

# Compound Specific Stable Isotope Analyses (CSIA)

*Identification of multiple sources of chlorinated solvents of a groundwater plume*



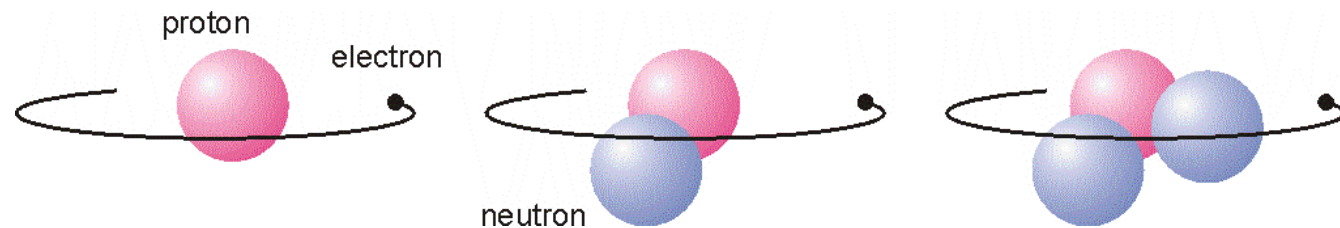
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*Patrick Jacobs, Tauw, Germany*  
*Siegmund Ertl, Hydroisotop, Germany*  
*Ralf Engelhardt, Tauw, Germany*  
*Frank Volkering, Tauw, The Netherlands*  
*Teresa Roza, Grupo EPA, SP, Brasil*  
*Sérgio Rameh, Grupo EPA, SP, Brasil*  
*Aline Nagata, Grupo EPA, SP, Brasil*

# Isotopes - Fundamentals

- Isotopes = species of the same element (same number of protons and electrons) but with a different number of neutrons.
- Chemical properties are virtually the same for isotopes of the same element but the mass differs according to the number of nucleons.
- Most chemical elements have two or more isotopes which may be stable or radioactive, e.g.:
  - Carbon:  $^{12}\text{C}$  (stable, 12 u),  $^{13}\text{C}$  (stable, 13 u),  $^{14}\text{C}$  (radioa., 14 u)
  - Hydrogen:  $^1\text{H}$   $^2\text{H}$   $^3\text{H}$



# Stable Isotopes - Background

- Specialized isotope laboratory separate different chemical species (e.g. PCE, TCE, DCE, VC) from a groundwater sample and subsequently determine the isotope ratios as  $^{13}\text{C}/^{12}\text{C}$  and/or  $^{37}\text{Cl}/^{35}\text{Cl}$
- Isotope ratios are expressed in ‰ relative to a reference standard

$$\delta_{sample} = 1000 \cdot \frac{R_{sample} - R_{standard}}{R_{standard}}$$



# Stable Isotopes - Background

- $^{13}\text{C}$ -PCE of  $-23.5\text{‰}$  means:  $^{13}\text{C}/^{12}\text{C}$  in the sample is 2,35 % lower than in the reference standard.

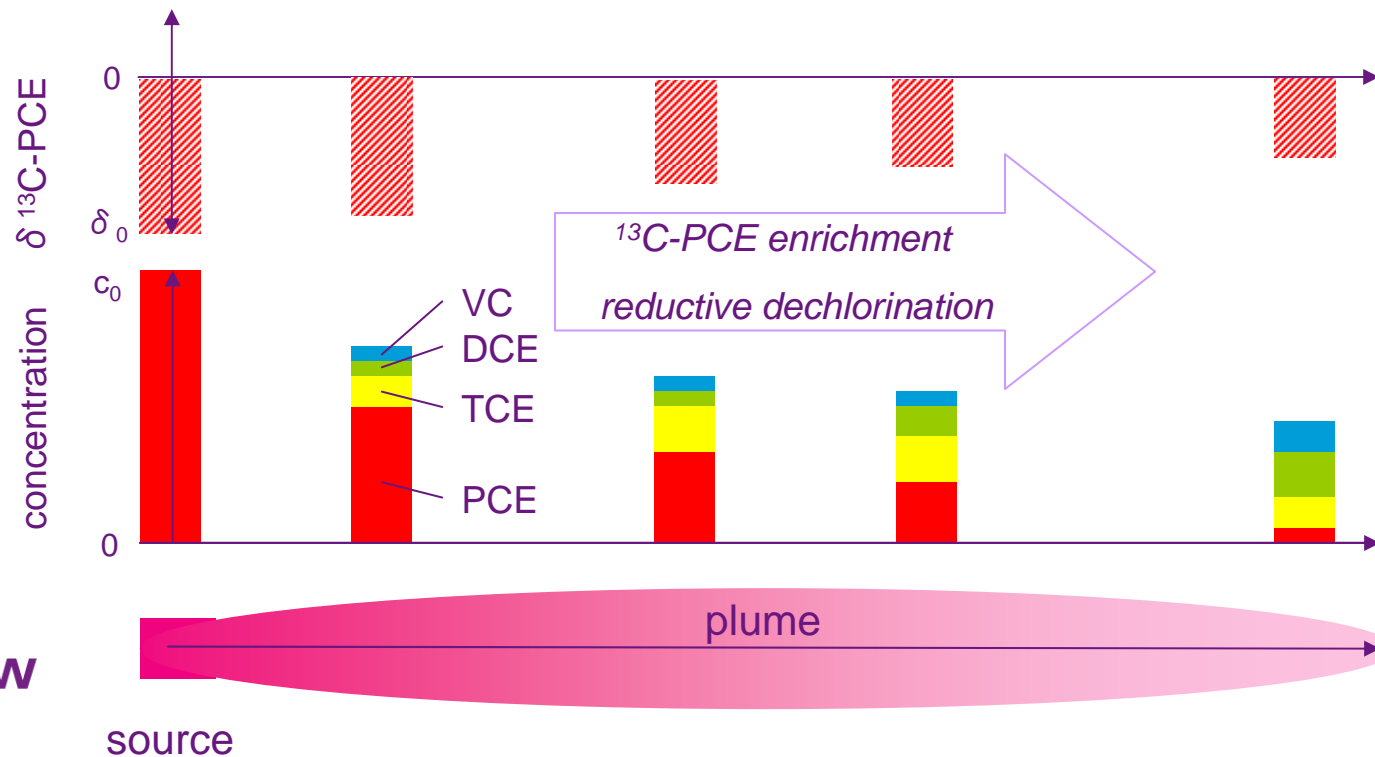
**$^{13}\text{C}$  standard:** VPDB (Vienna Pee Dee Belemnite); the ratio  $R=^{13}\text{C}/^{12}\text{C}=0,0112372$  is defined by IAEA (International Atomic Energy Agency)

**$^{37}\text{Cl}$  standard:** SMOC (Standard mean ocean chlorine) the ratio  $R=^{37}\text{Cl}/^{35}\text{Cl}=0,2422$  is defined by IUPAC (International Union of Pure and Applied Chemistry; Coplen 2002)



# Isotopic ratios in environmental samples

- Isotopic ratios are a function of the starting material and its manufacturing process.
- Stable isotope ratios change in systematic ways during the course of biodegradation or other processes.



# Compound Specific Stable Isotope Analysis

- CSIA measures these small changes in isotopic ratios very precisely.
- Those changes can be exploited to gain robust information about the source, transport, and fate of a compound.



# Analytical methods used

- $\delta^{13}\text{C}$  of chlorinated hydrocarbons and ethene:

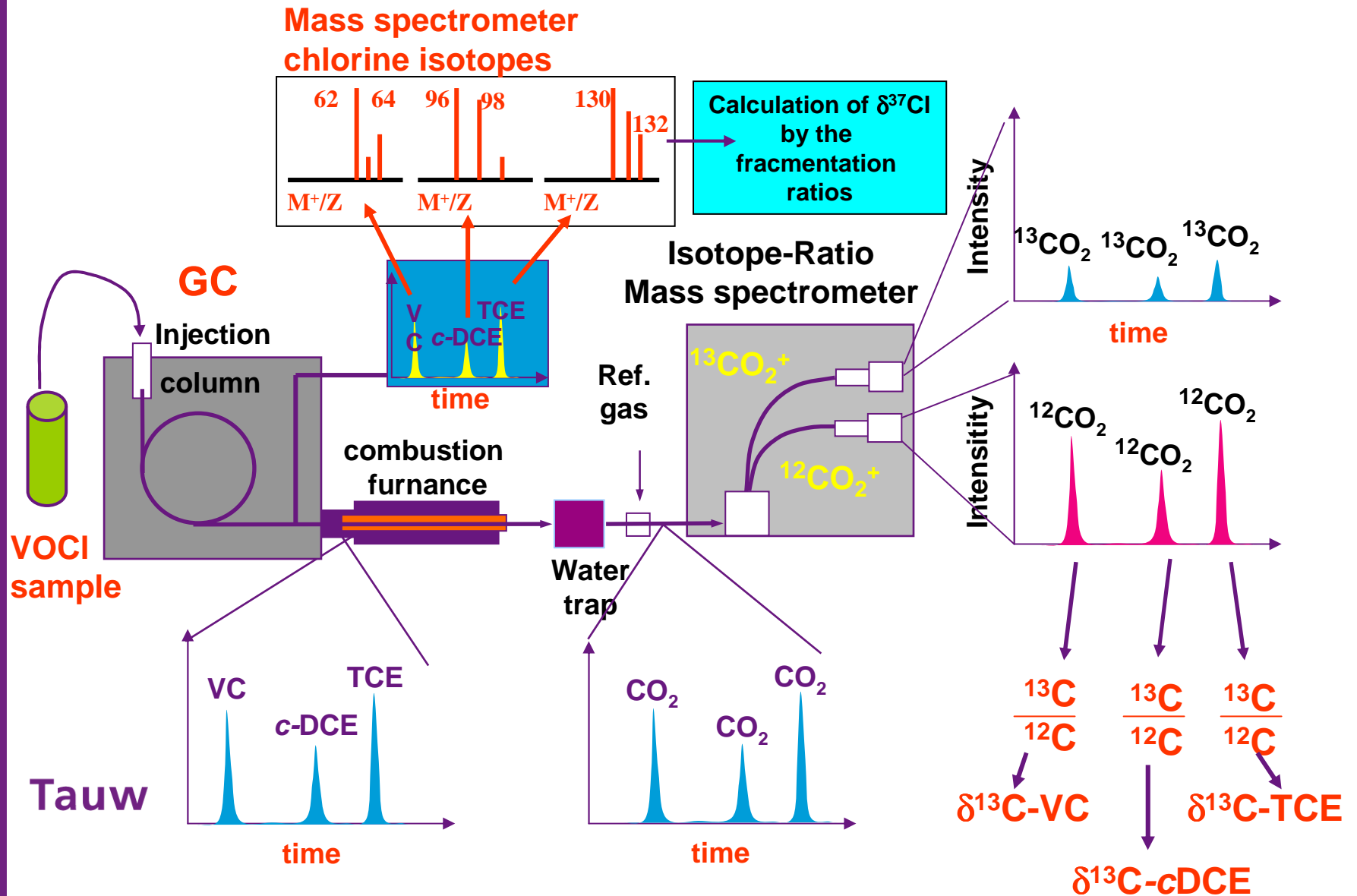
Purge-and-Trap and **GC Combustion Isotope Ratio Mass Spectroscopy (P&TGC-C-IRMS)**

- $\delta^{37}\text{Cl}$  of PCE:

Purge-and-Trap and **GC Mass Spectroscopy (P&T-GC-MS)**.

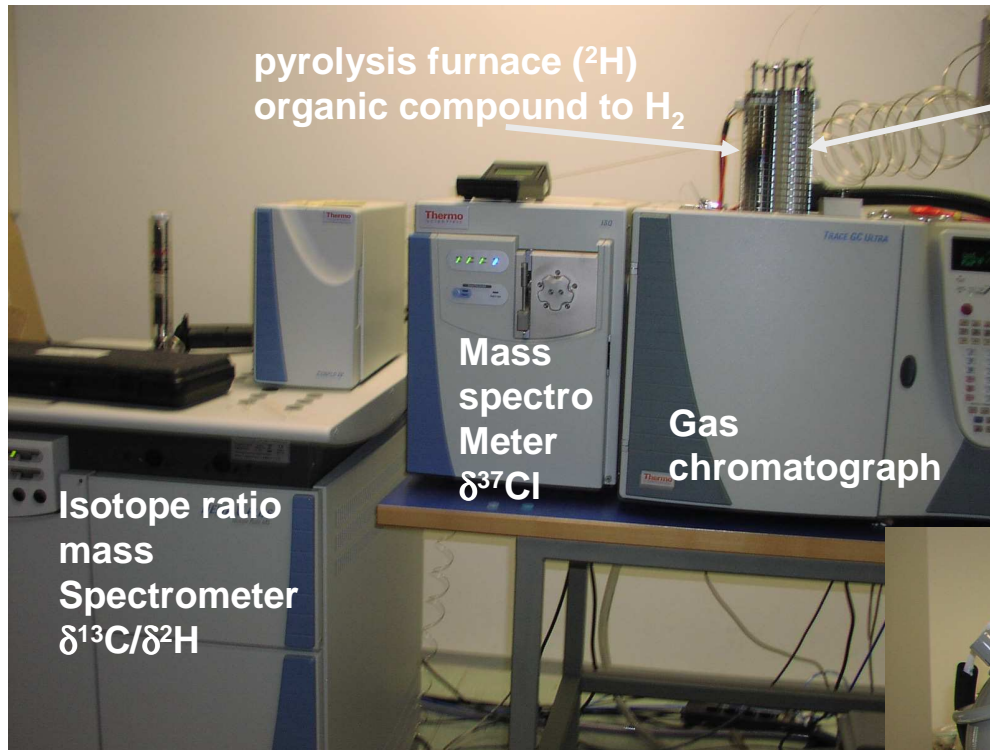


# Analytical methods used





# Analytical methods used



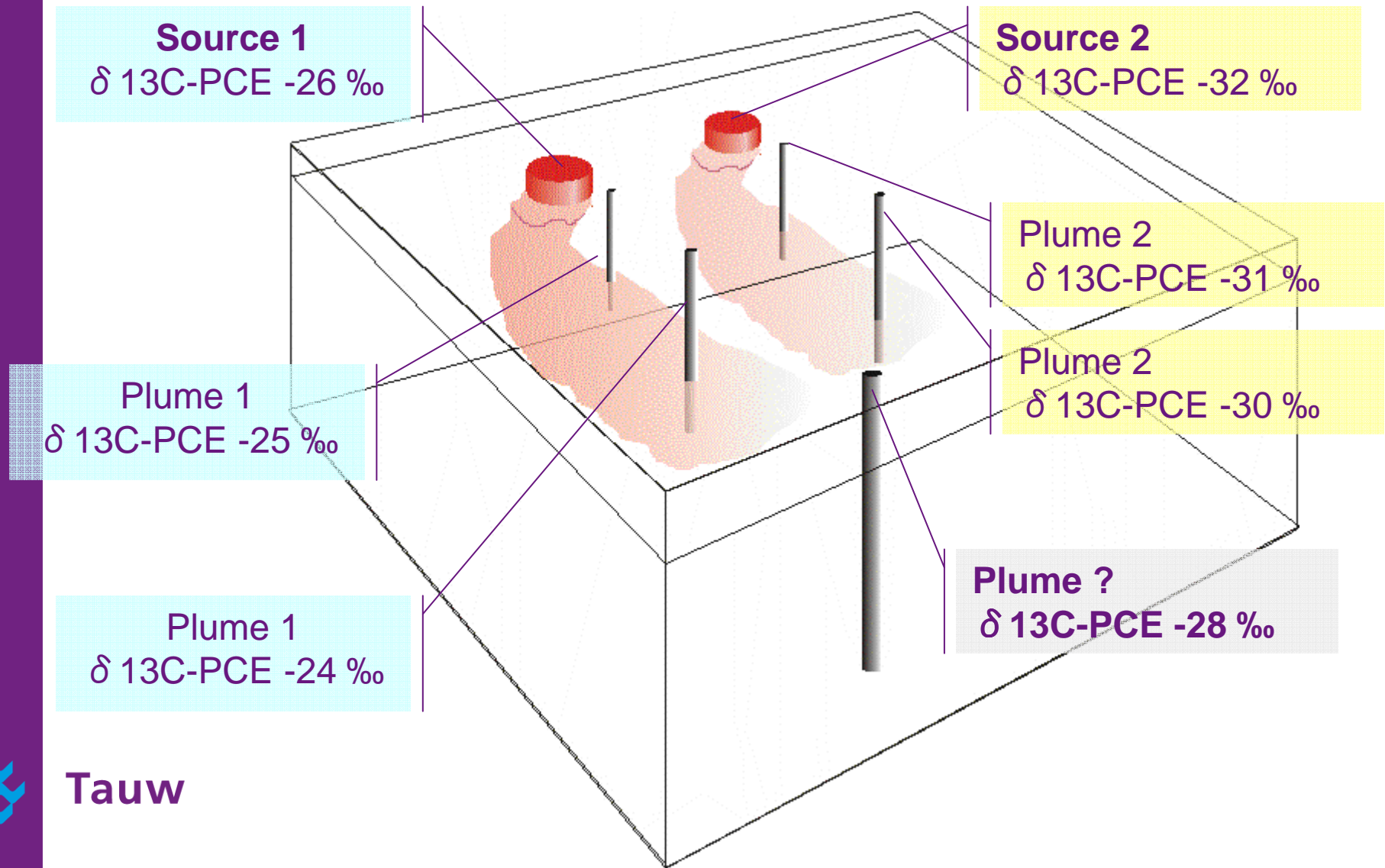
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# CSIA - application

- CSIA can give evidence which type of substance has been spilled.
- CSIA can reveal whether or not microbial or abiotic degradation of organics are taking place.
- CSIA can help identify multiple sources of the same substance and the respective plumes.



# Forensic approach



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# Example study

- The CSIA approach as shown was applied successfully on a site in Brazil.
- For the sake of confidentiality, however, the example given here does not present the real site. The example details the technical approach and data interpretation.



# Example site settings



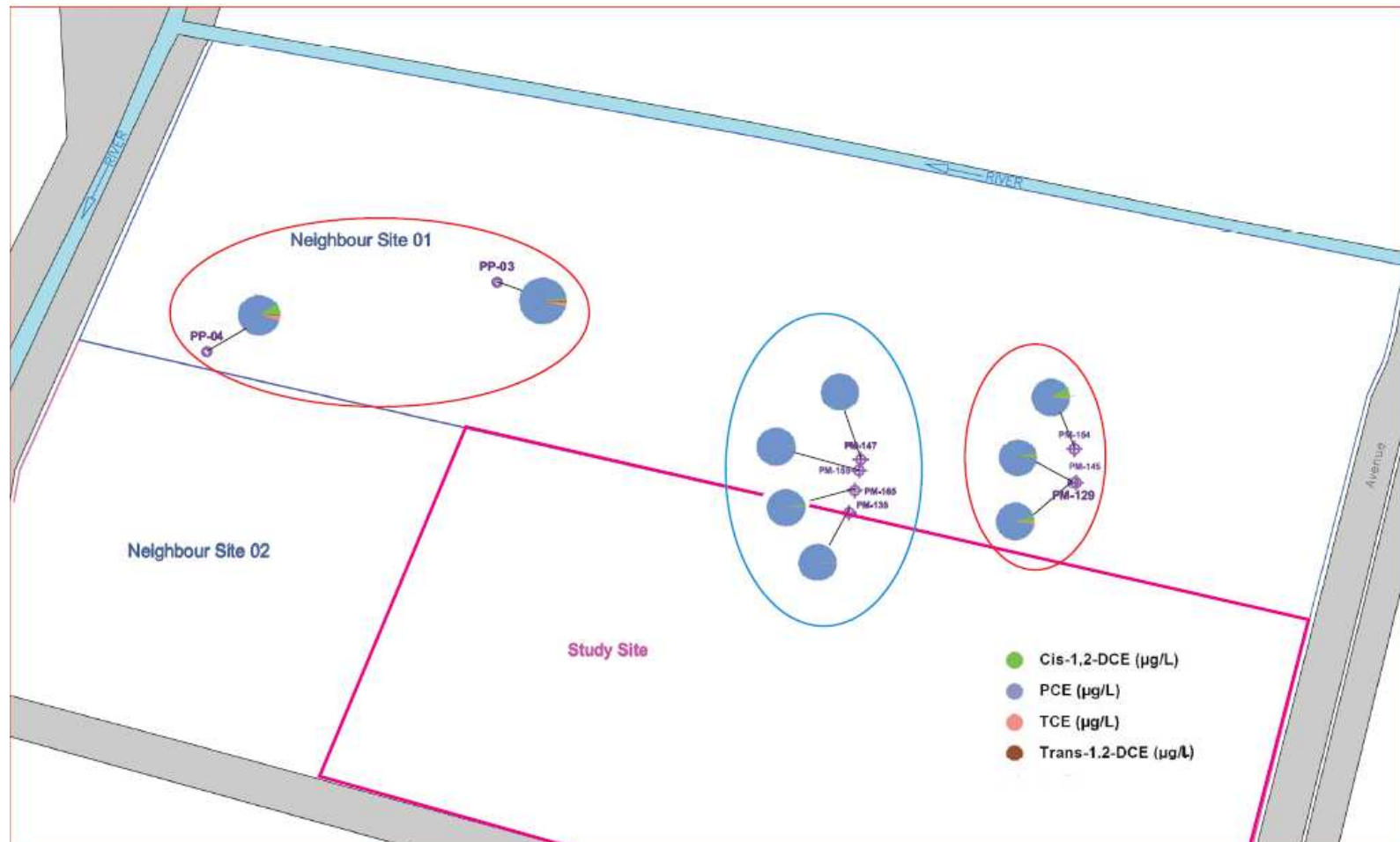
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# Example site settings



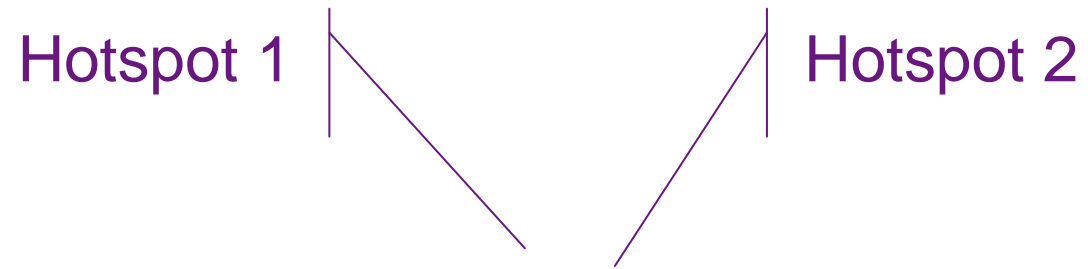
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# Example site settings



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# Cross section



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# Interpretation

- **First thesis:**
  - Hotspot 1 = source
  - Hotspot 2 = plume emanating from Hotspot 1
  - Contamination of downstream deep wells = plume emanating from Hotspot 1
- Extensive transport modeling (FEFLOW) does not provide satisfactory explanation for contaminant distribution
  - Contaminant transport not directed to Hotspot 2 nor to deep well!
  - Comparably negligible contamination in intermediate aquifer!

→ First thesis not plausible!

→ **Second thesis:** multiple sources with uncertain contribution to plumes

How to falsify first thesis?

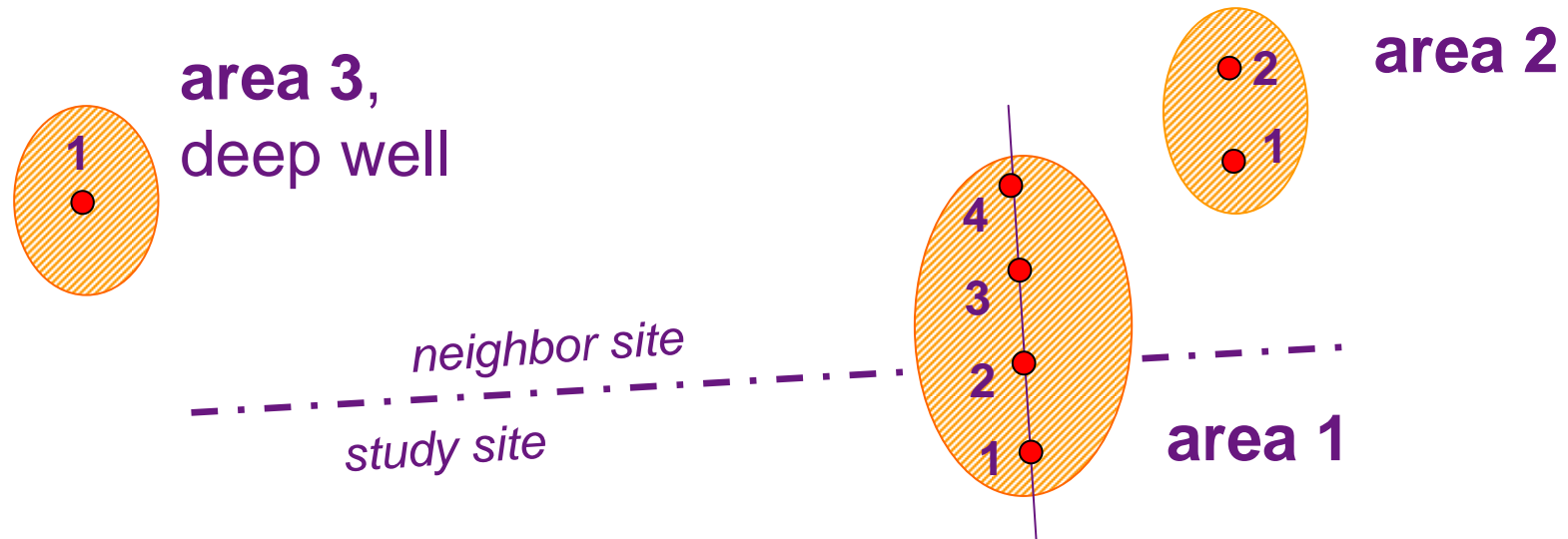
How to verify the second thesis?

} → **CSIA**



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# Investigation Concept

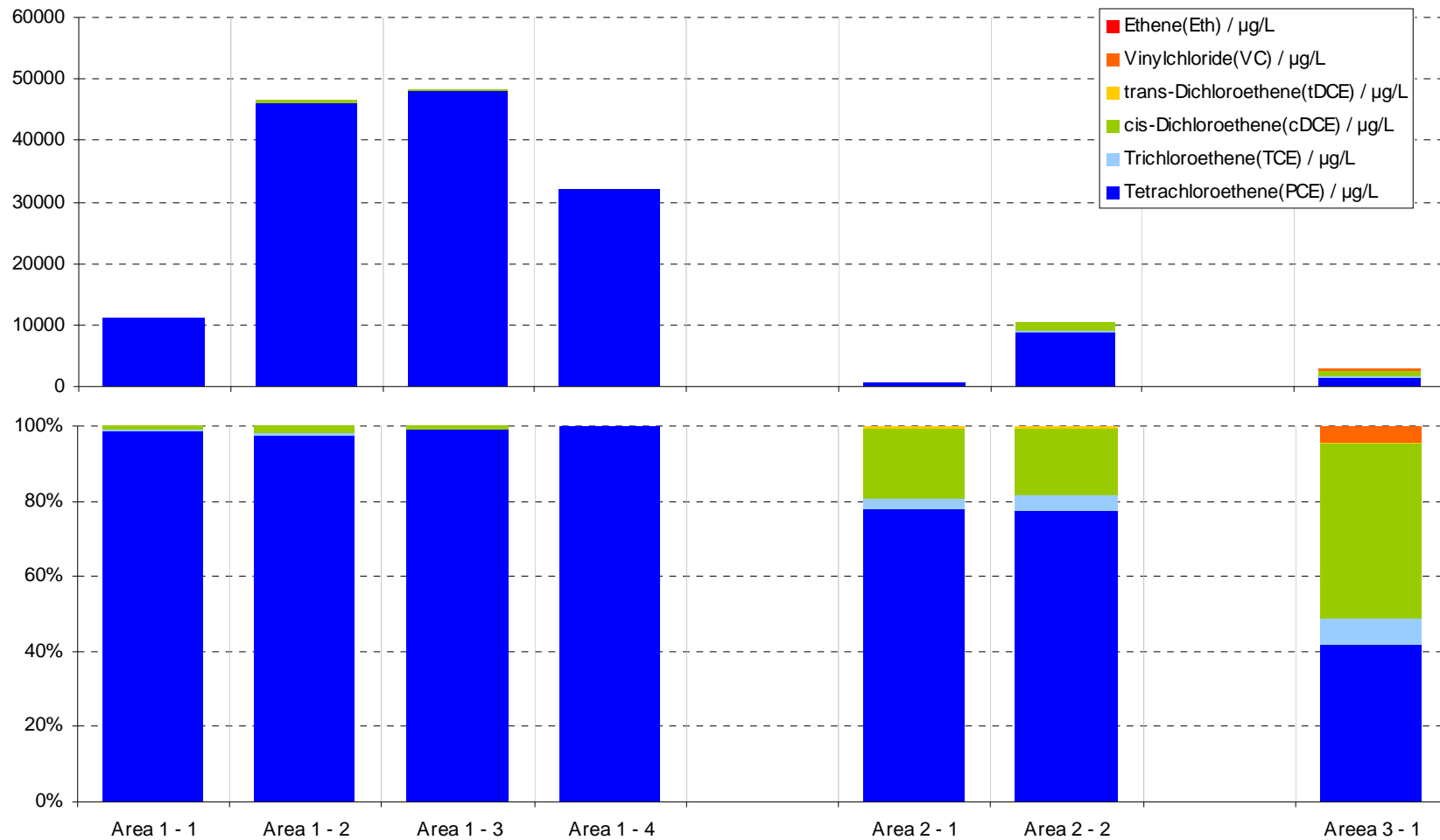


	$\delta^{13}\text{C}$ (PCE-VC + Eth)	$\delta^{37}\text{Cl}$ (PCE)
area 1 - 1	✓	✓
area 1 - 2	✓	
area 1 - 3	✓	
area 1 - 4	✓	✓
area 2 - 1	✓	✓
area 2 - 2	✓	
area 3 - 1	✓	✓



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# VOCI concentrations: totals and percentage



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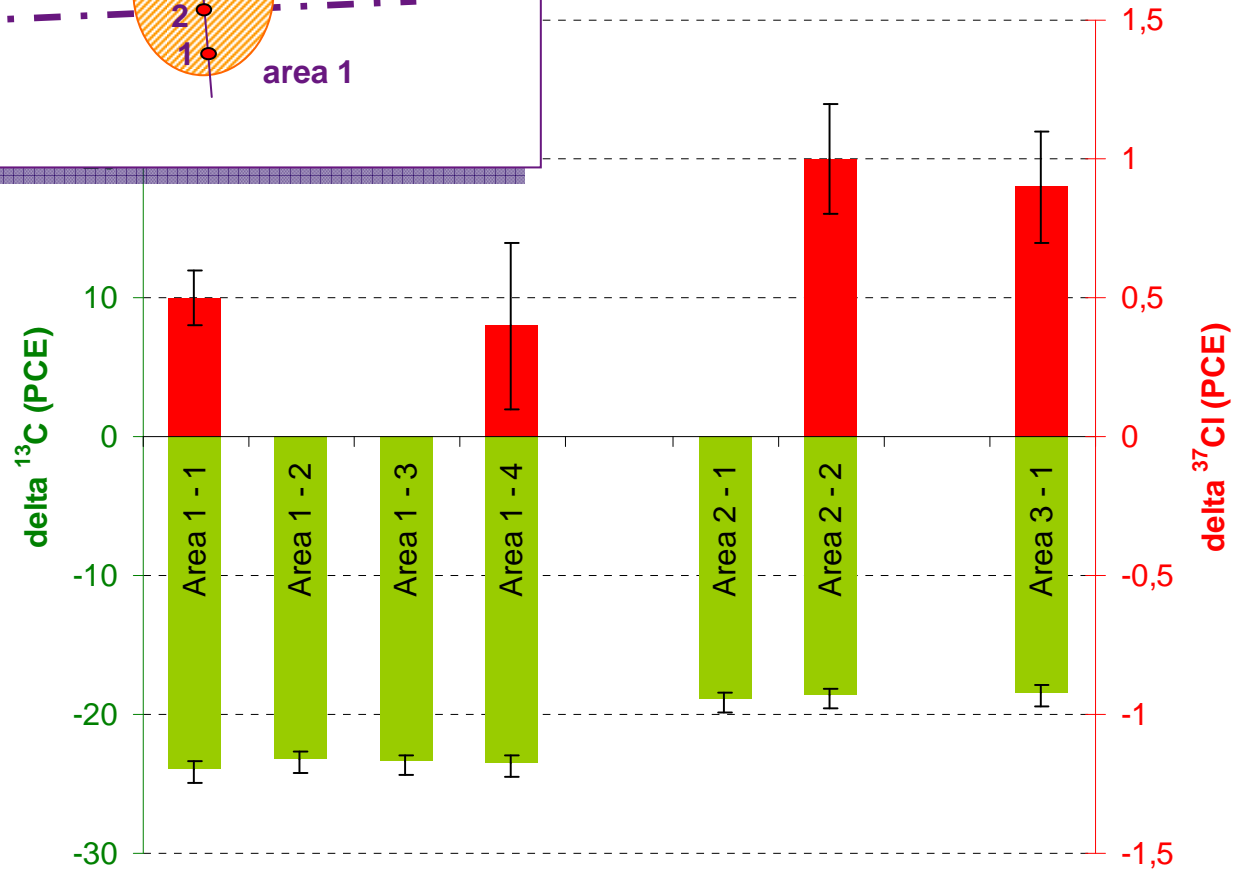
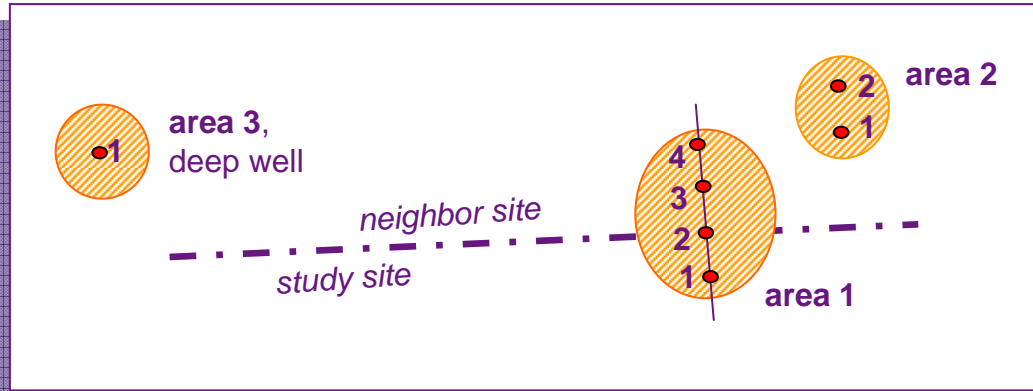
~ no degradation

weak d.

moderate d.

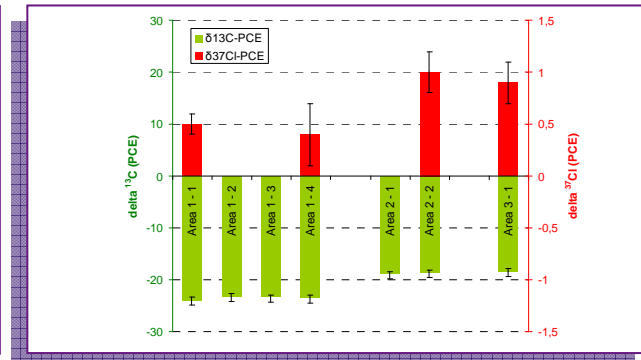


# CSIA results



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# CSIA results



## Observation:

- Isotopic fingerprints within area 1 consistent
- Isotopic fingerprints of area 2 and area 3 are significantly different from area 1

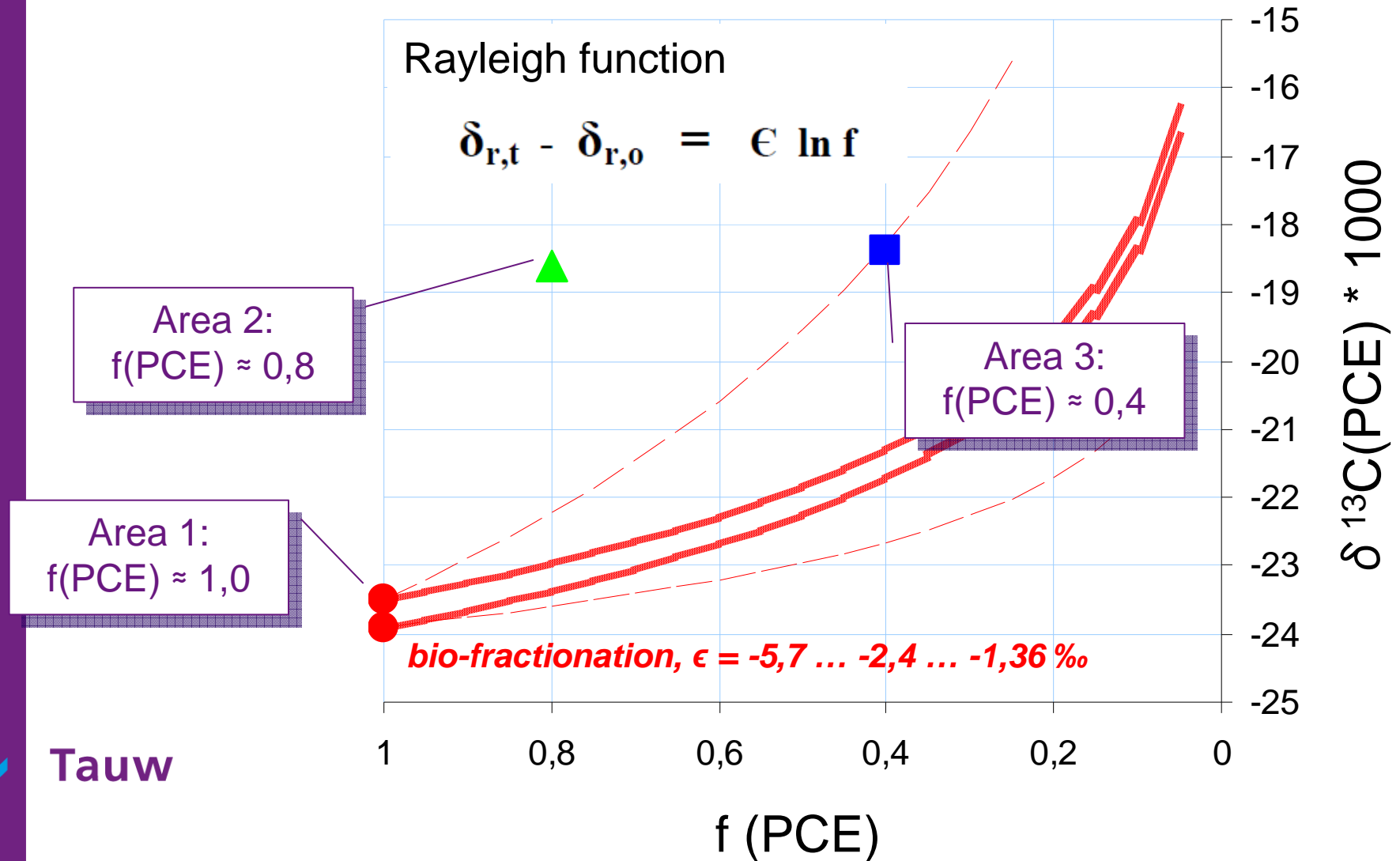
## Conclusion:

- Contamination in area 1 most likely has only one common source
- PCE in area 2 and in area 3 are heavier (less negative  $\delta^{13}\text{C}$ ) but:
  - this is not necessarily due to different sources!
  - Also fractionation during biodegradation depletes  $^{12}\text{C}$  over  $^{13}\text{C}$ !

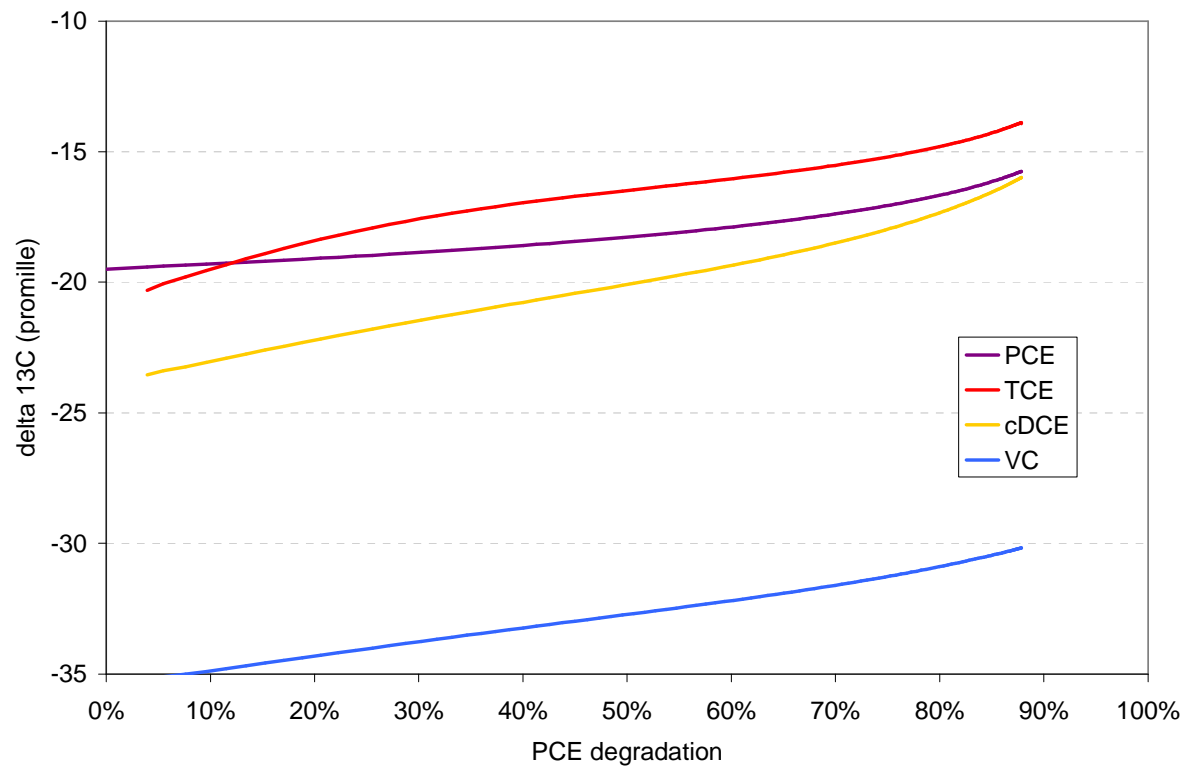


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# Multiple sources vs. bio-fractionation

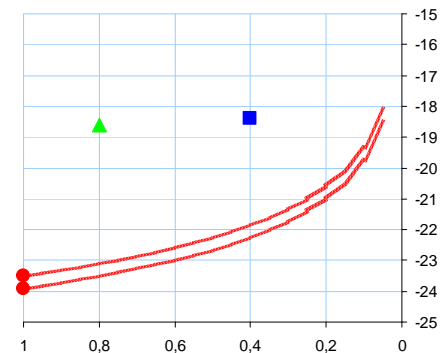


# Fitting of area 3 „fingerprint“



Optimized fit parameters

	$\epsilon$
<b>PCE</b>	<b>-1,8 ‰</b>
TCE	-3,5 ‰
DCE	-12 ‰

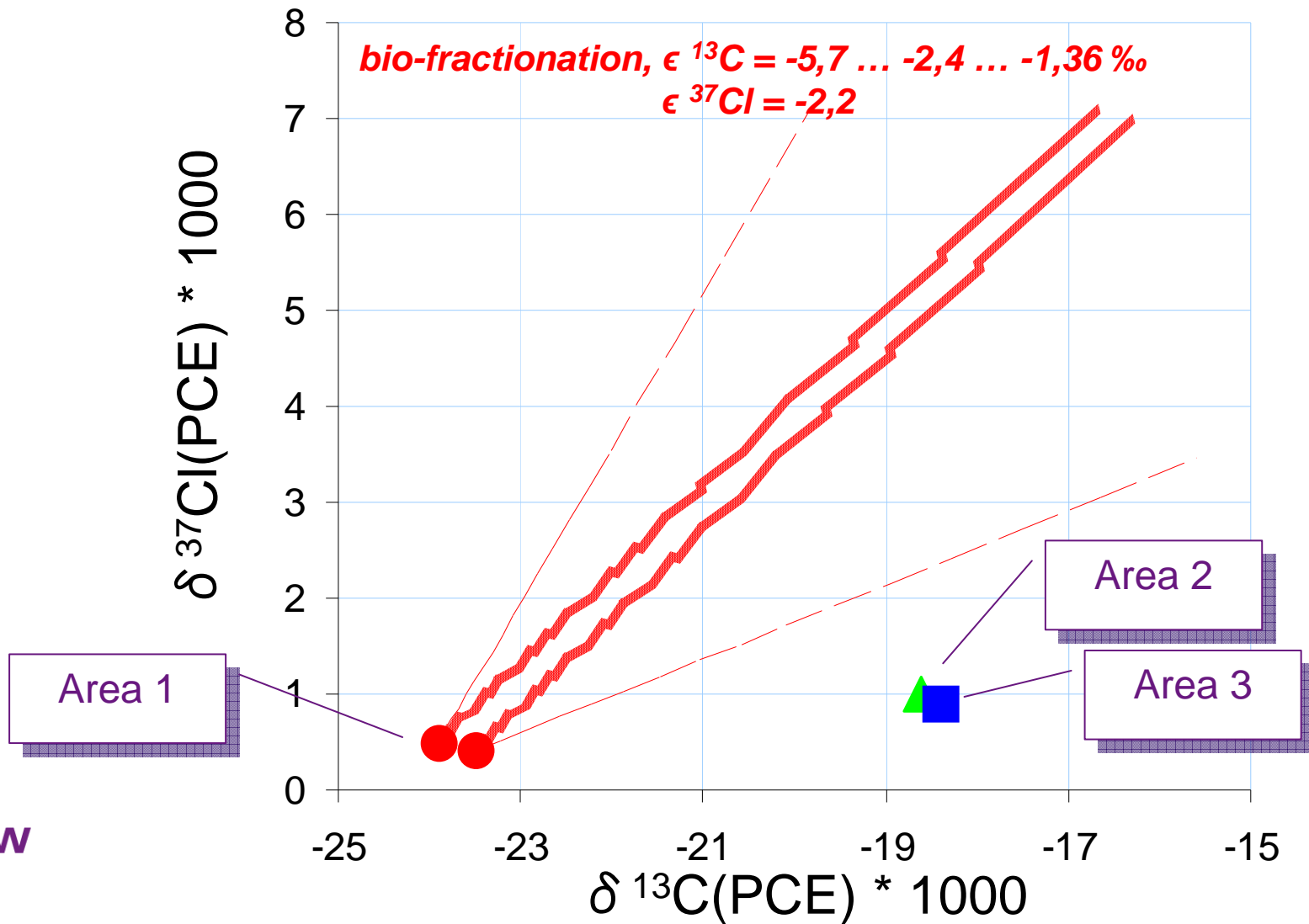


- Fractionation model (PHREEQC) including all chlorinated ethenes according to analyzed species distribution area 3.
- The resulting  $\epsilon$ -factor falls into the lower/medium range



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# Multiple sources vs. bio-fractionation



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# Conclusion (1)

- The CSIA campaign clearly proved:
  - **Area 1** is caused by a single PCE source as both  $^{13}\text{C}$ -PCE and  $^{37}\text{Cl}$  signatures do not show relevant variation within the area
  - **Area 2** is not caused by the same source as area1. The isotopic composition of PCE in area 2 cannot result from biotic degradation of the source material when assuming plausible enrichment factors.
    - Postulating a sufficient enrichment of  $^{13}\text{C}$ -PCE ( $\epsilon \approx -22!$ ) would go along with an extremely light daughter product composition, which is not found on site.



## Conclusion (2)

- The CSIA campaign clearly proved:
  - **Area 3** is not caused by the same source as area1. Its isotopic composition of PCE could only result from biotic degradation at extremely strong enrichment factors.
    - Fitting the isotopic fingerprint using a fractionation model shows that rather “normal” enrichment factors must be assumed.
    - At these enrichment factors, the isotopic ratios at area 3 cannot be derived from the same source material as present at area1



# END



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