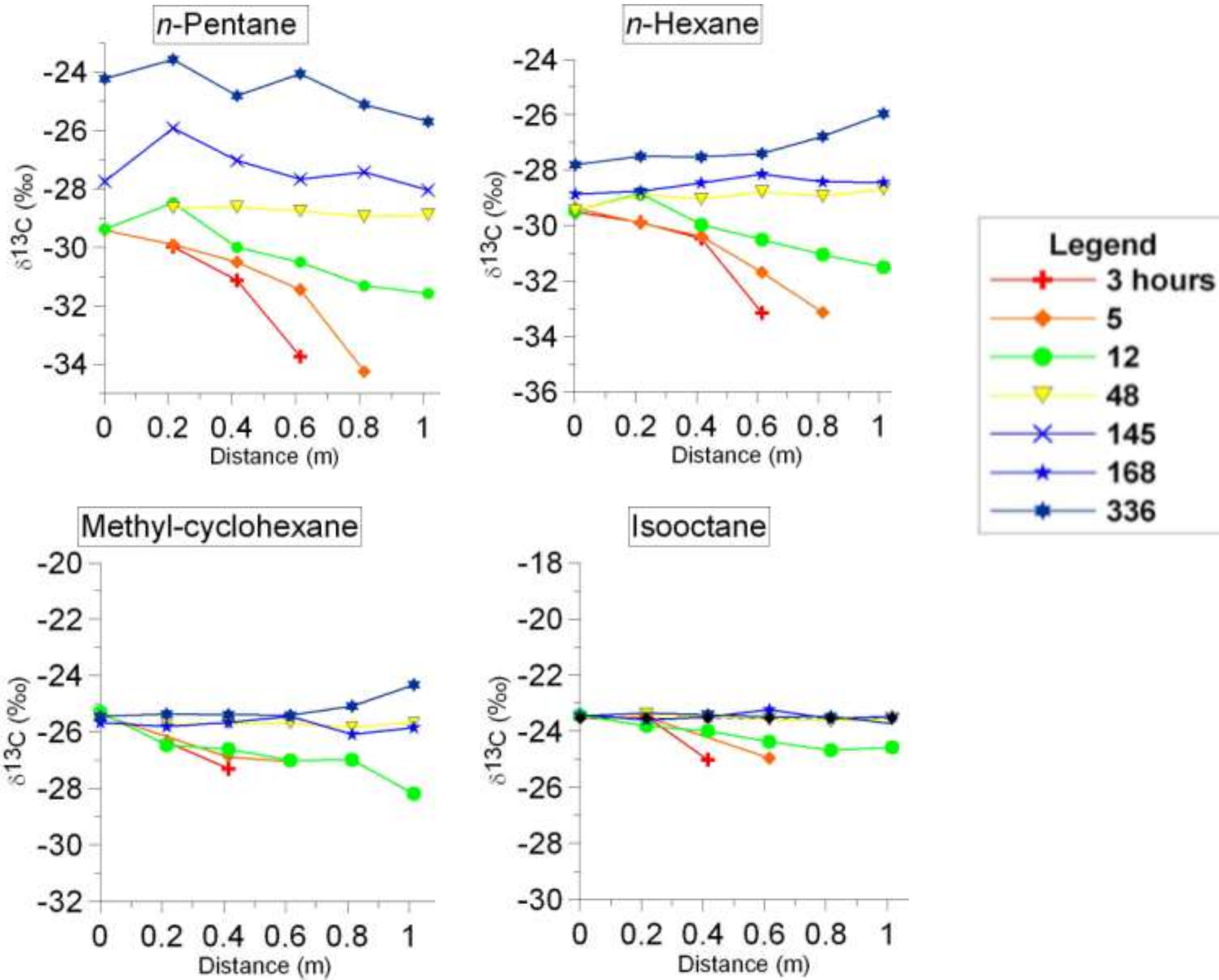


Column experiment

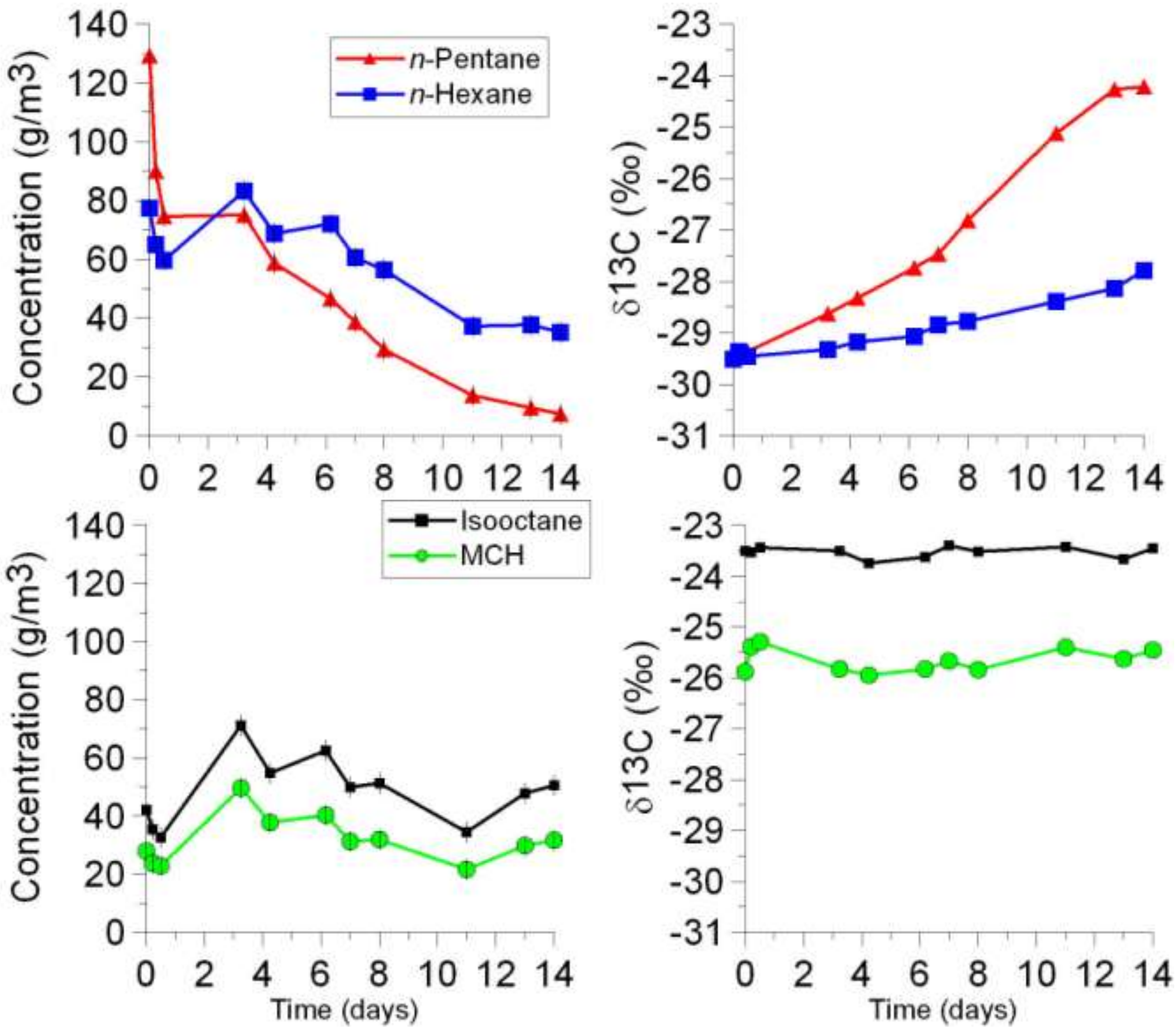
- Experimental set up
  - Alluvial sand
  - Source of 10 VOCs



Carbon isotope ratios in column



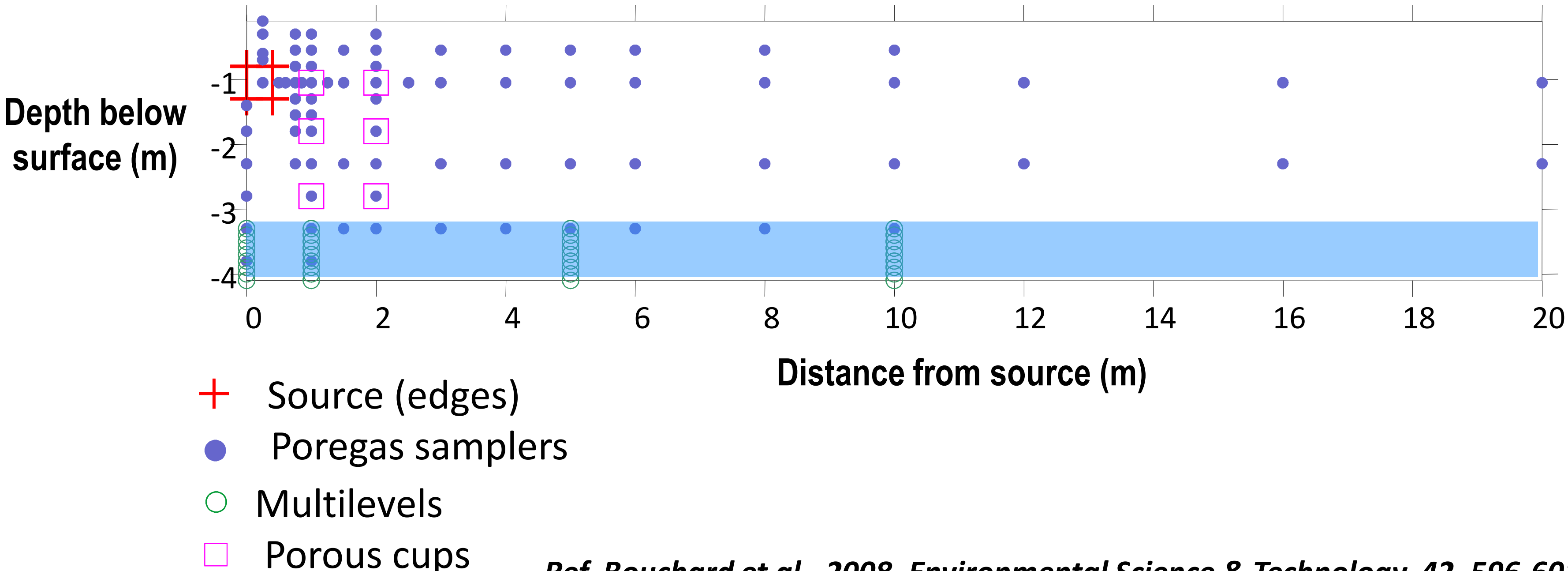
Isotope evolution at source



Field site location

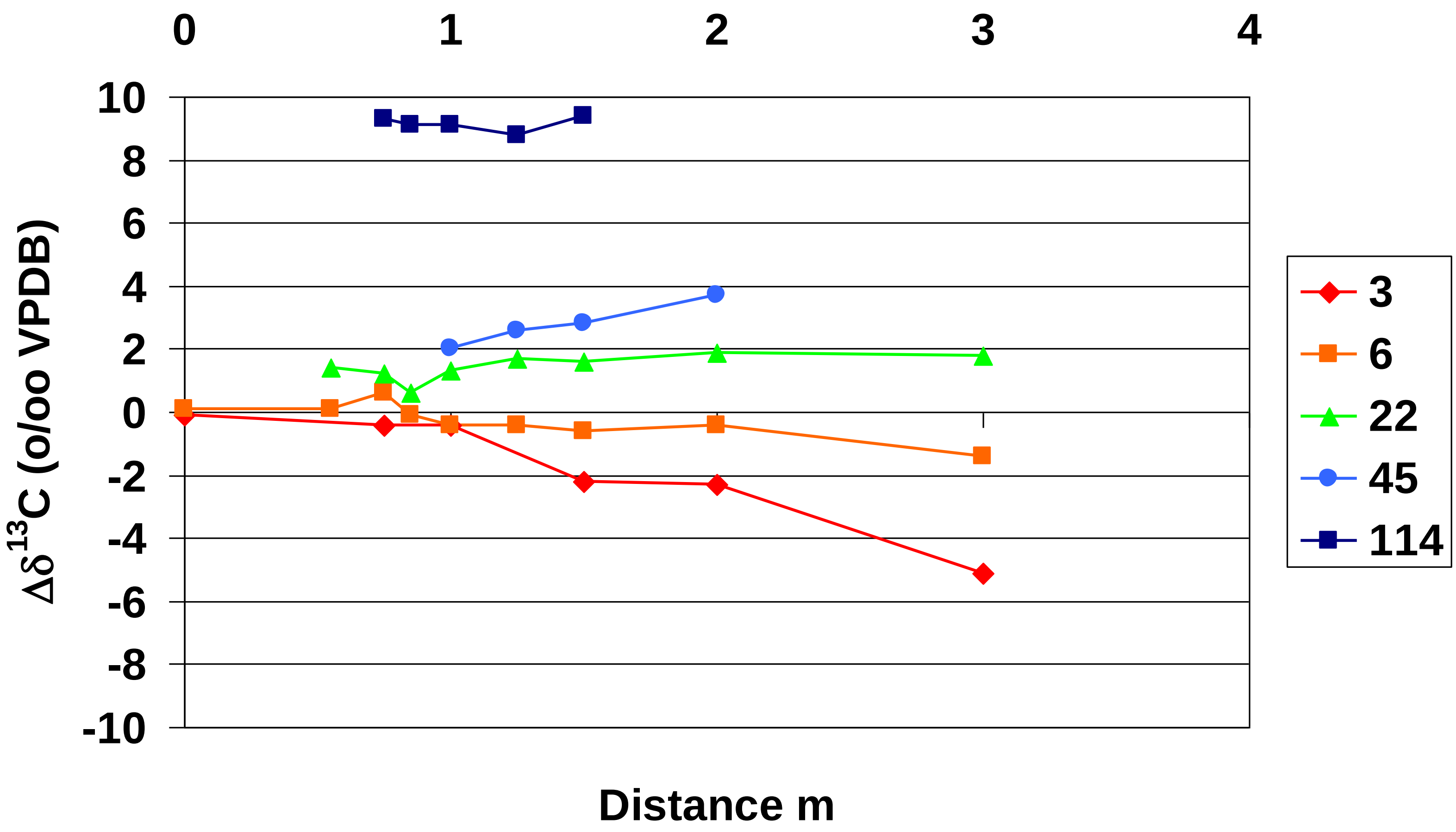
Værlose unsaturated zone experiment

- Carried out by Danish Technical University, GRACOS project
- Artificial gasoline mixture placed at 1.2 m depth below surface
  - BTEX, TMB
  - Alkanes, Cycloalkanes
  - CFC113



Ref. Bouchard et al., 2008, Environmental Science & Technology, 42, 596-601

Carbon isotope ratio of Hexane



Maximal shift in $\delta^{13}C$ and isotopic enrichment factors ε

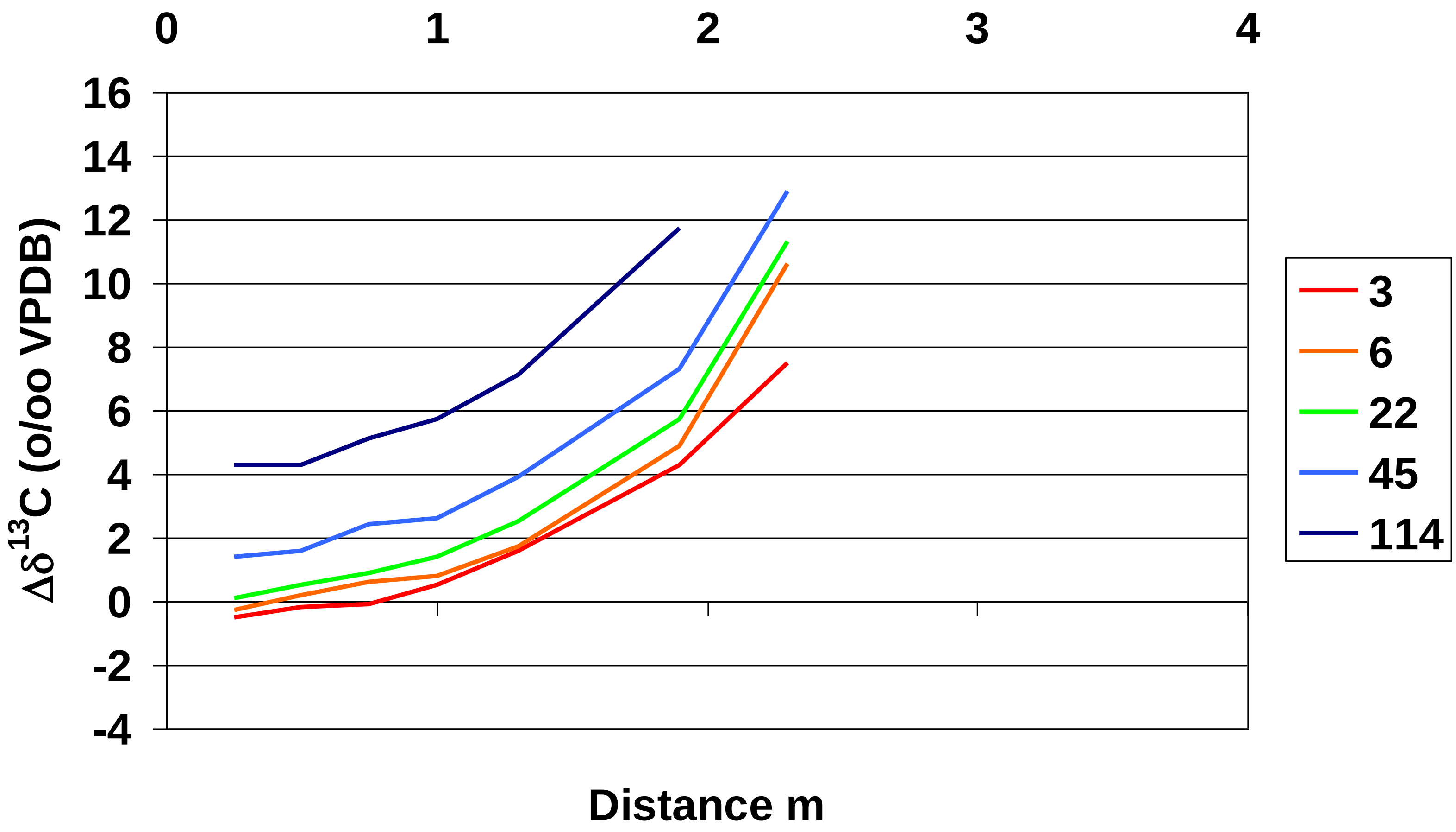
	$\Delta\delta^{13}C$ max neg. (‰)	**$\Delta\delta^{13}C$ max pos. (‰)**	**ε (‰)**
Hexane	**-5.1**	**9.4**	**-2.2** ± 0.63 (12)
Octane	**-2.8**	**5.7**	**-0.9** ± 0.13 (10)
3-Methylpentane	**-4.1**	**10.6**	**-1.5** ± 0.08 (2)
Methylcyclopentane	**-5.7**	**8.0**	**-1.1** ± 0.04 (3)
Methylcyclohexane	**-3.2**	**4.5**	**-1.0** ± 0.28 (3)
Benzene	**-2.6**	**7.7**	**-3.1** ± 0.63 (6)
Toluene	**-3.2**	**5.1**	**-0.7** ± 0.27 (6)
m-Xylene	**-2.2**	**1.4**	**-0.8** ± 0.12 (3)
1,2,4-TMB	**-2.1**	**0.1**	

Modeling scenarios

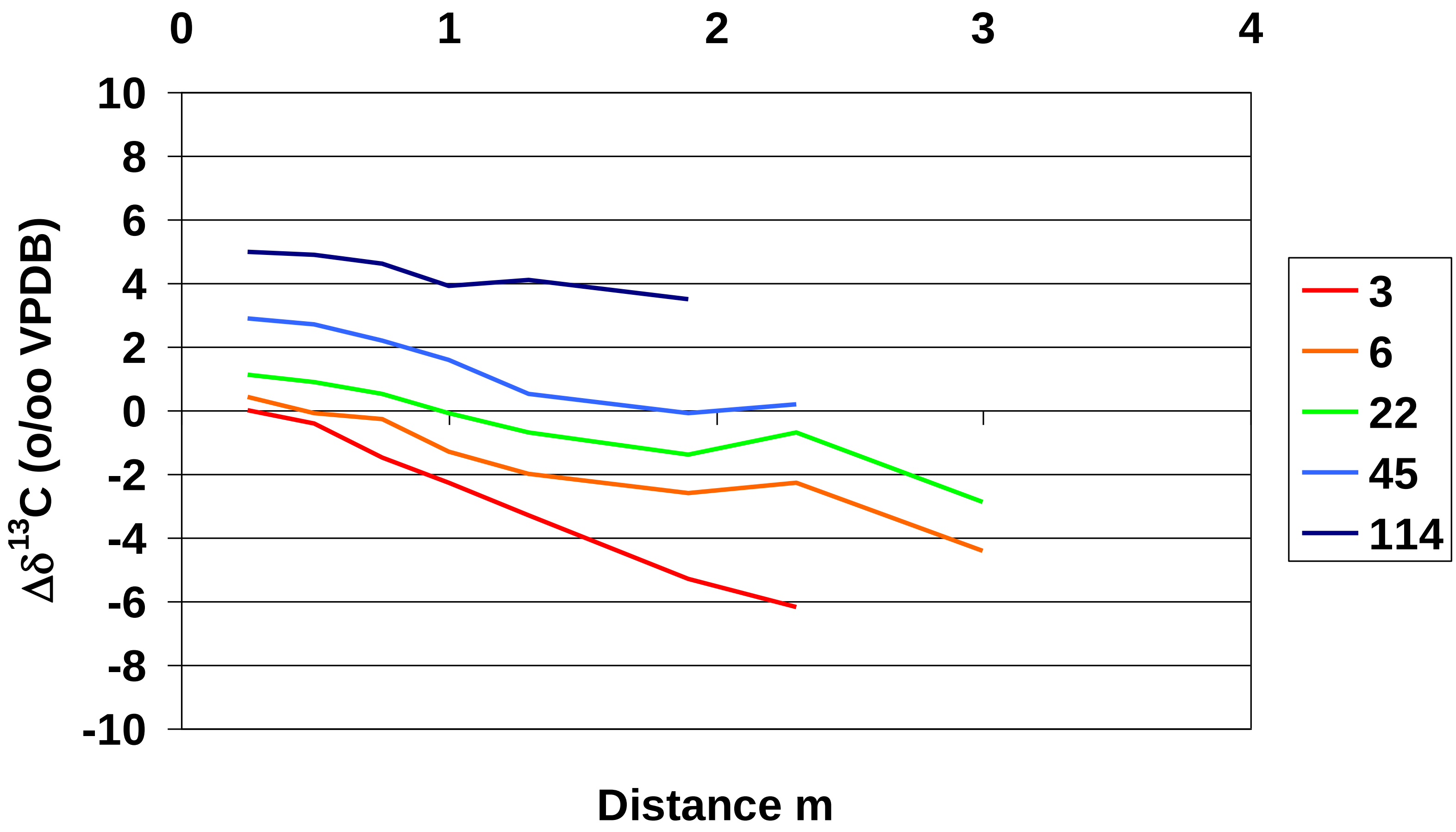
- Degradation rate estimated from concentration data

- Scenarios
  1. Only biodegradation fractionates
  2. Only diffusion fractionates
  3. Biodegradation and diffusion fractionate

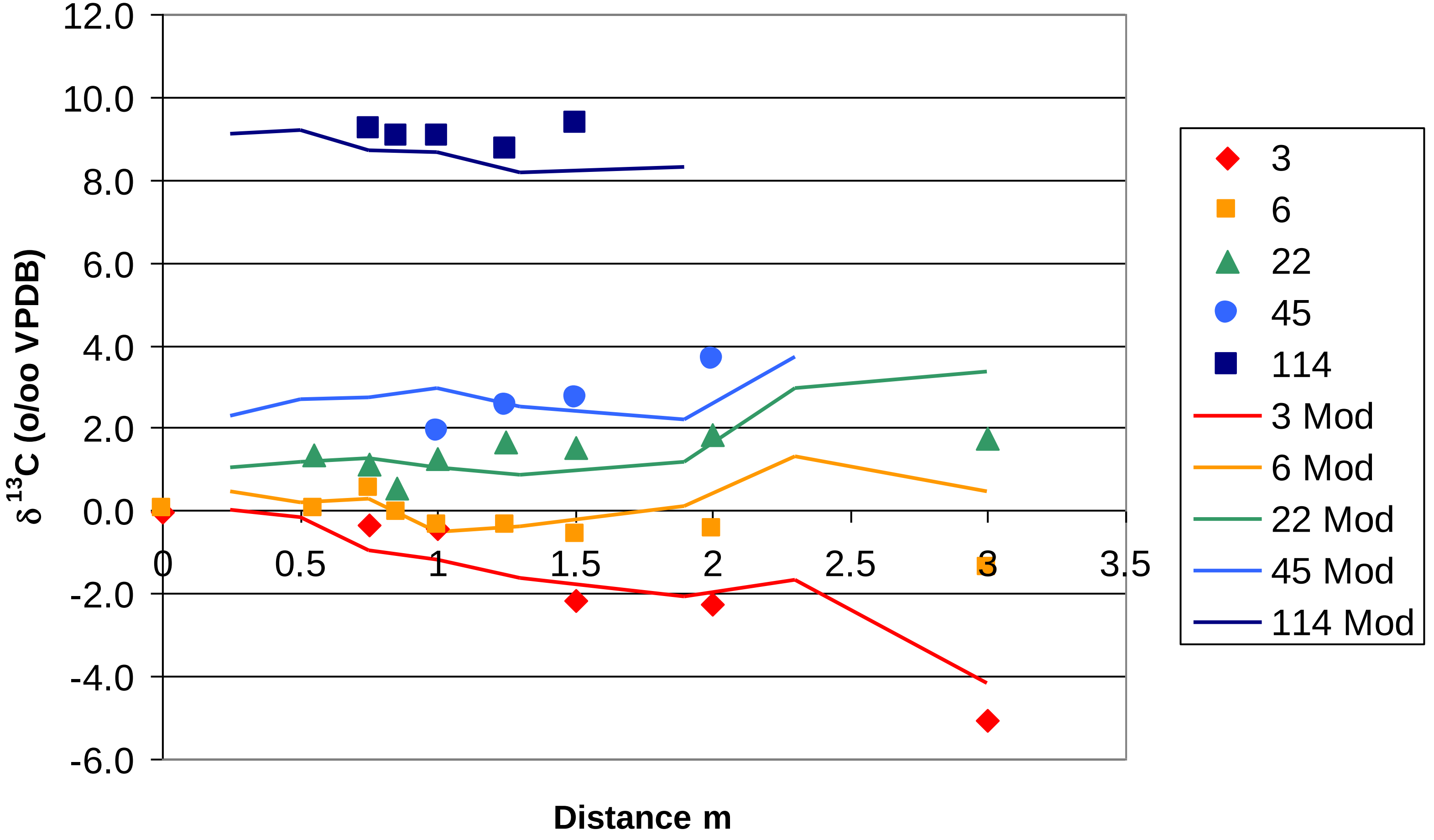
Scenario 1
Only biodegradation fractionates



Scenario 2
Only diffusion fractionates



Comparison Model/Measurements
Biodegradation and diffusion fractionate



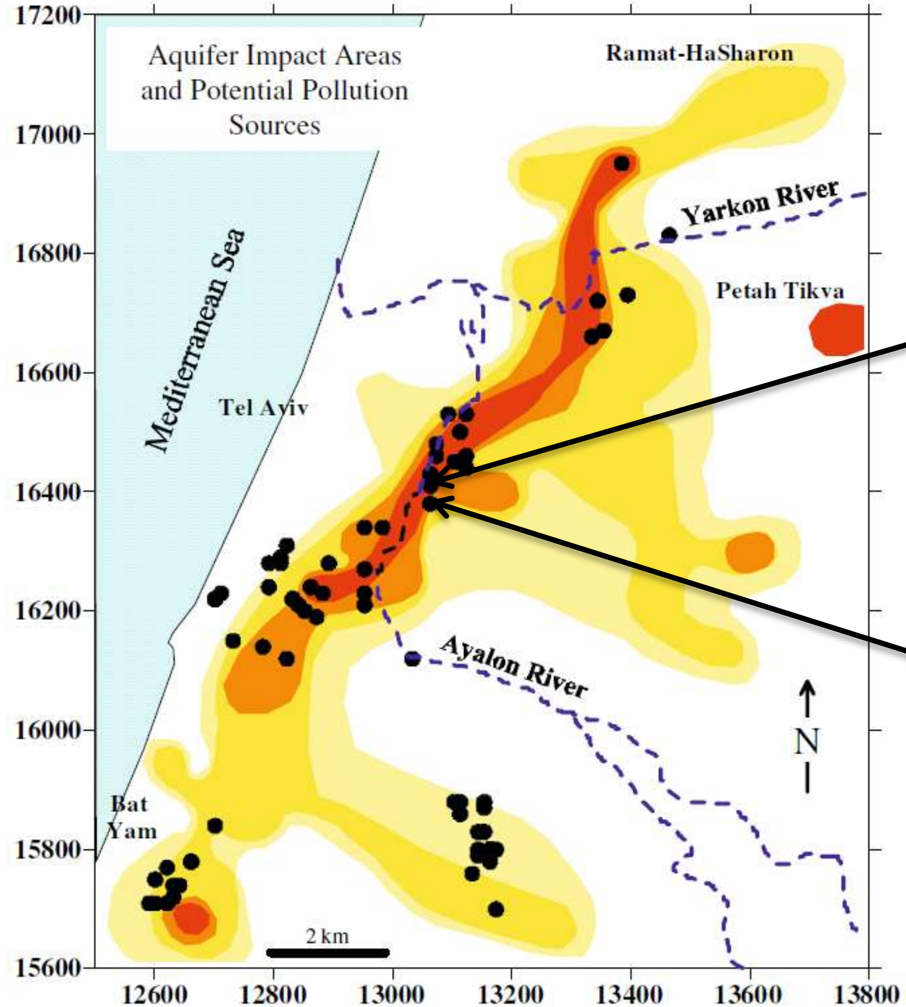
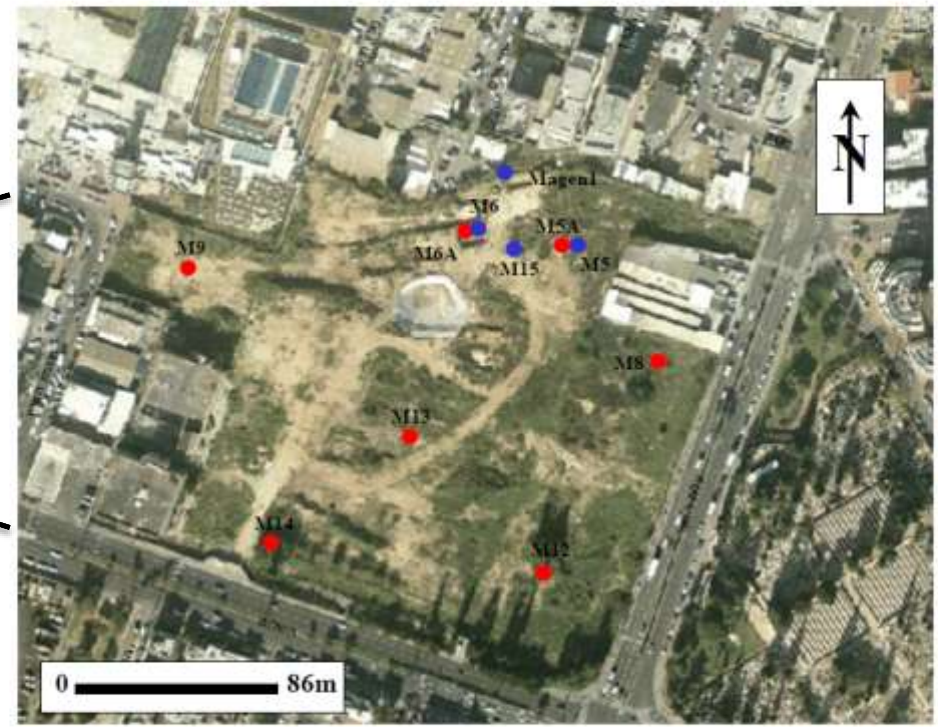


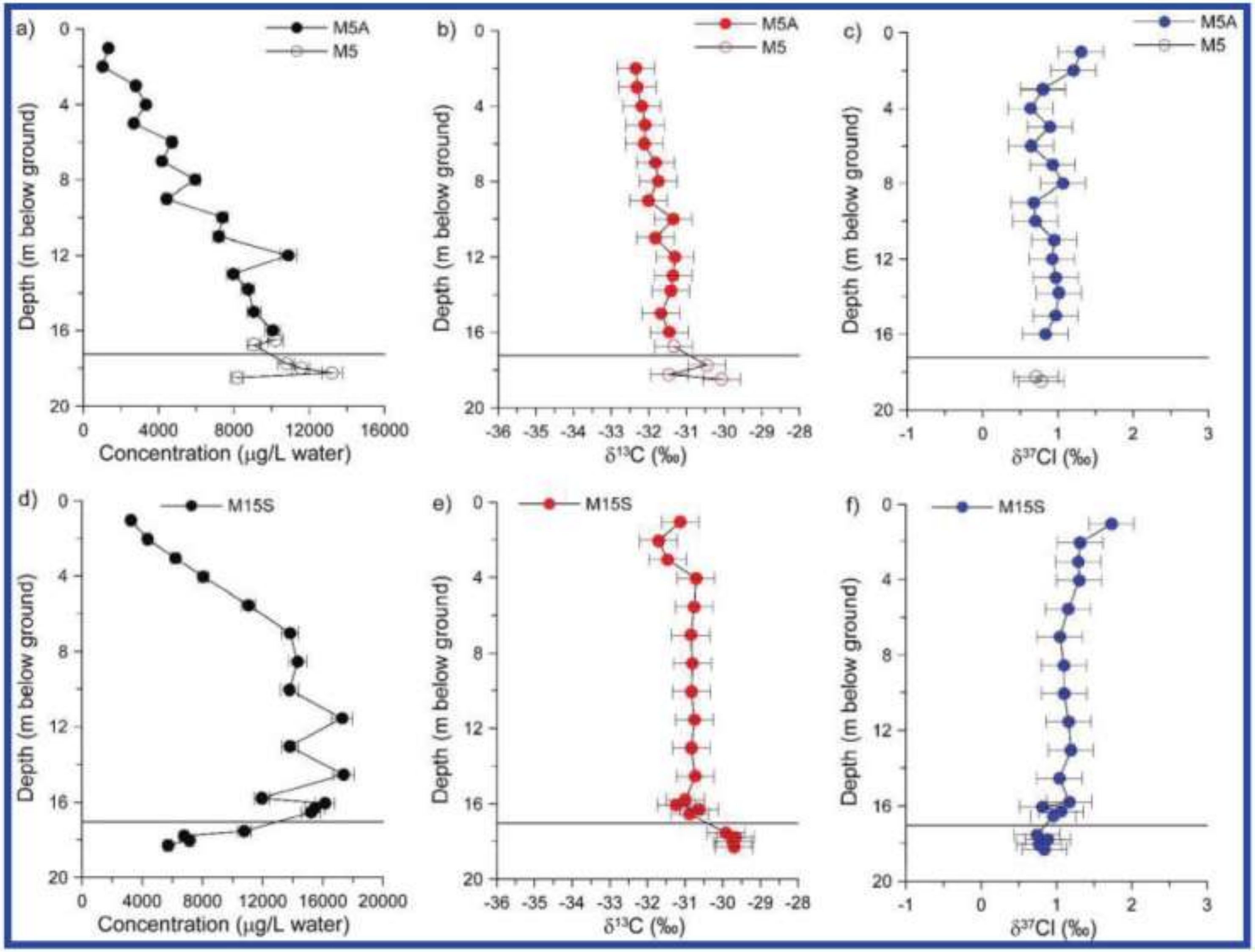
Fig. 5 Four aquifer impact areas based on the concentration of the Cl-VOC component that was greatest in relation to its Israel drinking water standard (IDWS) for the period 1999 to 2001: area I (*red*) ≥ 100% IDWS; area II (*orange*) 50–<100% of IDWS; area III (*dark yellow*): 10–<50% of IDWS; area IV (*light yellow*): 0–<10% of IDWS. Potential sources of Cl-VOCs are shown as *filled black circles*



Existing monitoring wells at the Magen study area sampled in the course of this study; (●) wells that penetrate into the UZ; (●) wells that penetrate into both the saturated and unsaturated zones.

Hunkeler et al., 2011, ES&T

Passive multilevel passive sampler system
Diffusion Sampler



Concentration, stable carbon isotope ratio, and stable chlorine isotope ratio of TCE in monitoring wells M5A and M5 (a-c), and M15S (d-f). The concentrations in the unsaturated zone correspond to equivalent aqueous phase concentrations. The horizontal line indicates the location of the water table

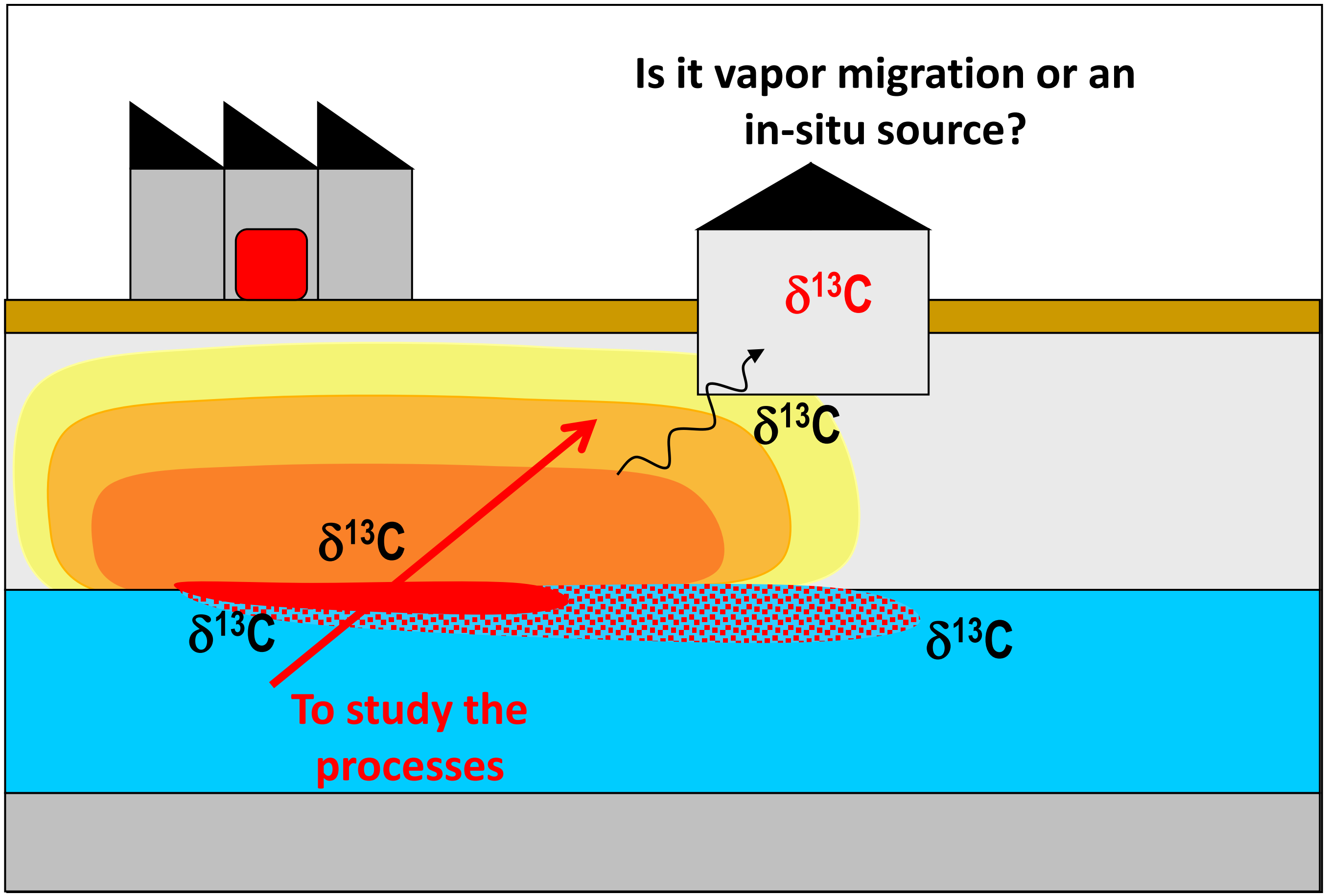
Conclusions unsaturated studies

- Under steady state diffusion (and in absence of biodegradation), isotope ratios are expected to be constant in space
  -> Linking vapor plumes to sources

- Isotope enrichment due to biodegradation is partly counterbalanced by diffusion isotope effect
  -> Isotope ratios almost « conserved » for some isotopes (especially C) while significant trend expected for others (especially H)

- If significant mass has been removed from source, source becomes enriched or depleted in heavy isotope, depending on substance and isotope
  -> Tool to track degree of source removal in unsaturated zone

CSIA in a vapor intrusion process

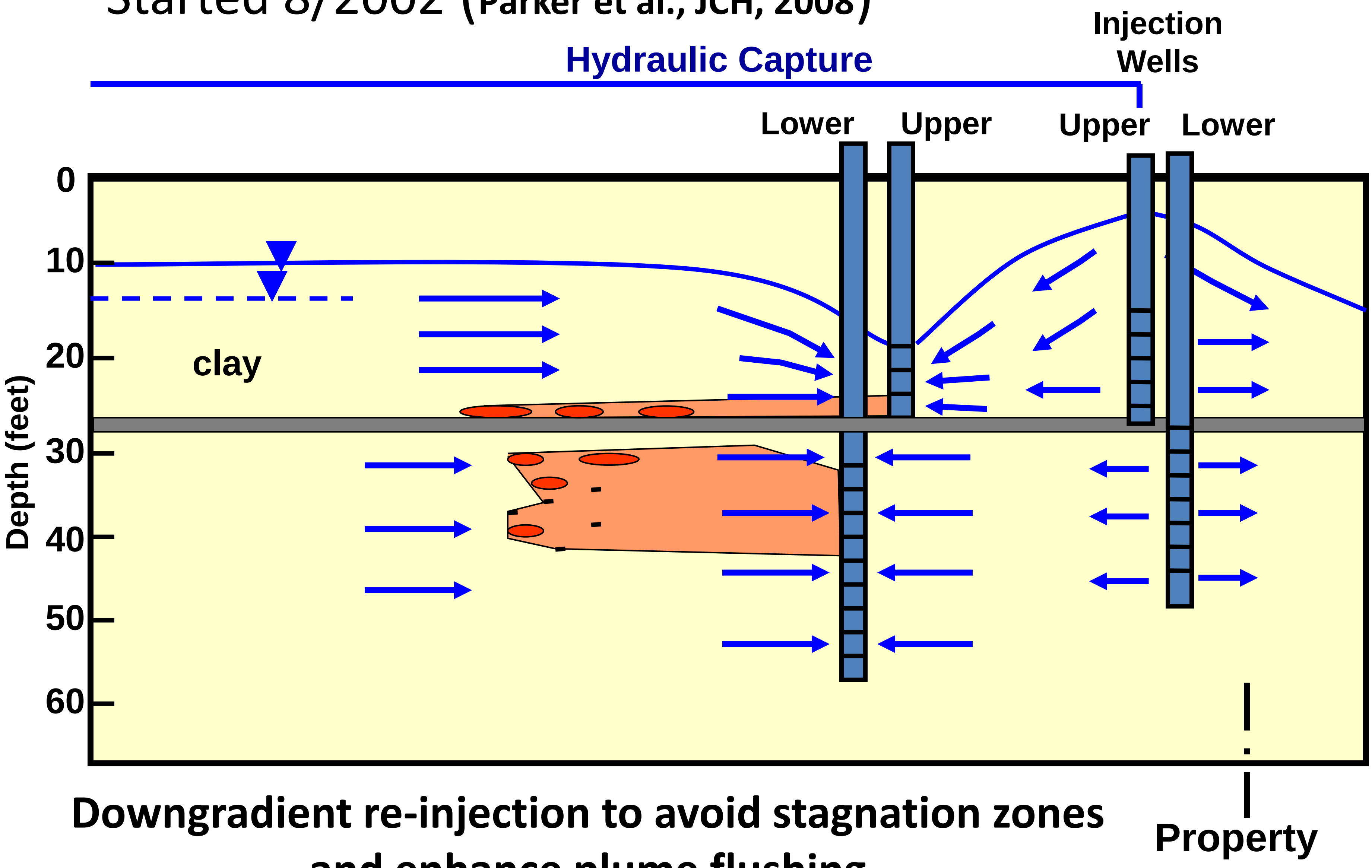


Sampling and analysis of vapor samples is challenging because of the low concentration levels (0.001 to 0.01 µg/L range)

Site and Downgradient Area

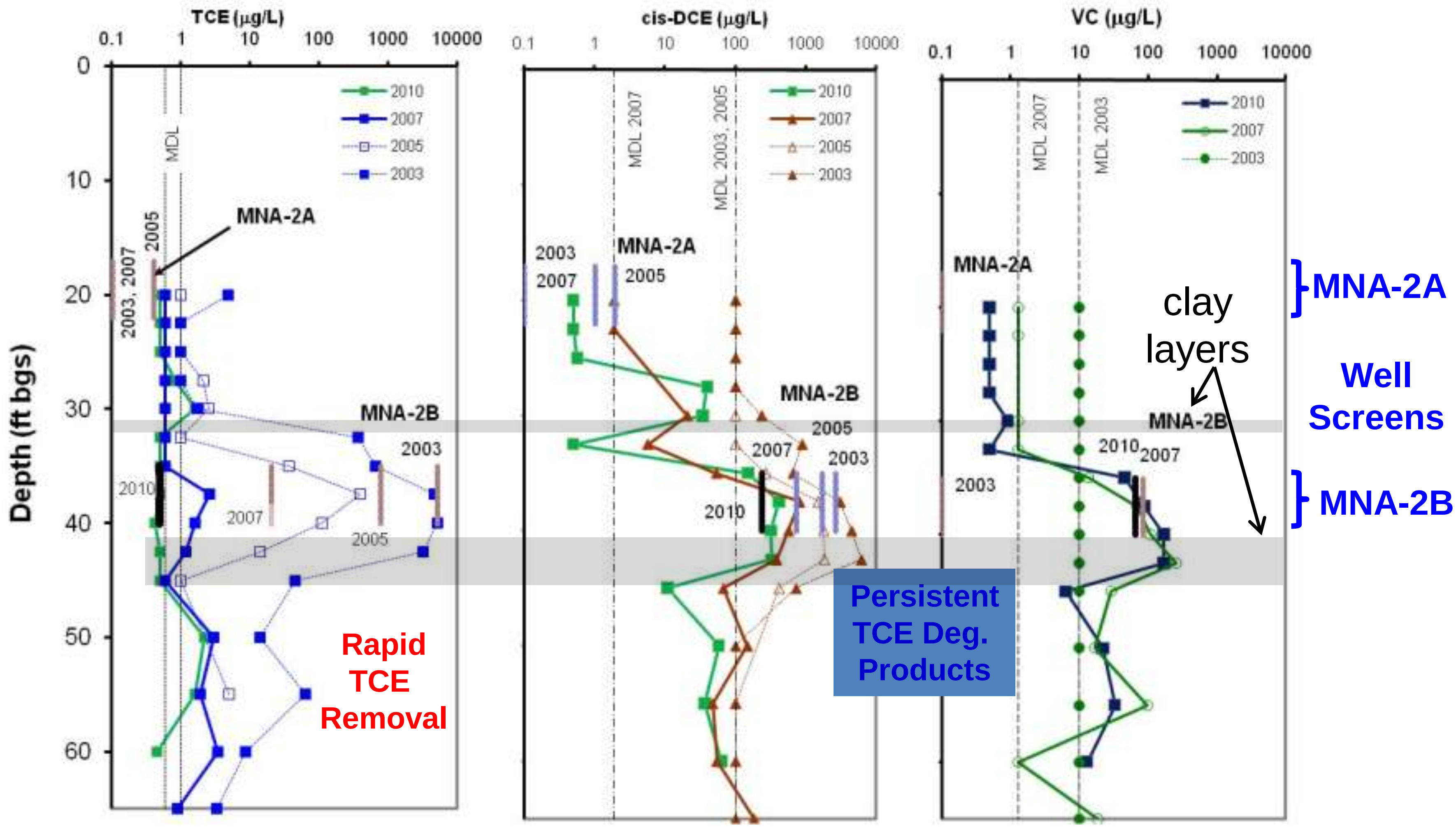
PFC Hydraulic Capture System

Started 8/2002 (**Parker et al., JCH, 2008**)



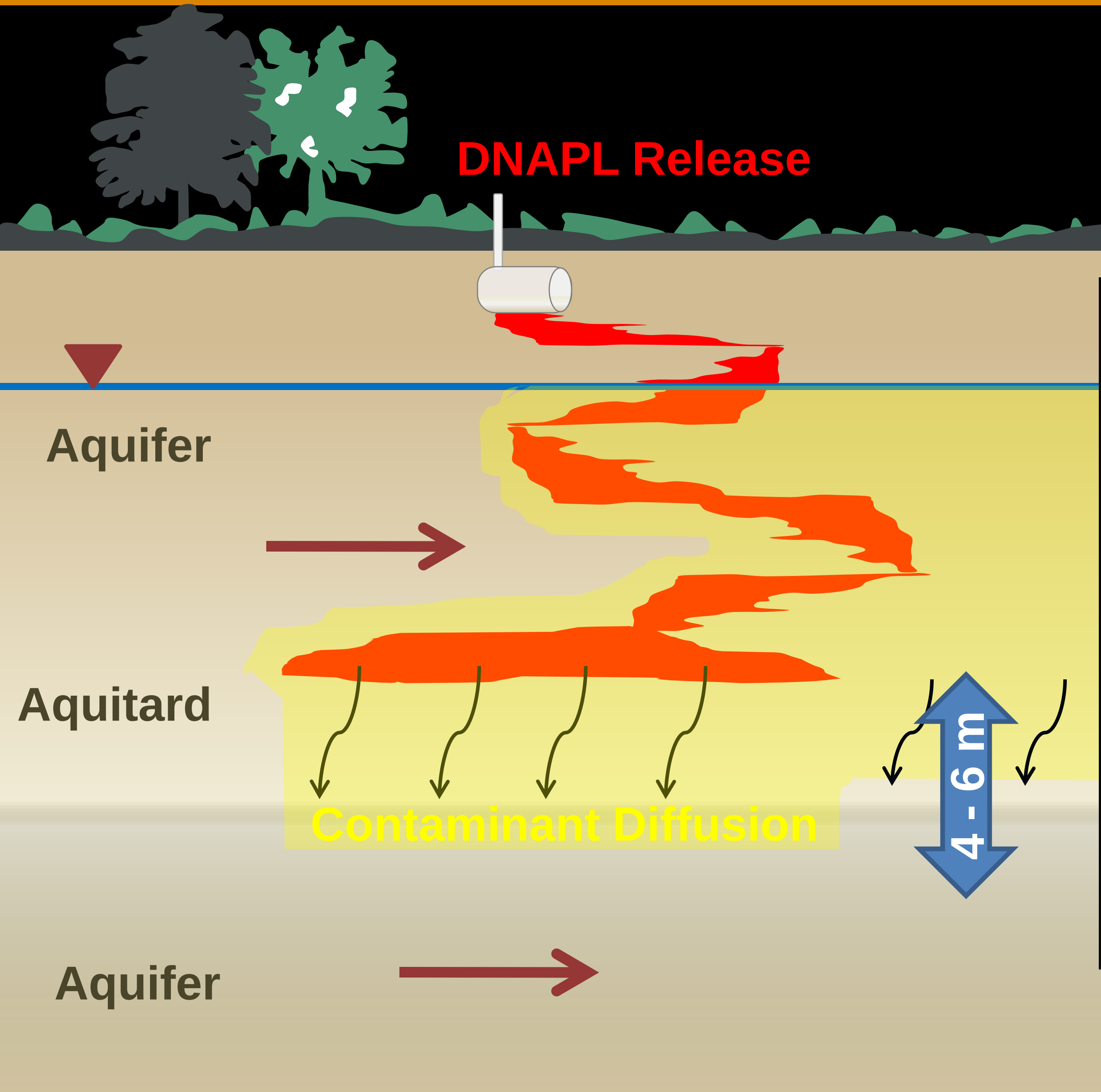
Downgradient re-injection to avoid stagnation zones and enhance plume flushing

Multilevel VOC Profile: WR Transect



Hydraulic capture system started 8/2002

Aquitard Protection to Aquifers



Factors Affecting the Degree of Protection

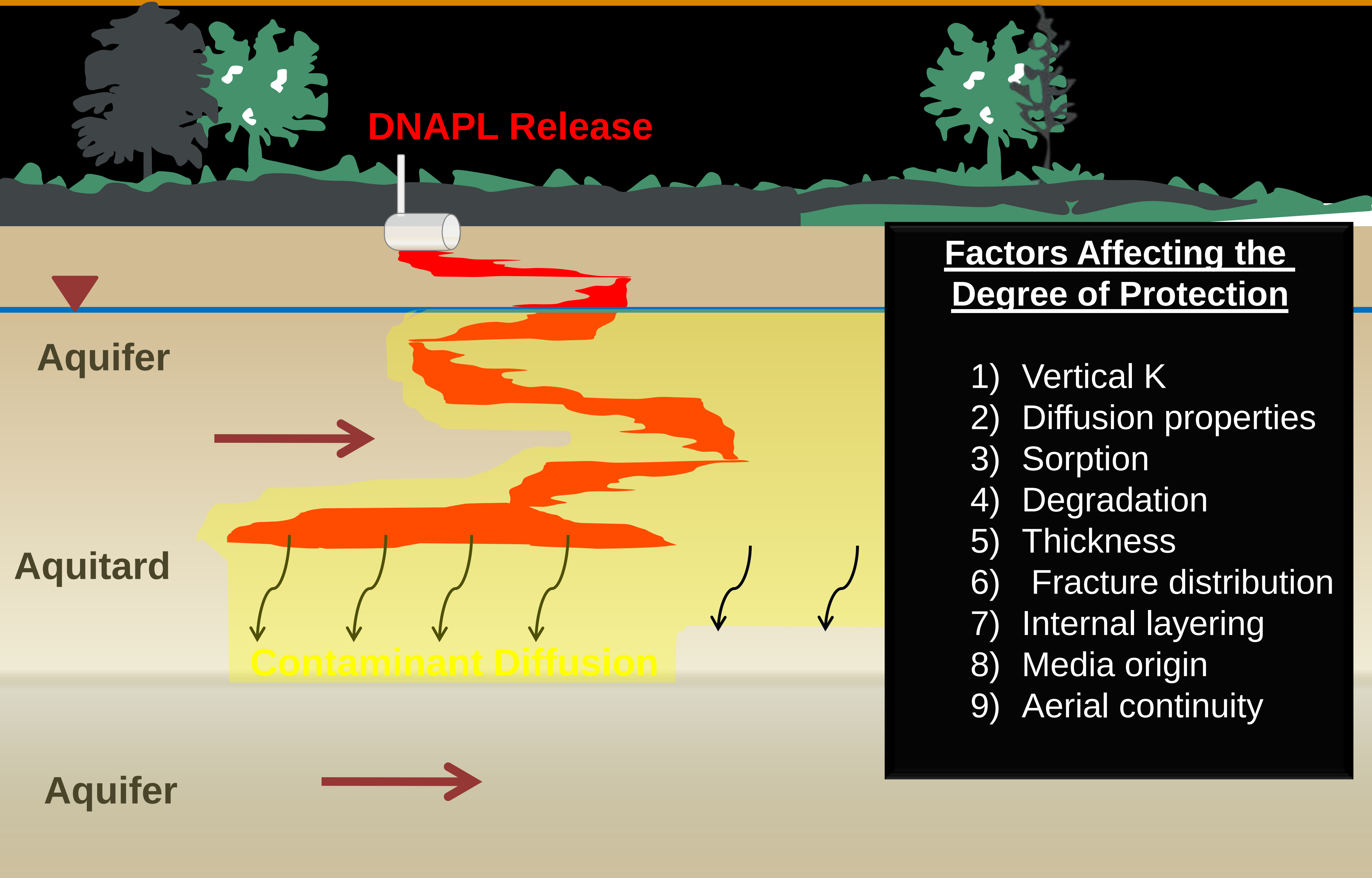
1) Vertical K
2) Diffusion properties
3) Sorption
4) Degradation
5) Thickness
6) Fracture distribution
7) Internal layering
8) Media origin
9) Aerial continuity

This Talk Will Present

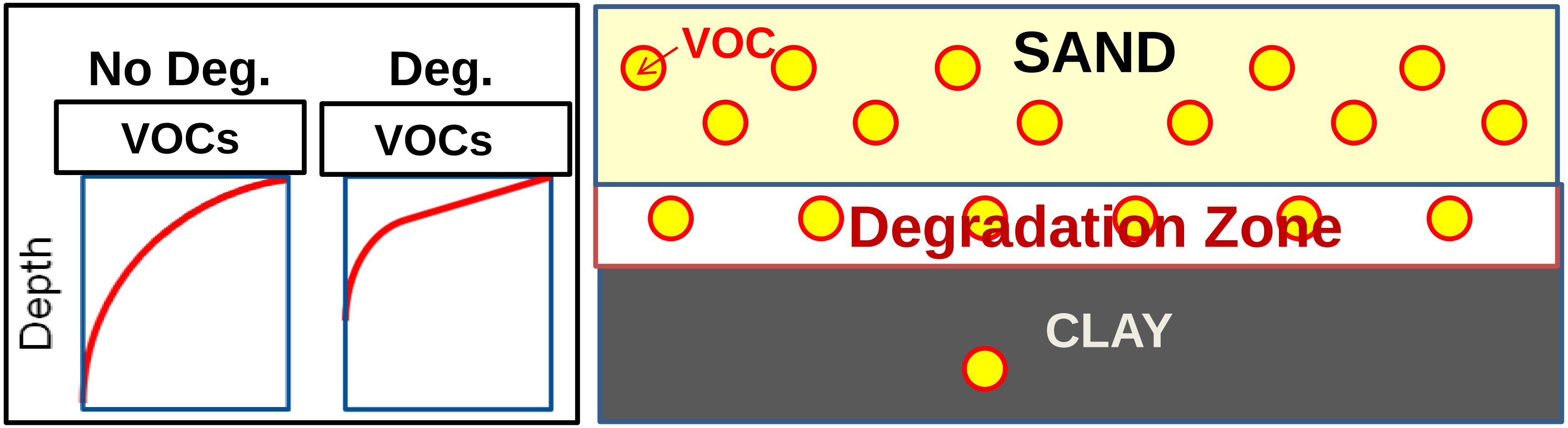
Evidence for contaminant degradation in silty/clayey aquitards

Implications for aquifer cleanup and protection

Aquitard Protection to Aquifers



Degradation Enhances Aquifer Protection



Thickness of Aquitard Biodegradation Zone

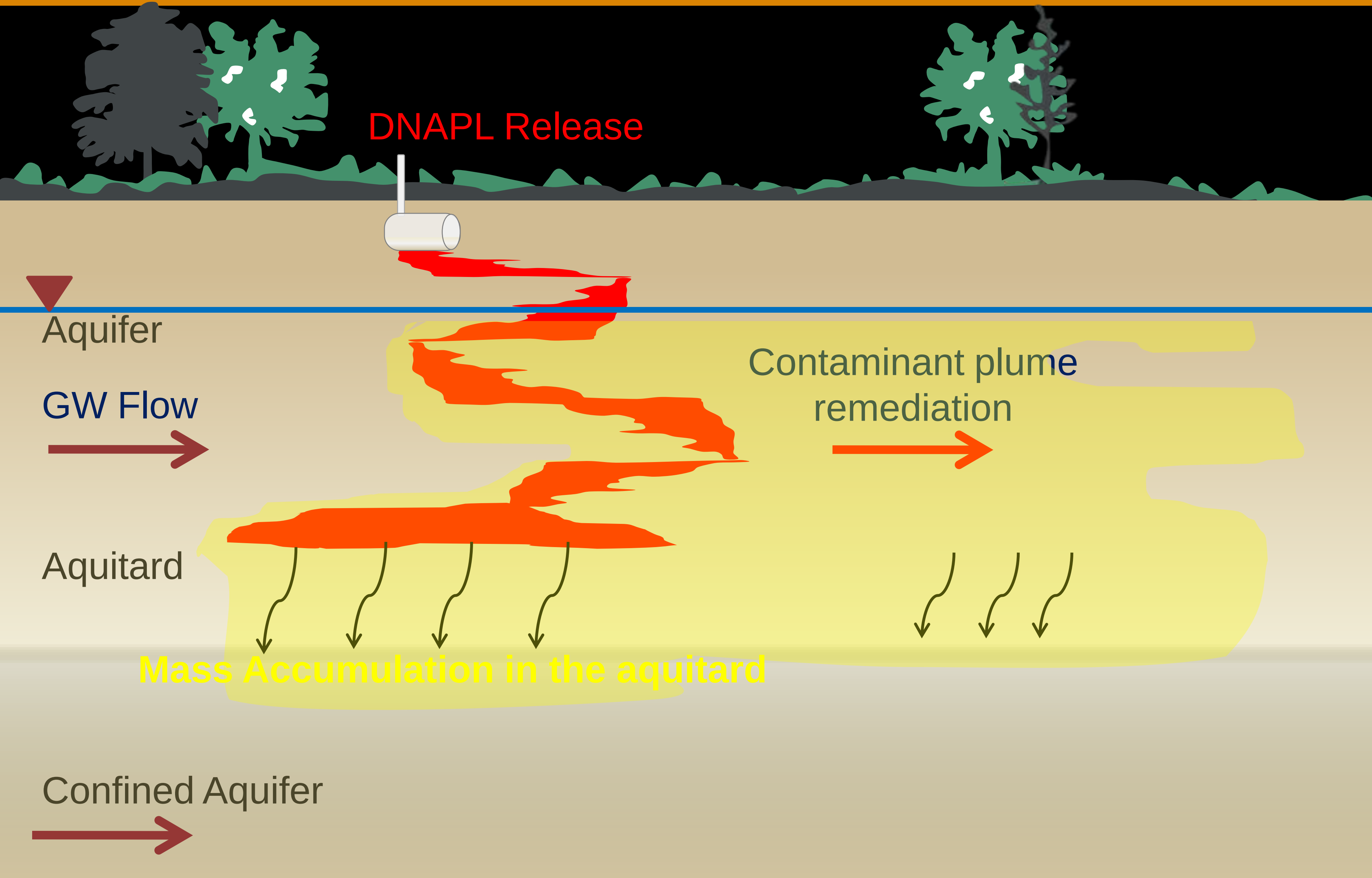
May be limited to a few cm into clay

Sleep (2007); Broholm *et al.* (2006); Takeuchi *et al.* (2011)

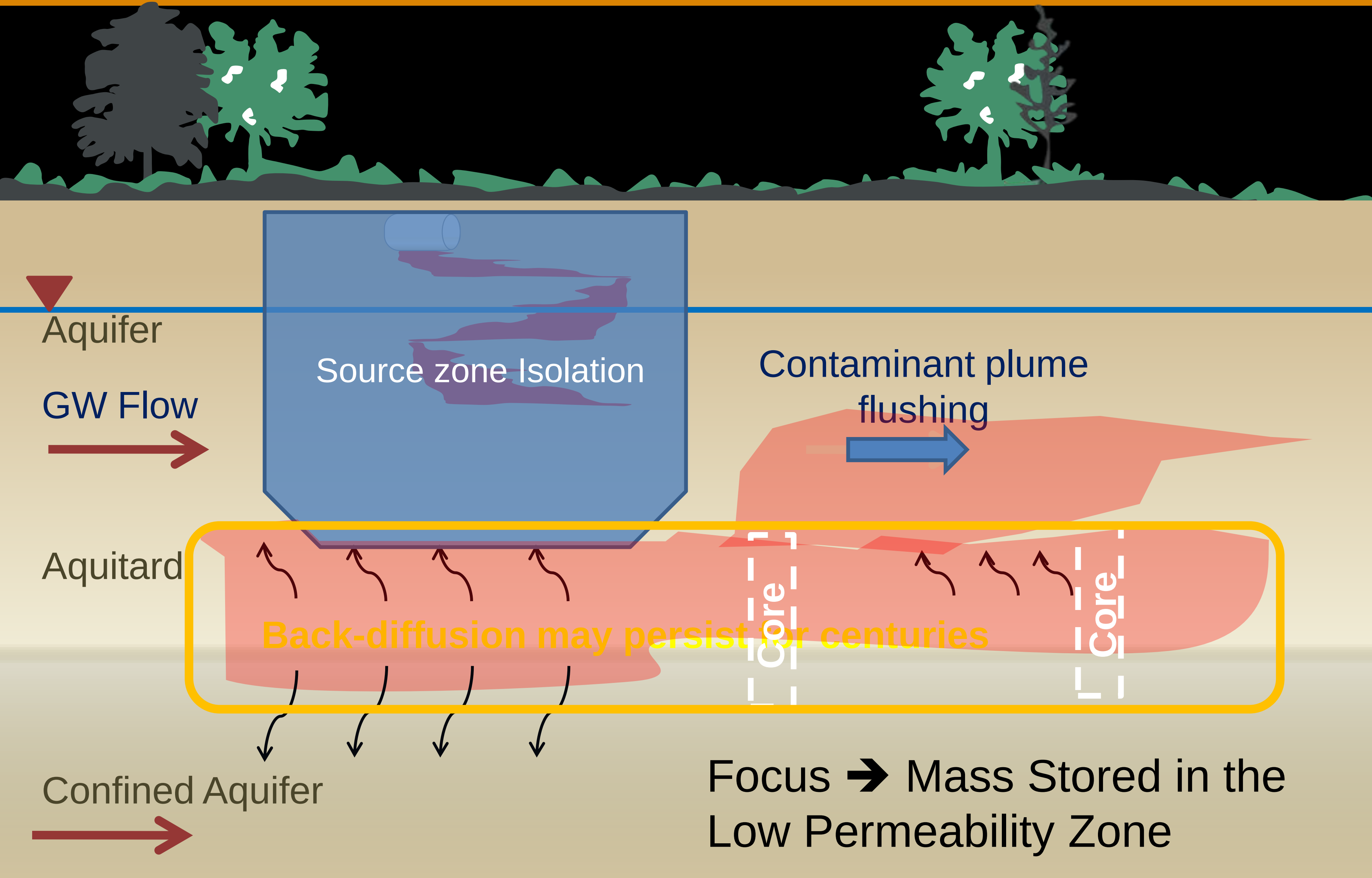
Observed the development of microbial communities capable of degrading contaminant mass stored

- Van Stempvoort et al (2009); Takeuchi et al. (2011)

Contaminant Mass "Trapped" in Aquitard

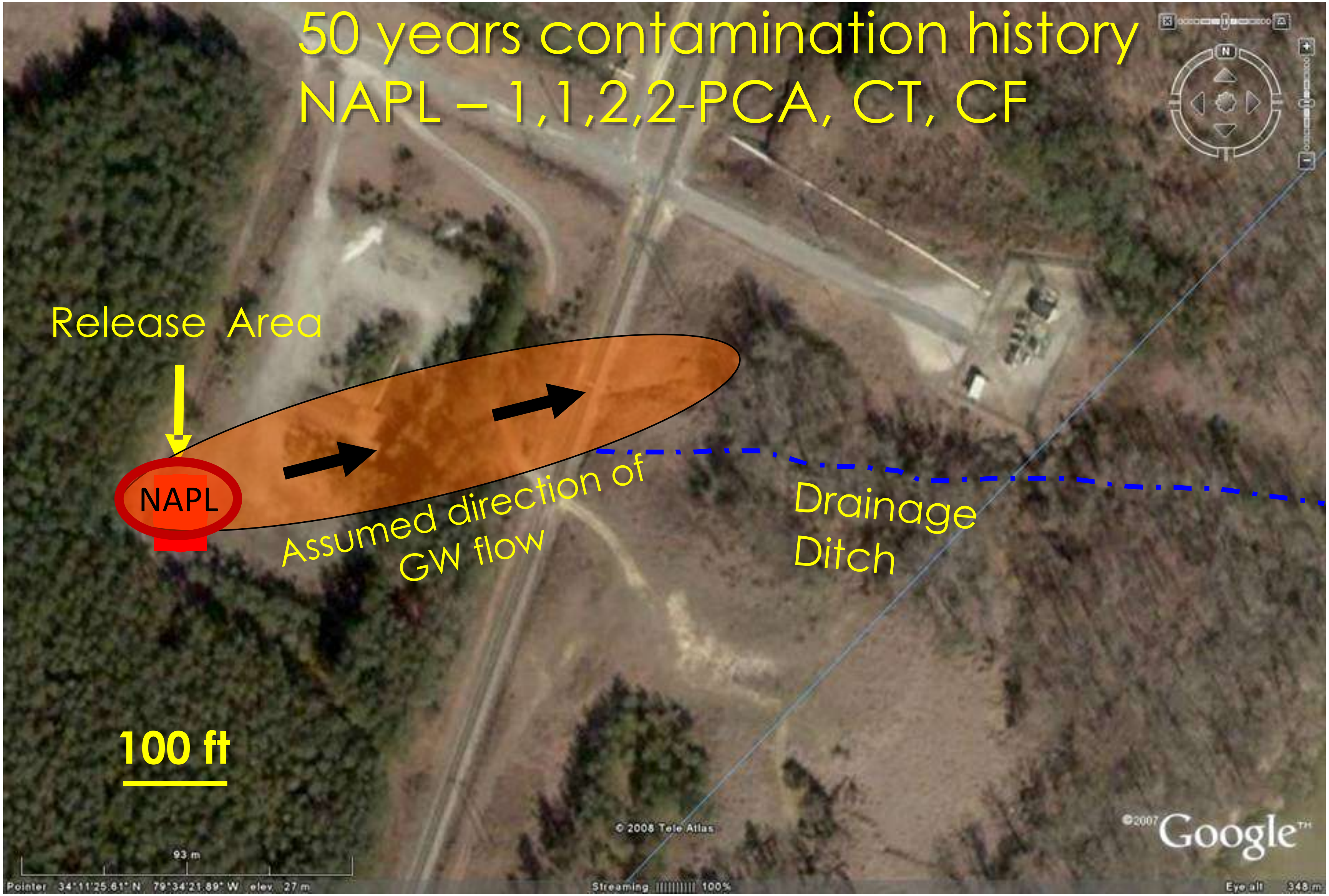


SZ Isolation + Aquifer Remediation

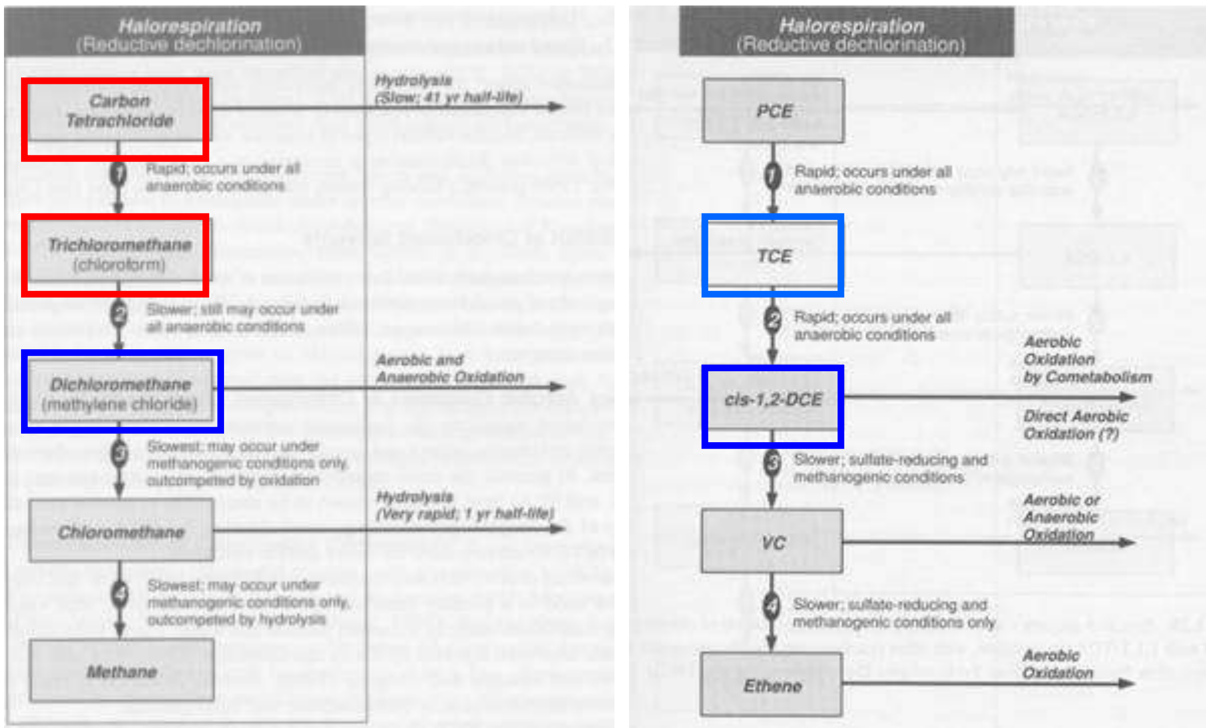


Focus ➔ Mass Stored in the Low Permeability Zone

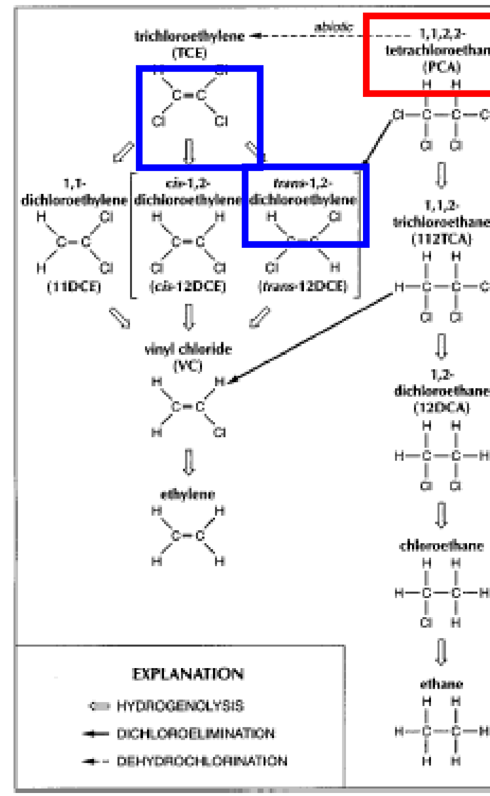
Case Study – South Carolina Site



Degradation Pathways



From Wiedemeier et al., 1999



From Lorah & Olsen, 1999

Released contaminants

Observed breakdown products

Case Study – South Carolina Site

Focus – Mass Stored in Aquitard

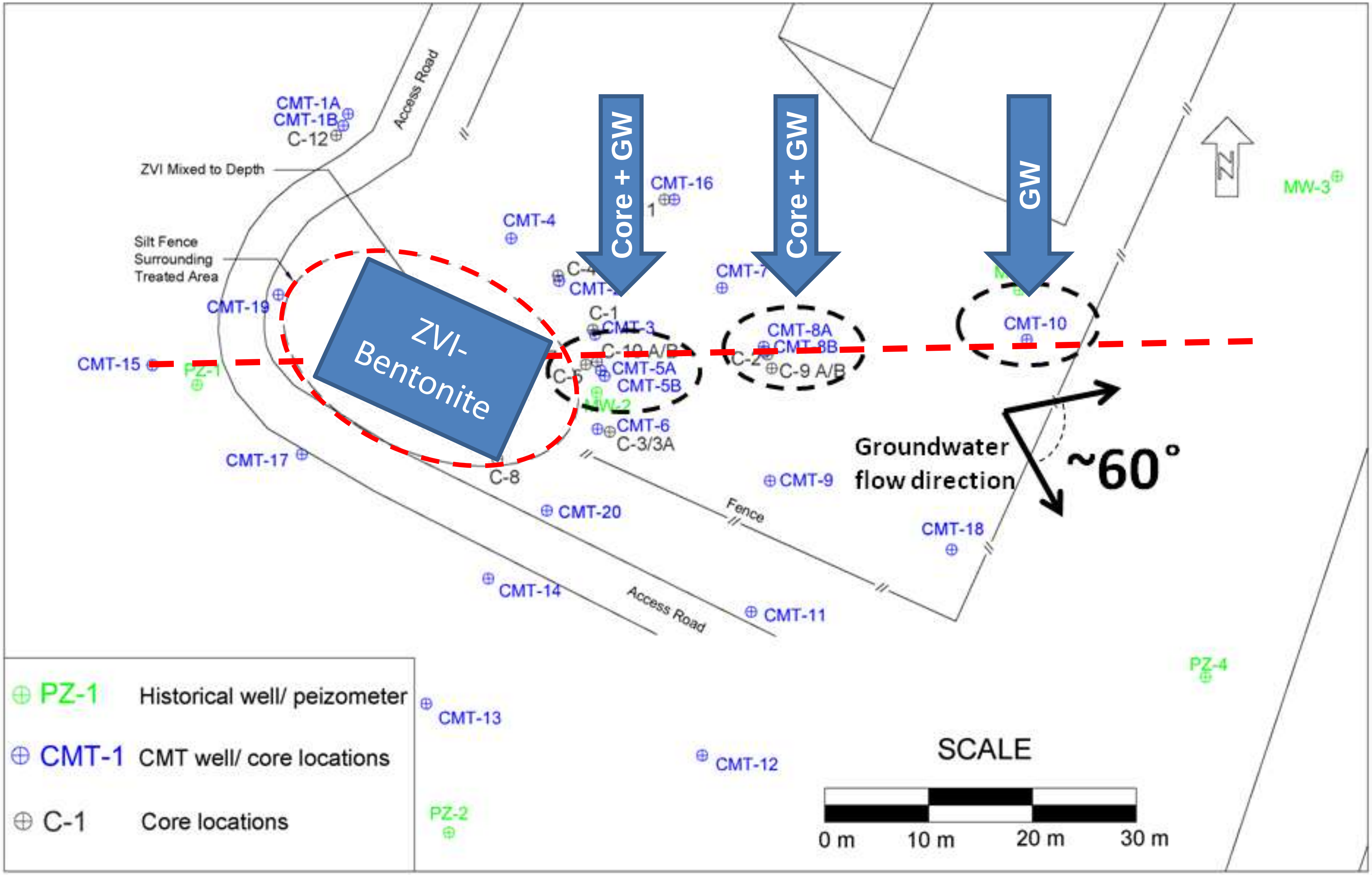
Sediment Core

- Detailed [VOC] distribution
- CSIA
- Microorganisms

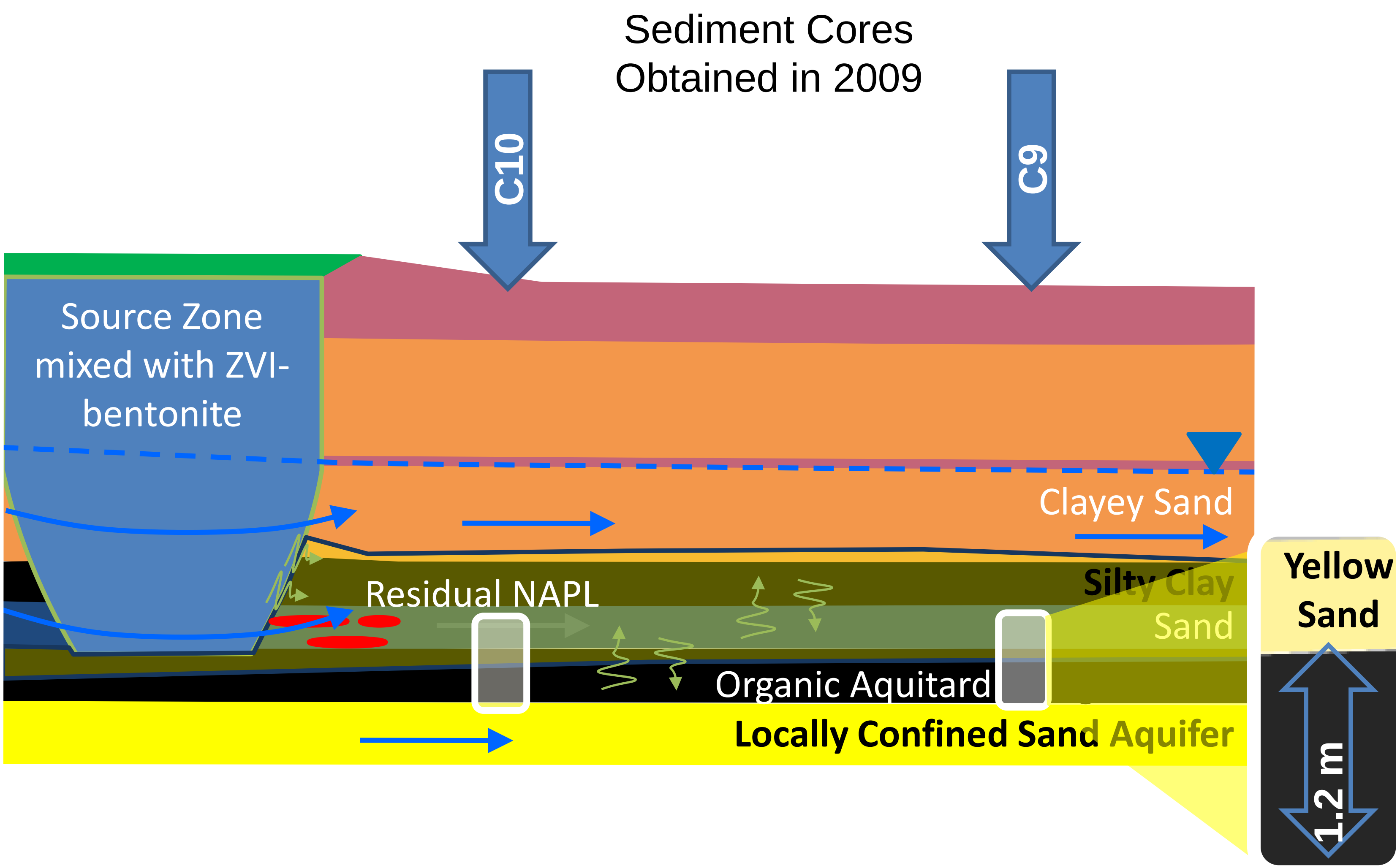
Aquifer Groundwater

- Redox conditions
- [VOC]
- CSIA

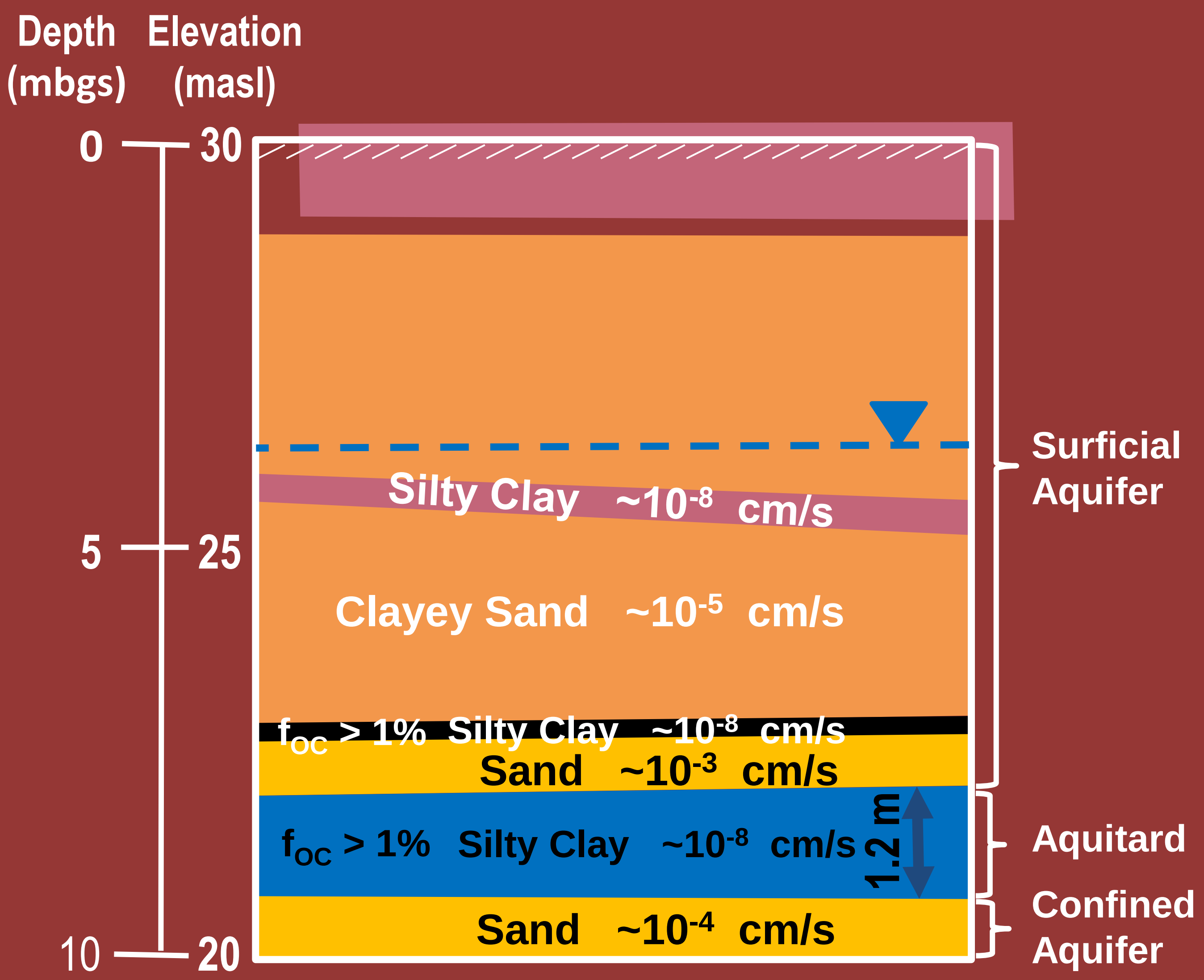
Monitoring Network



Source Isolation – December 2007

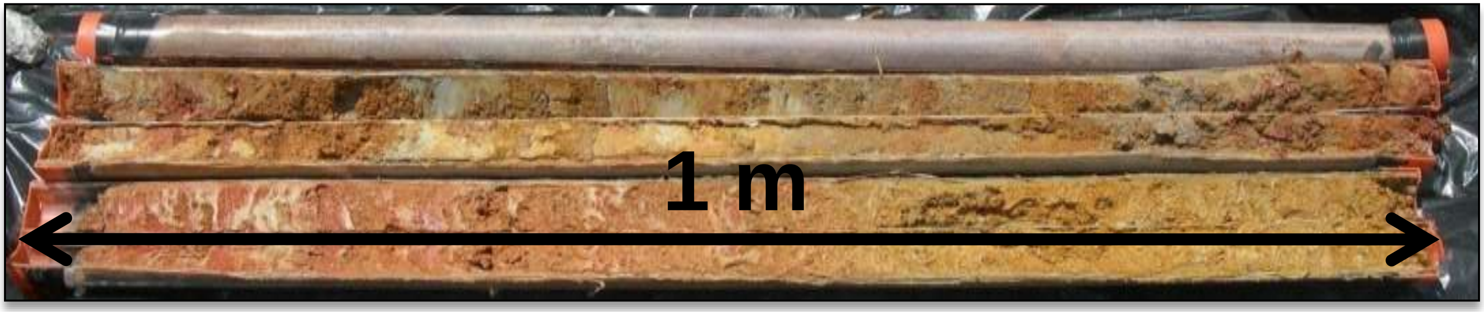


Lithology



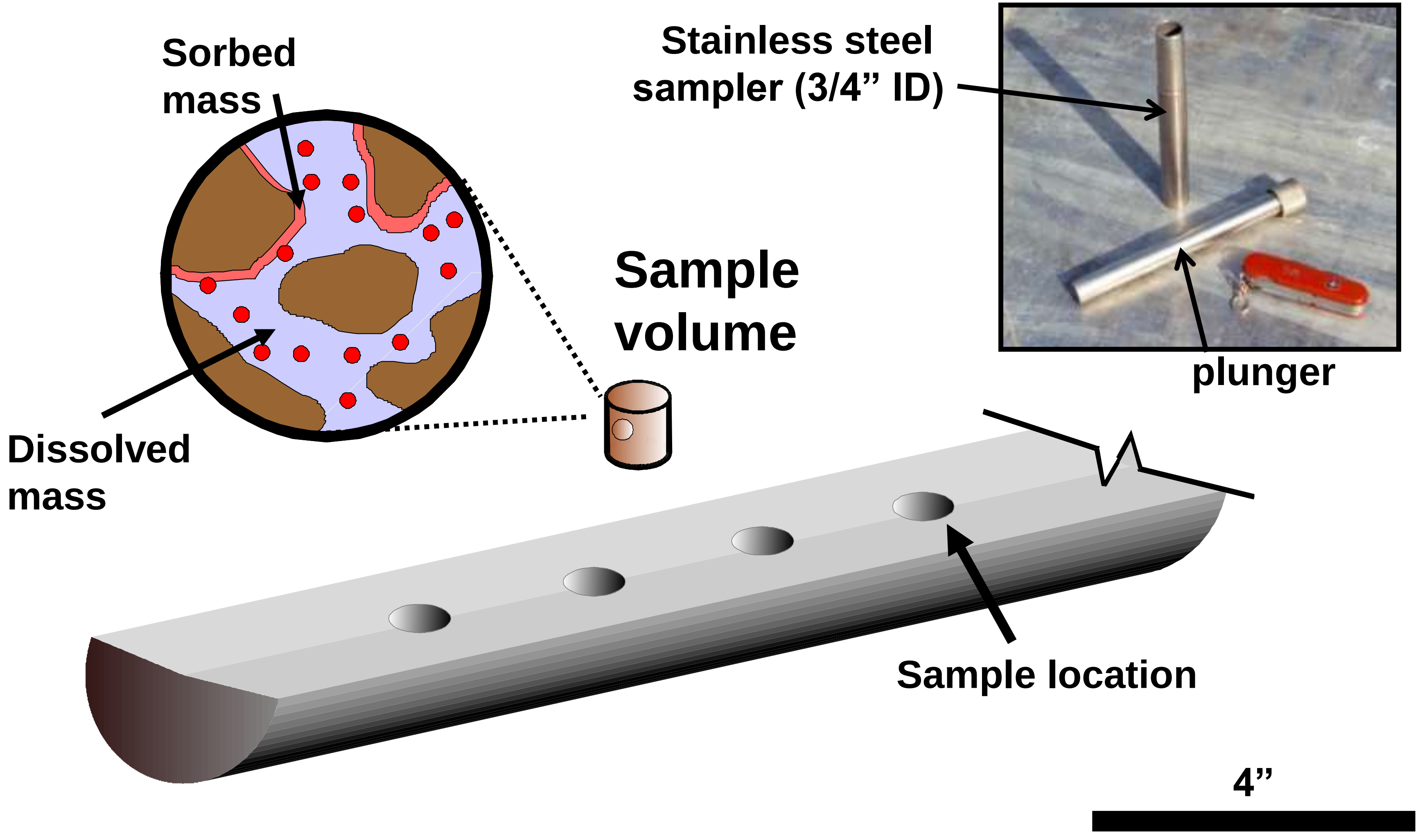
Depth (mbgs)
Elevation (masl)
0
30
5
25
10
20
Silty Clay ~10-8 cm/s
Clayey Sand ~10-5 cm/s
foc > 1% Silty Clay ~10-8 cm/s
Sand ~10-3 cm/s
foc > 1% Silty Clay ~10-8 cm/s
1.2 m
Sand ~10-4 cm/s
Surficial Aquifer
Aquitard
Confined Aquifer

Direct Push Coring – Enviro-Core Method



~ 100% Recovery

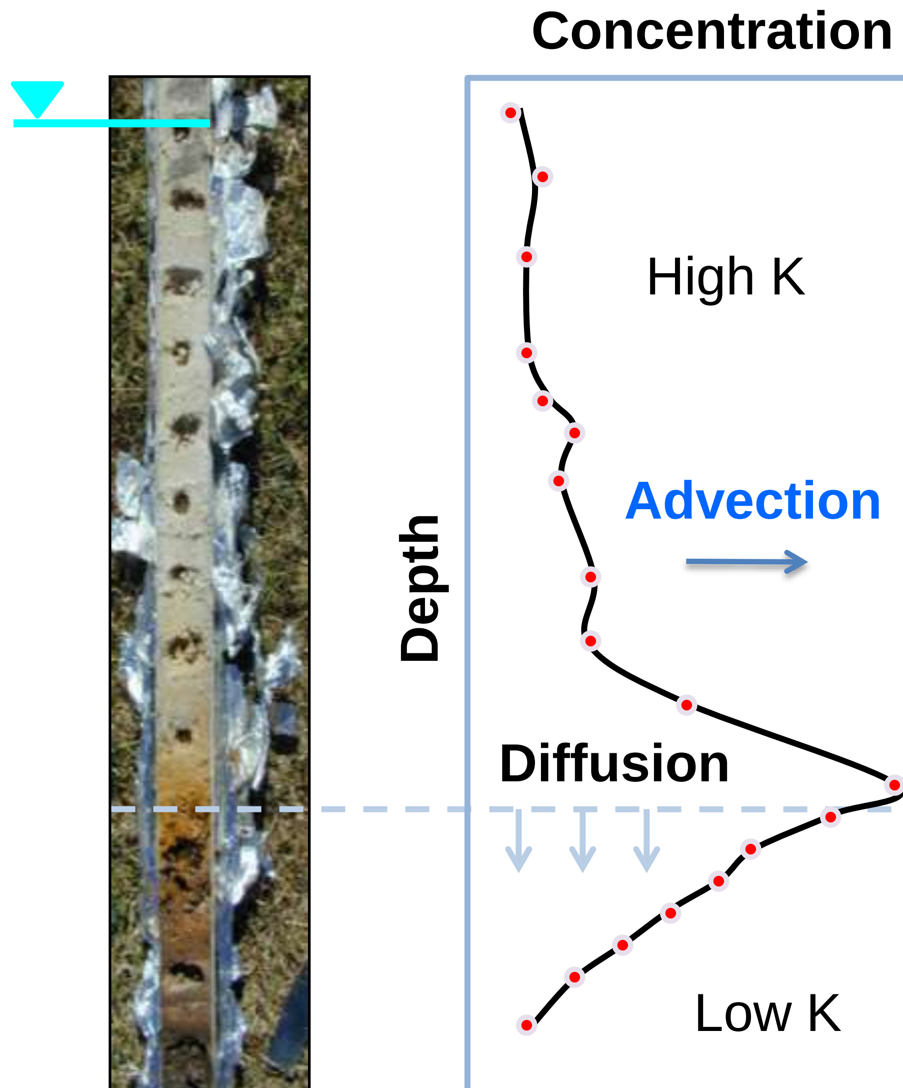
Sediment Core – Subsampling



Guilbeault, 1999

Sediment Core – Subsampling

Methanol preservation



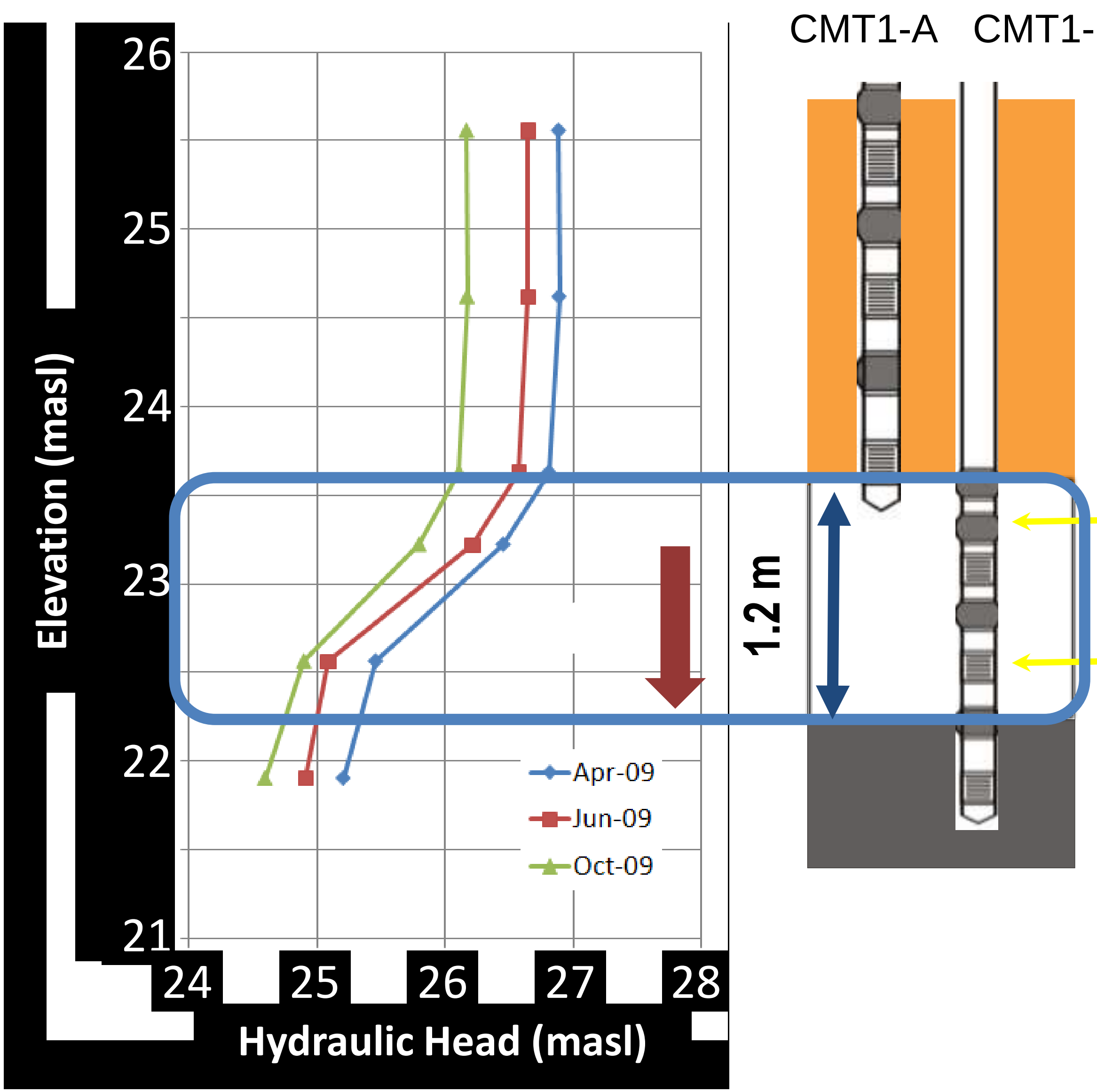
Results

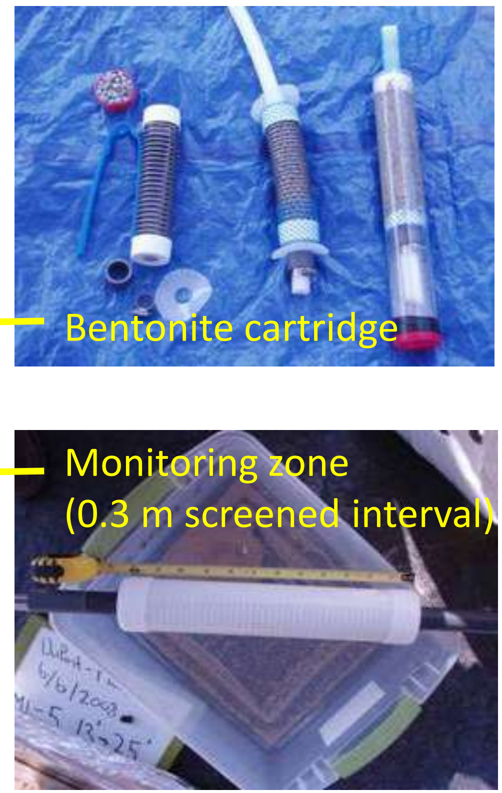
Aquitard hydraulic properties

Sediment core – VOCs, CSIA, and microorganisms

Groundwater- Redox,VOCs, and CSIA

Hydraulic Head Profiles





Hydraulic Head Profiles

Lack of connectivity between upper and lower aquifers

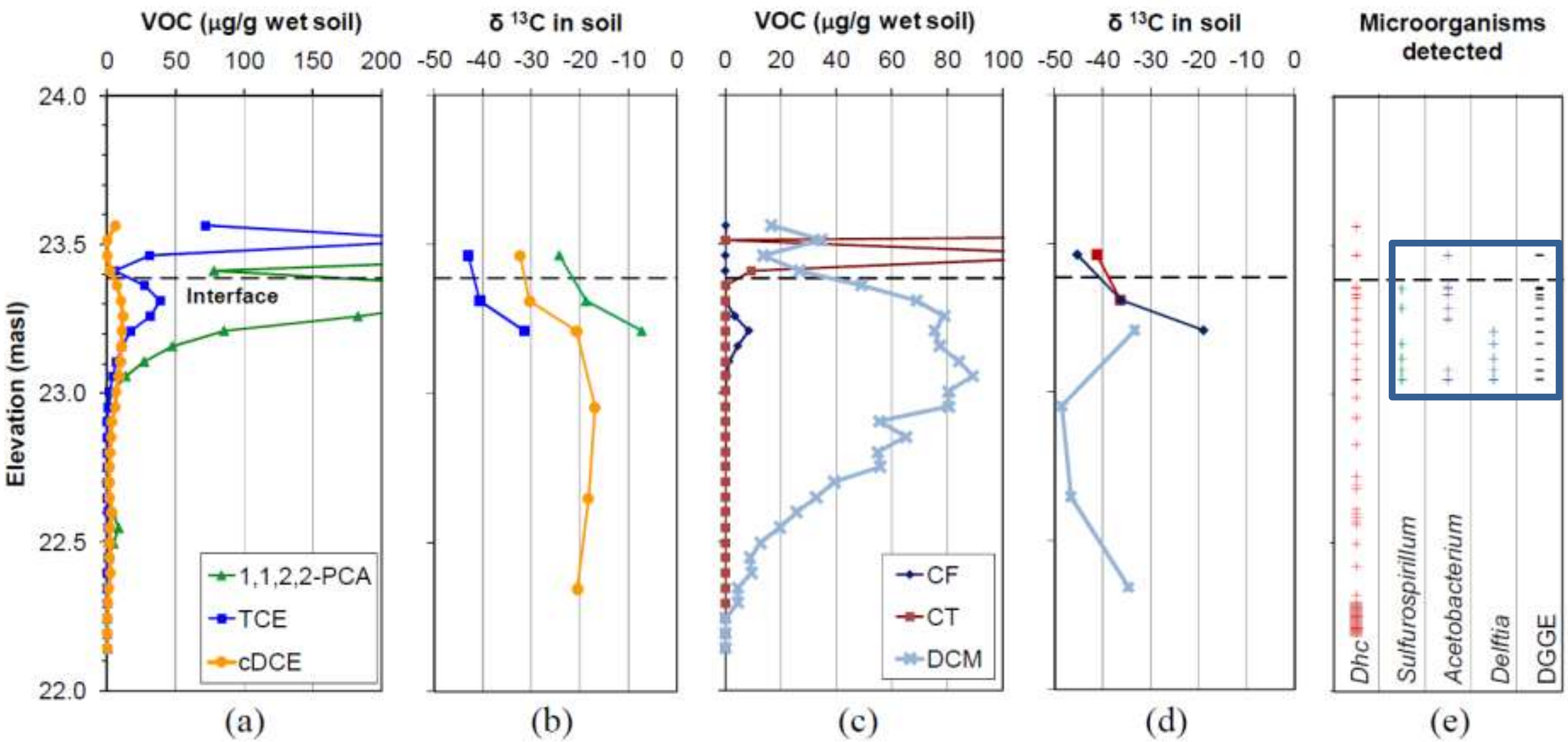
Low vertical hydraulic conductivity and apparent lack of fractures

Isotope Signatures of Parents and Potential Daughters Compounds at the Study Site

Compound	$\delta^{13}C$ (‰)	References
1,1,2,2-PCA	-33.04	(*1*, *2*)
PCE	-23.19 to -33.84	(*3*, *4*)
TCE	-24.45 to -31.90	(*3*-*5*)
CT	-38.6	(*6*)
CF	-45.3	(*6*)
DCM	~-50.0	(*7*)

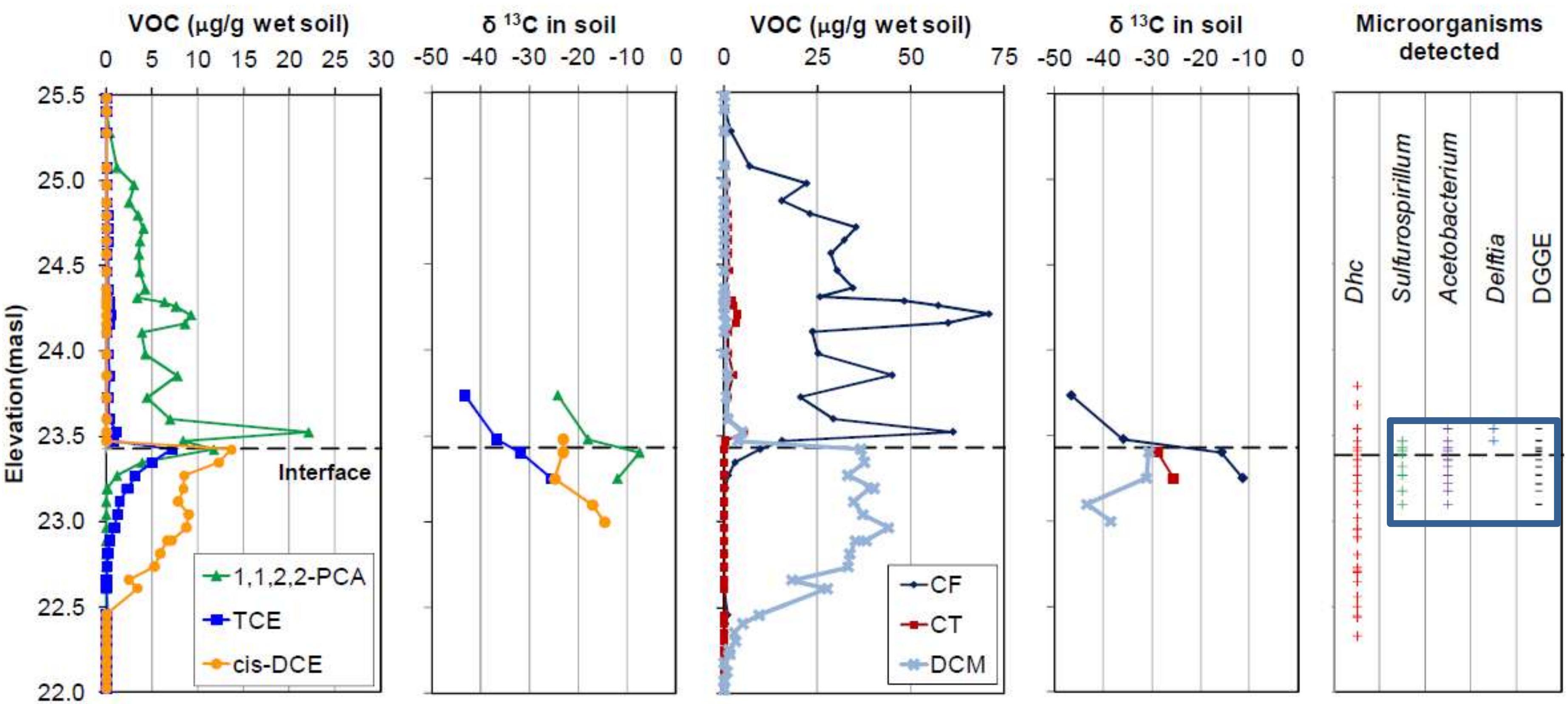
[VOC] + CSIA + Microbiology

C10

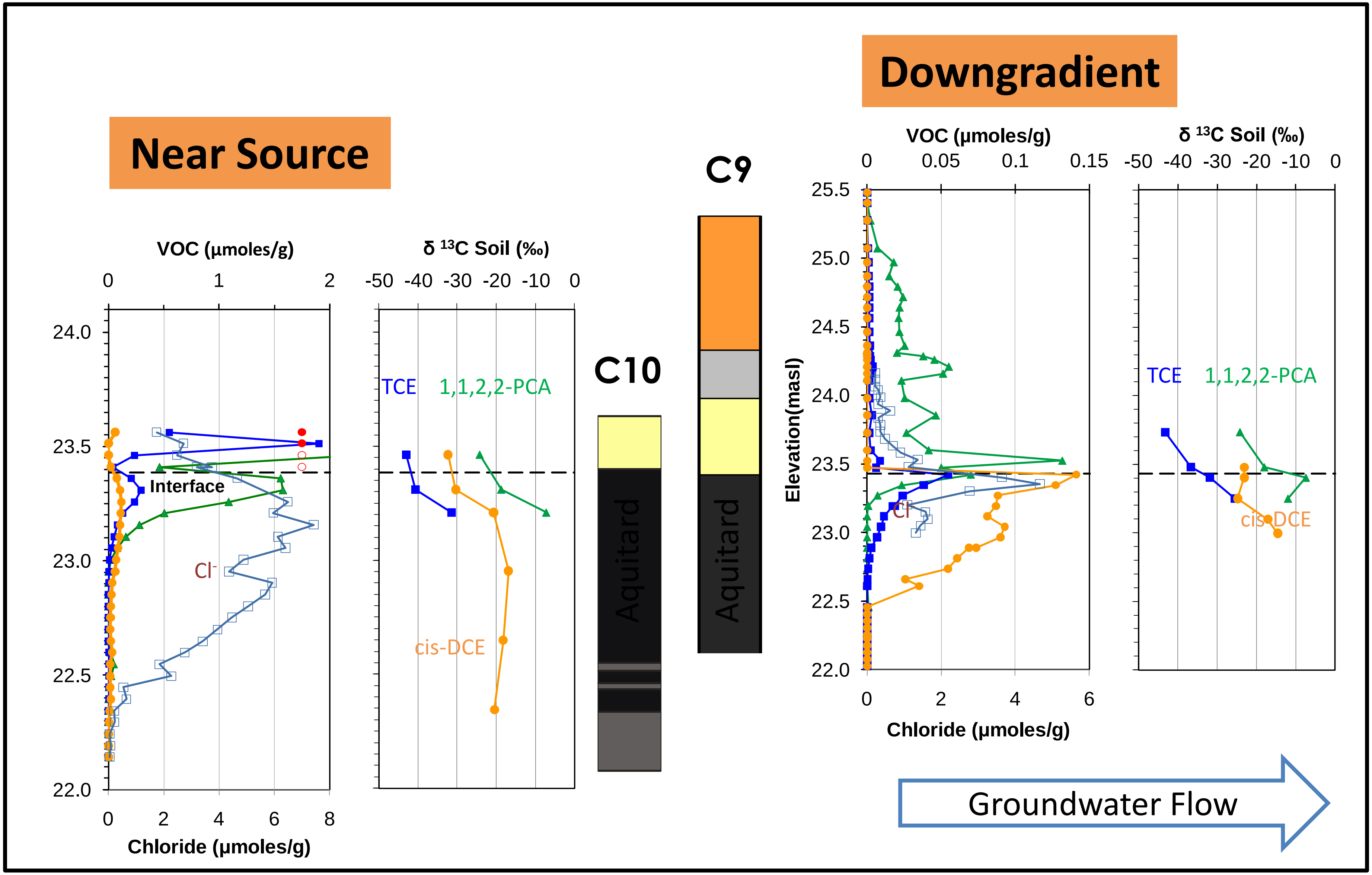


[VOC] + CSIA + Microbiology

C9



Sediment Core Samples – Comparison

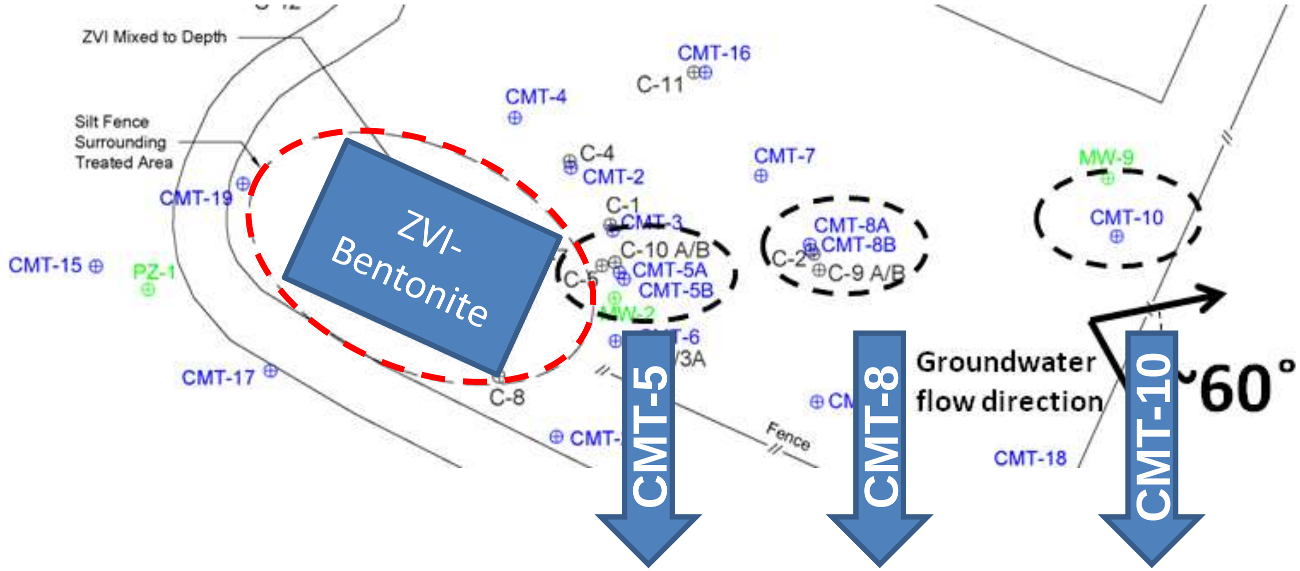


Aquitard vs. Aquifer

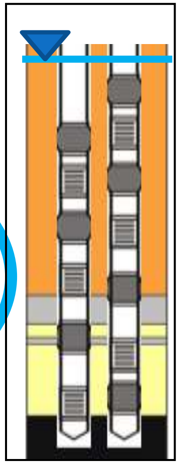
Up to here we saw that there is degradation in the aquitard.

What is going on in the aquifer?

Groundwater – Dissolved H_2



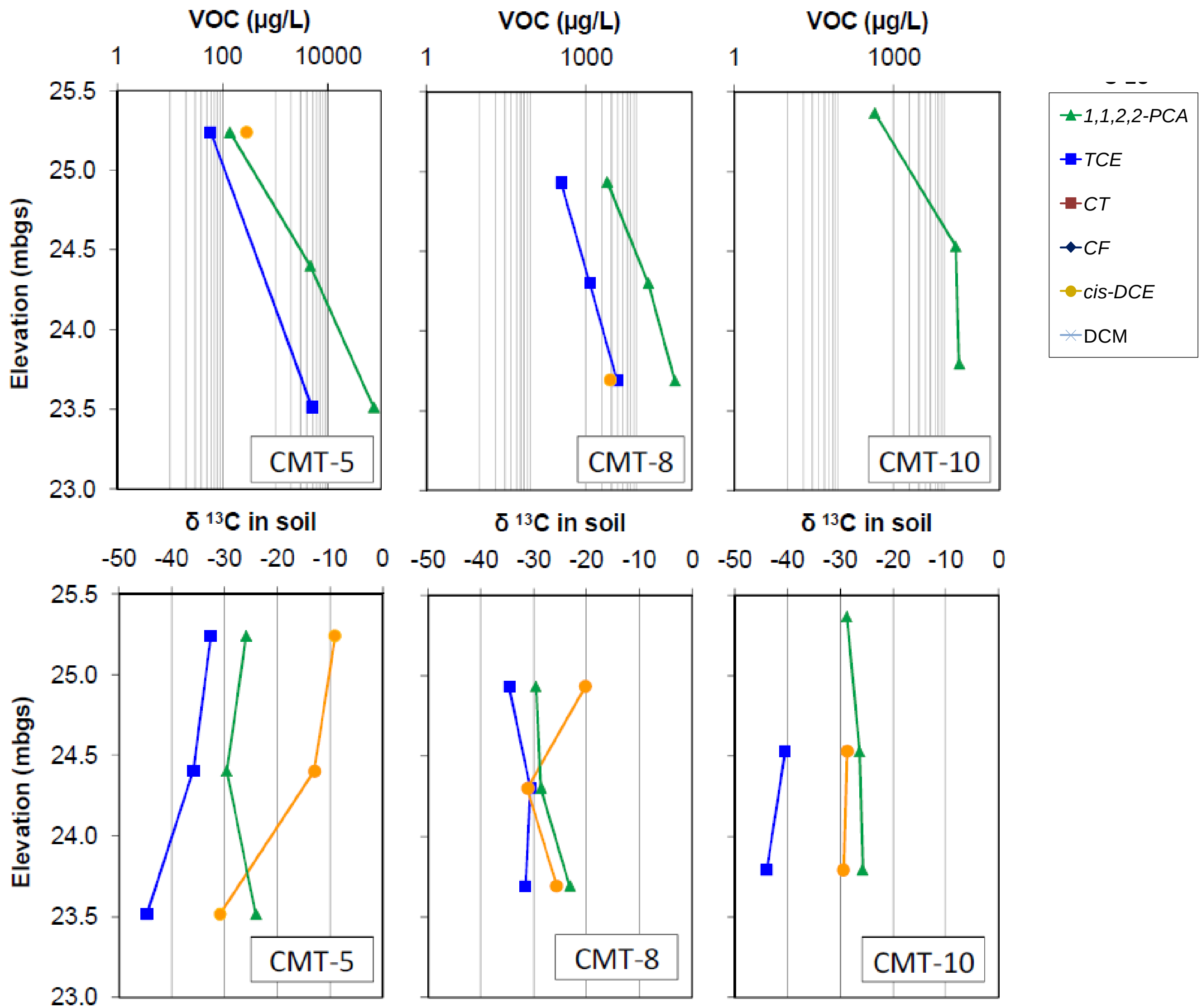
Approx. Elevation	CMT-15 [nM]	CMT-5 [nM]	CMT-8 [nM]	CMT-10 [nM]
25.5	<0.600	4.5	7.2	1.2
24.5	0.640	5.2	-	19
24.0	-	17	1100	-
23.5	-	17000	3400	-



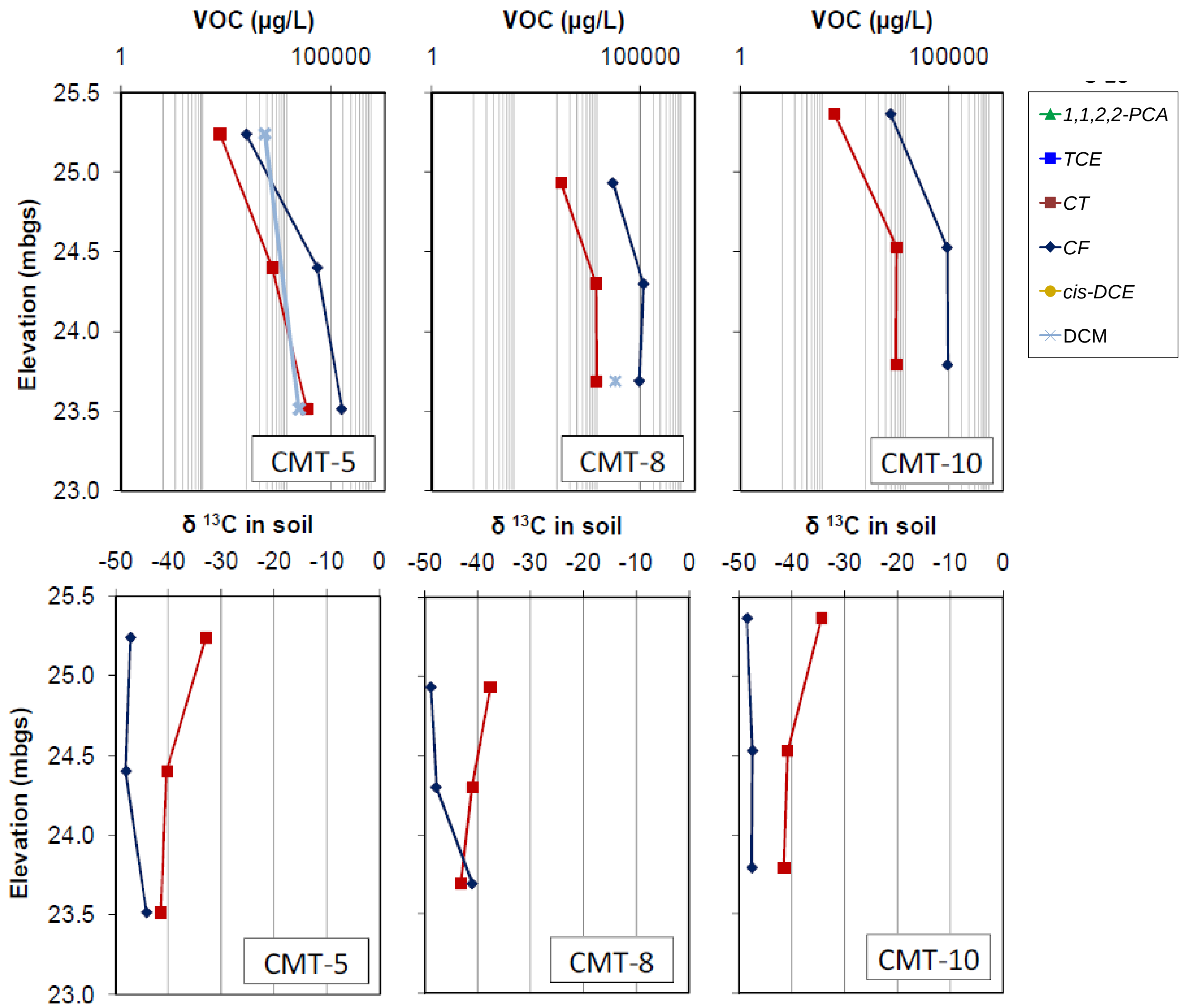
Groundwater – Redox Conditions

Locatior	Point	Elevation masl	Cl mg/L	NO_3^- mg/L	Fe(II) mg/L	SO_4^{2-} mg/L	Mg mg/L	TOC mg/L	Ethane µg/L	Ethene µg/L	H_2 nM	CH_4 µg/L
CMT-15	1	25.50	11	60	<1	5.2	0.051	<5	0.033	<0.01	<0.6	0.084
CMT-15	2	24.50	11	46	<1	8.6	0.046	<5	<0.01	0.016	0.64	0.32
CMT-5A	1	25.24	49	<0.5	14	1.7	0.083	<5	27	3.9	4.5	2800
CMT-5A	2	24.40	25	<0.5	1.9	<1	0.075	<5	23	3.9	5.2	960
CMT-5B	3	23.83	52	<0.5	1.8	1.2	0.35	<5	37	7	17	1600
CMT-5A	3	23.51	72	<0.5	4.8	2.5	0.46	5.9	37	6.3	17000	1000
CMT-8B	1	25.51	11	<0.5	5.4	1.7	0.016	<5	51	6.8	7.2	520
CMT-8A	1	24.93	11	<0.5	7.7	1.6	0.029	<5	32	4.7	12000	380
CMT-8A	2	24.30	14	<0.5	1.1	<1	0.074	<5	13	2.5	260	62
CMT-8B	3	23.99	34	1.2	1.4	1.2	0.19	<5	12	2.3	1100	42
CMT-8A	3	23.69	130	<0.5	<1	2.9	0.79	<5	6.2	3	3400	16
CMT-10	1	25.37	5.7	<0.5	1.4	1.9	0.01	<5	7	1.3	1.2	71
CMT-10	2	24.53	29	<0.5	2.2	<1	0.074	<5	2.8	0.75	19	8.6
CMT-10	3	23.79	49	<0.5	1.2	1.7	0.16	<5	0.47	0.28	?	5.1

[VOC] + CSIA, Groundwater- Chlorinated ethanes



[VOC] + CSIA, Groundwater- Chlorinated methane



Summary

1. Parent compounds dominate concentrations in aquifer
2. Daughter products dominate concentrations in aquitard
3. Cl^- in aquitard ~70× background

Summary

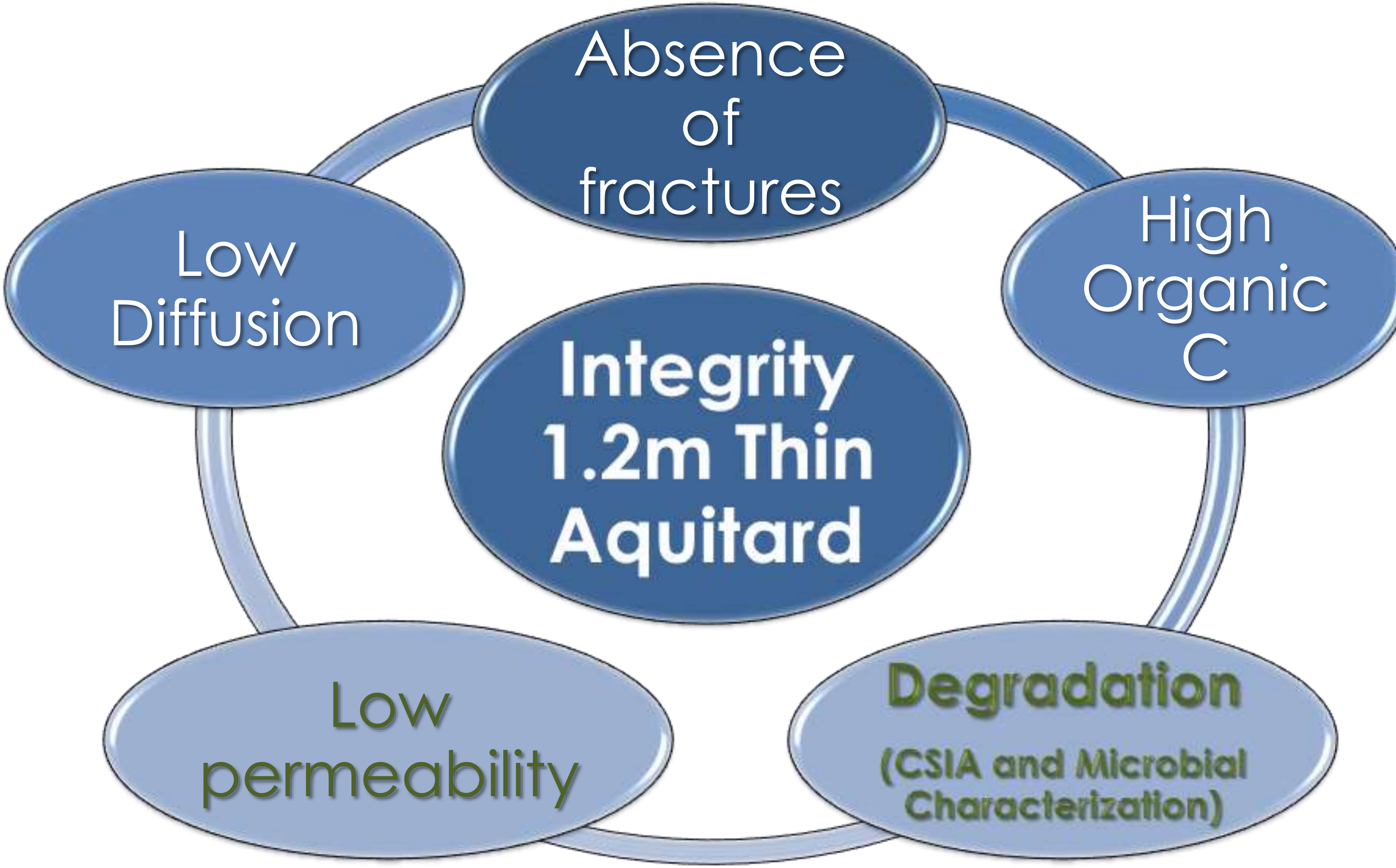
4

- CSIA – substantial fractionation occurs in the aquitard

5

- CSIA + microbial analyses: evidence of biodegradation within aquitard

Conclusion


Absence of fractures
High Organic C
Low Diffusion
Integrity 1.2m Thin Aquitard
Low permeability
Degradation
(CSIA and Microbial Characterization)

Application of the Waterloo Membrane Sampler (WMS) for Isotope Ratio Analysis in Vapor Samples

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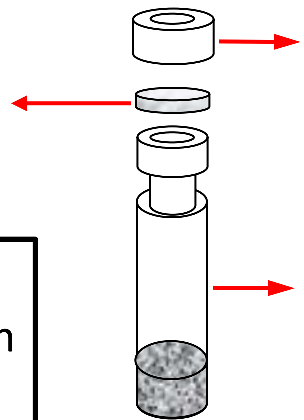
University Consortium for Field-Focused Groundwater Contamination Research Program for Annual Progress Meeting: June 12-14, 2012 The Arboretum, University of Guelph

Waterloo membrane sampler (WMS)



Turned upside down before use

WMS sampler

$$C_0 = \frac{kM}{t}$$

***C_0* - analyte concentration in the studied medium**

***k* - calibration constant (time/volume)**

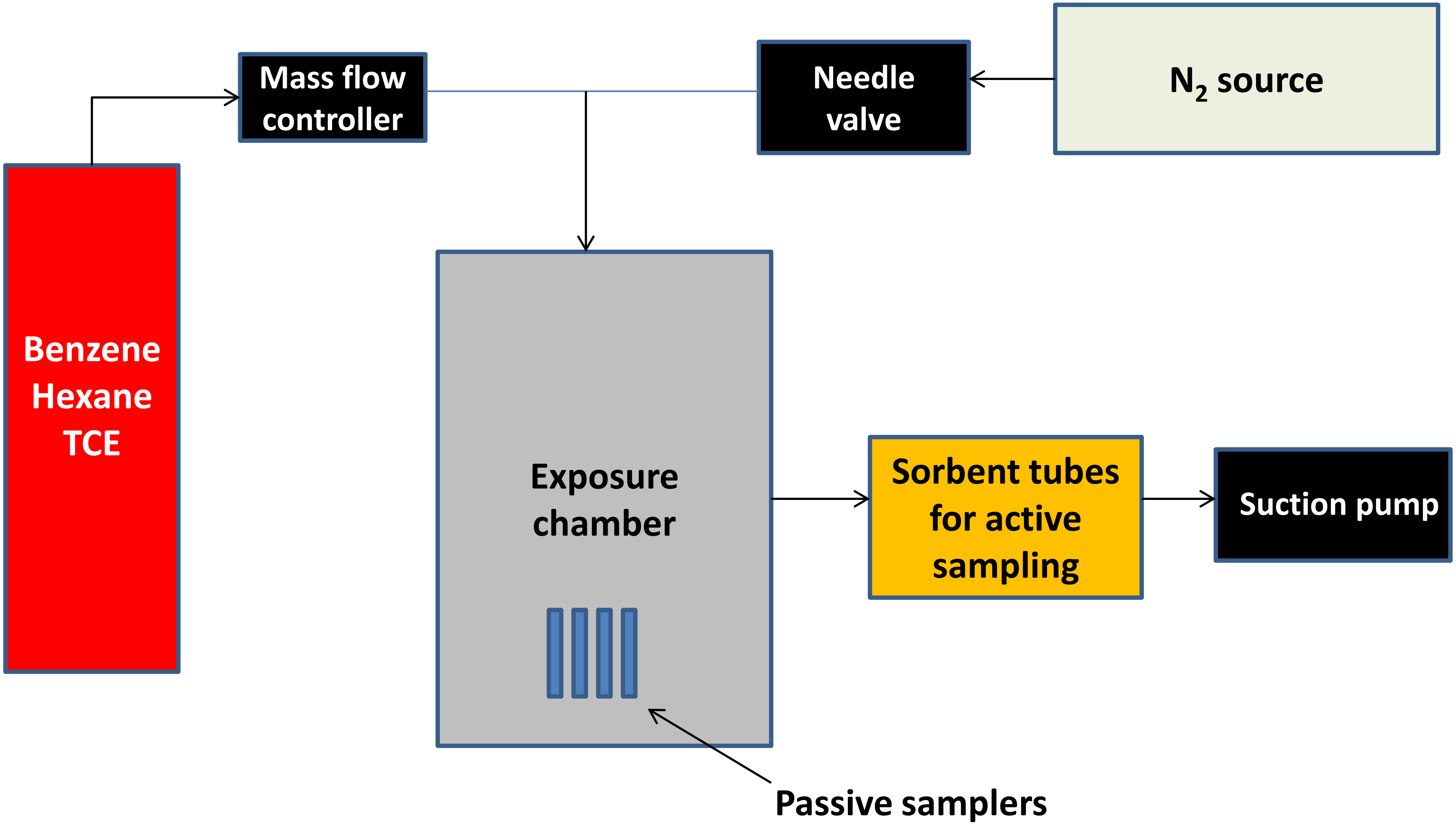
***M* - collected mass of the analyte**

***t* - time of exposure**

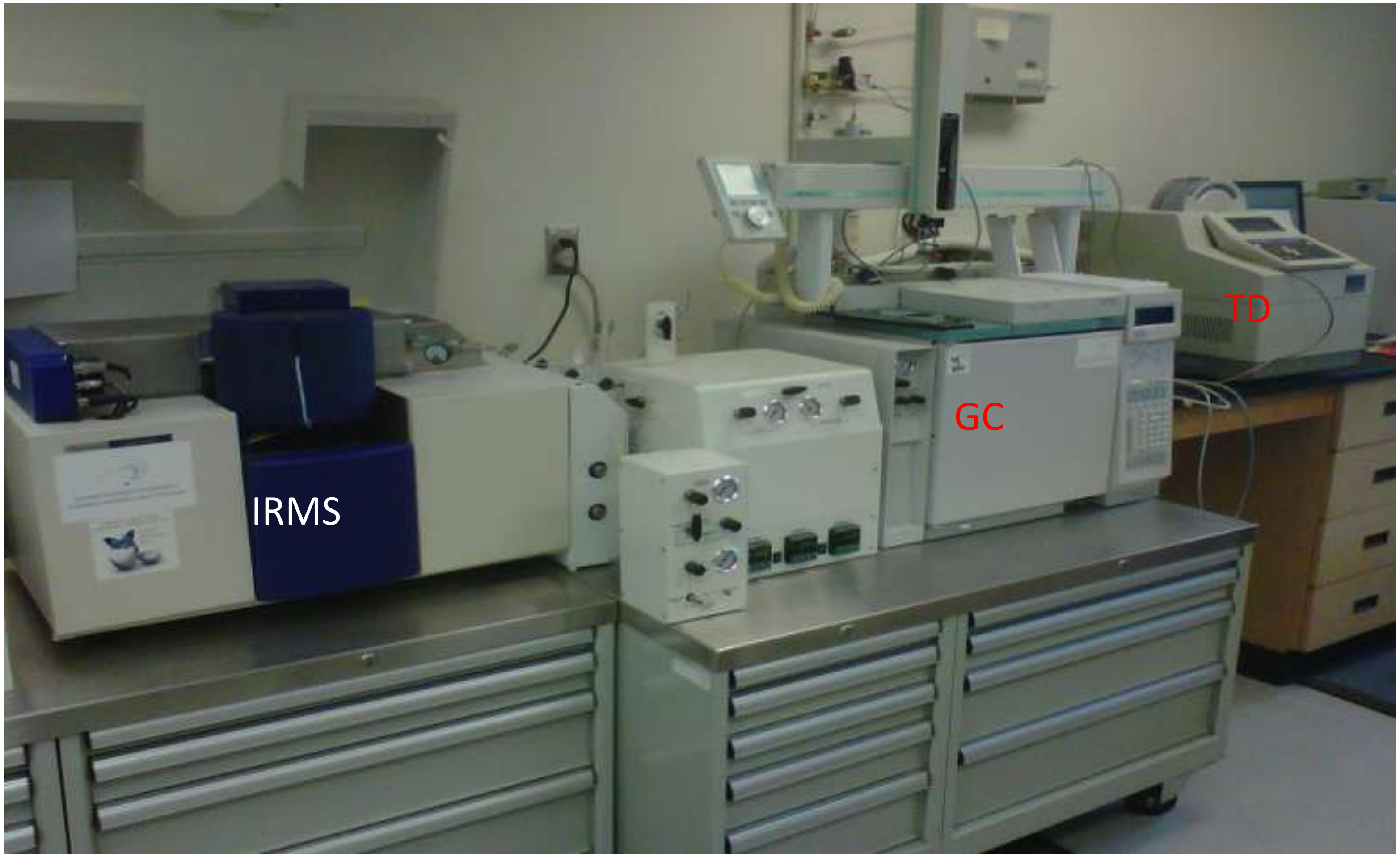
WMS and CSIA

- **In order to introduce the required amount of the contaminant necessary in the CSIA analysis, the WMS was combined with thermal desorption (TD)**
- **WMS was employed under controlled conditions for measurements of carbon isotope composition ($\delta^{13}C$) of analytes of interest that are contained in a standard gas mixture**

Experimental set-up



TD-GC-IRMS



Preliminary experiments

- **Target contaminants investigated: benzene, hexane and TCE**

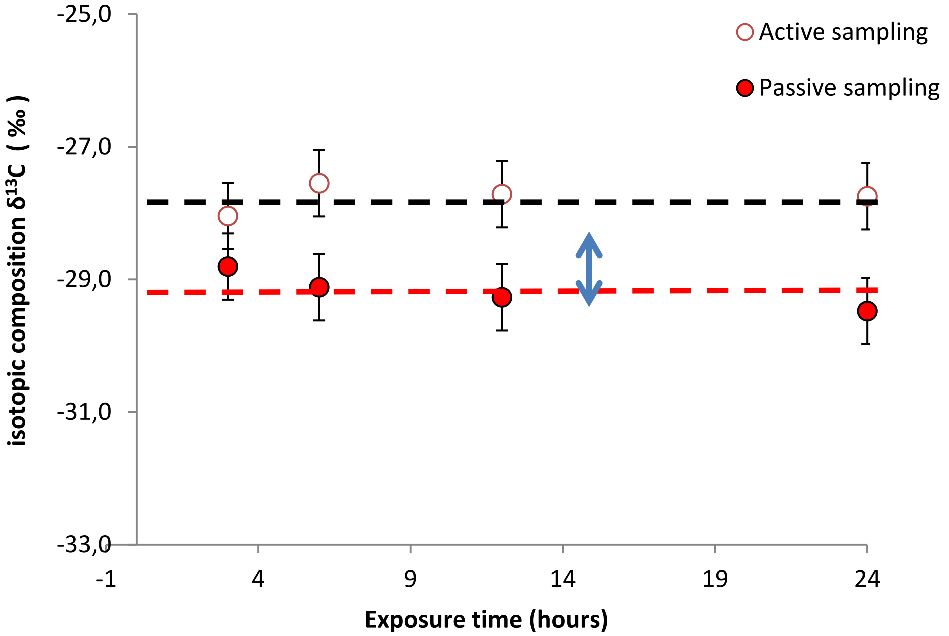
- **Exposure times: 3, 6, 12 and 24 hours**

- **Concentration of the analytes in the exposure chamber was adjusted for various exposure times (for each exposure time the target amount collected by the passive sampler was the same)**

Results

	Passive sampling	Active sampling	Passive sampling	Active sampling	Passive sampling	Active sampling
Time of exposure	HEXANE	HEXANE	BENZENE	BENZENE	TCE	TCE
(h)	$\delta^{13}C$	$\delta^{13}C$	$\delta^{13}C$	$\delta^{13}C$	$\delta^{13}C$	$\delta^{13}C$
3	-28.8	-28.0	-31.1	-30.4	-32.5	-31.3
6	-29.1	-27.6	-29.0	-27.6	-32.1	-30.8
12	-29.3	-27.7	-29.0	-27.8	-32.8	-31.5
24	-29.5	-27.7	-29.9	-28.2	-32.4	-31.3
Average	-29.2	-27.8	-29.8	-28.5	-32.4	-31.2
Standard deviation	0.3	0.2	0.5	0.3	0.3	0.3
Difference between passive and active sampling	-1.4		-1.3		-1.2	

HEXANE

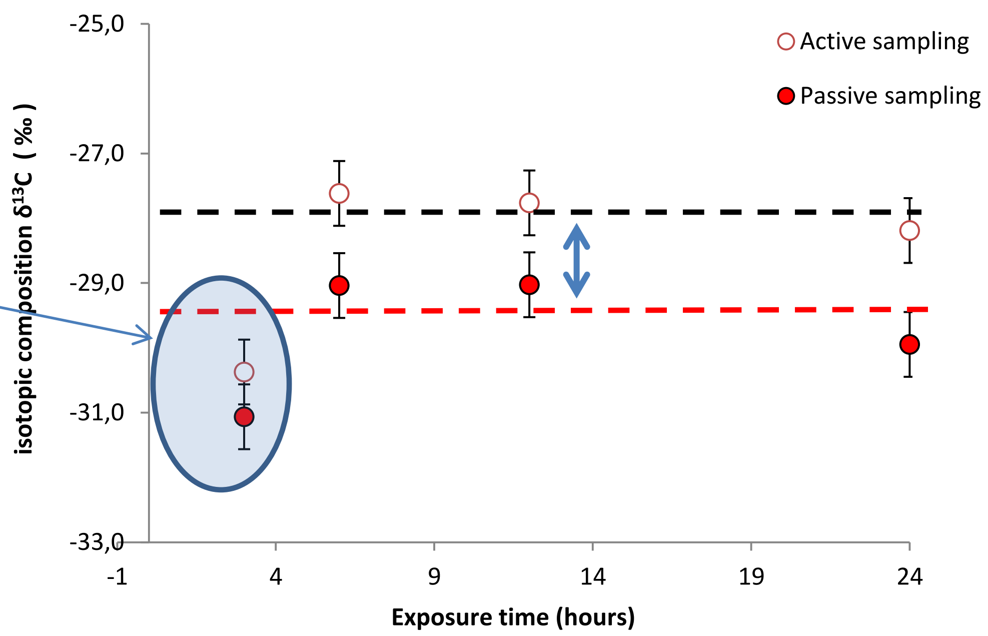


All the values obtained for passive and active sampling are in the range of the error of 0.5 ‰

The difference in between the average values for passive and active sampling is around 1.4 ‰

BENZENE

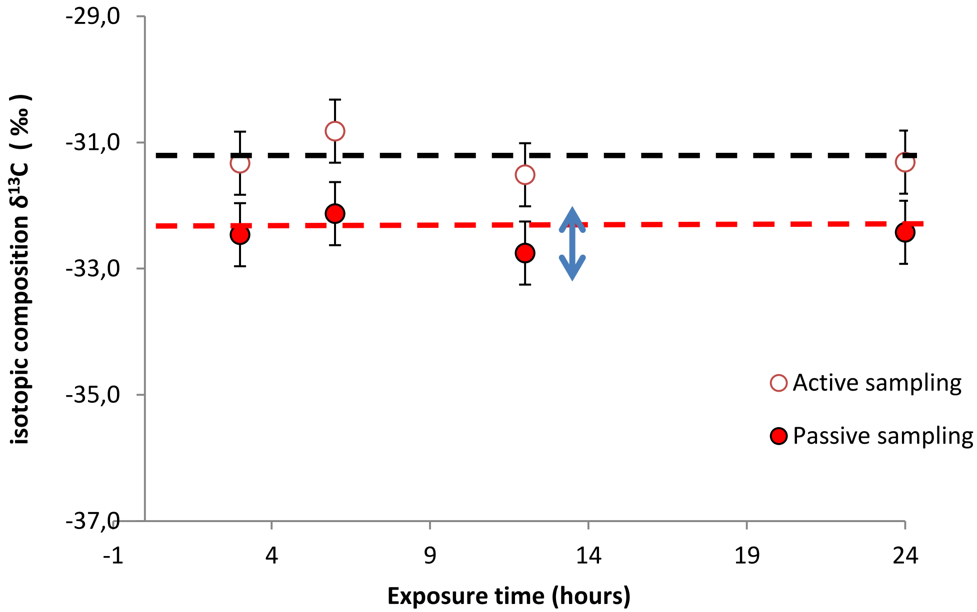
This 3 h exposure should be repeated



Excluding the dataset for 3h exposure again the values obtained for passive and active sampling are in the range of the error of 0.5 ‰

The difference in between the average values for passive and active sampling is around 1.5 ‰

TCE



As for benzene and hexane, the TCE values obtained for passive and active sampling are in the range of the error of 0.5 ‰

The difference in between the average values for passive and active sampling is around 1.2 ‰

Conclusions

- **The results are consistent and the standard deviations for all the compounds are below the common error accepted (0.5 ‰)**
- **The difference between the values from passive and active sampling seems to be practically constant in the timeframe studied**
- **The results indicate that WMS could be a useful tool for fingerprinting applications based on CSIA**

Future work

- **Perform the same experiments for longer exposure times**
- **Determine the applicability of the method to real field projects**