# Integrated Assessment of Anaerobic Reductive Dechlorination of Chlorinated Ethenes by Stable Isotope Analysis and Microbial Techniques

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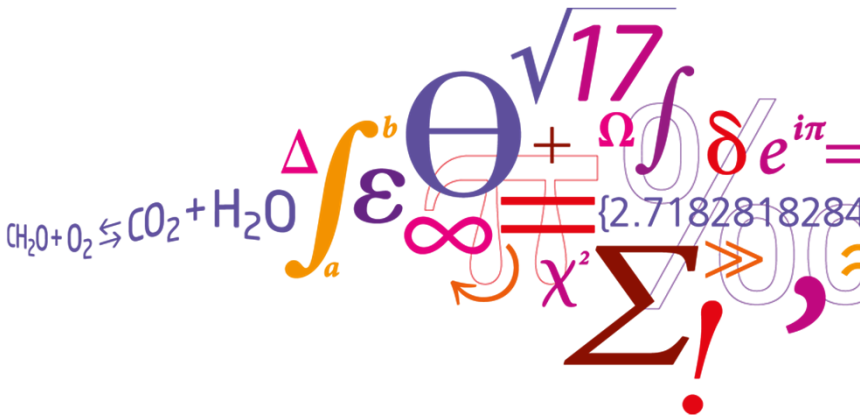
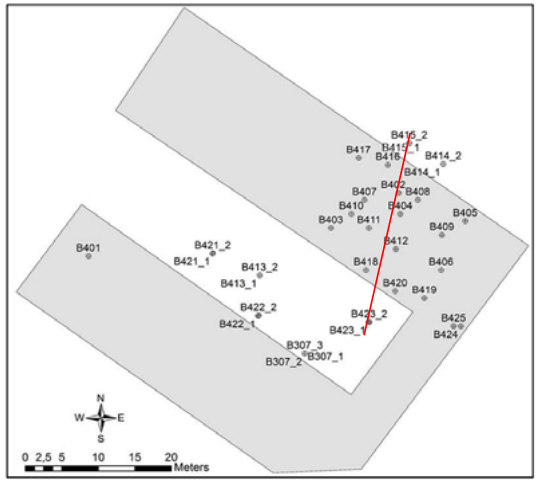


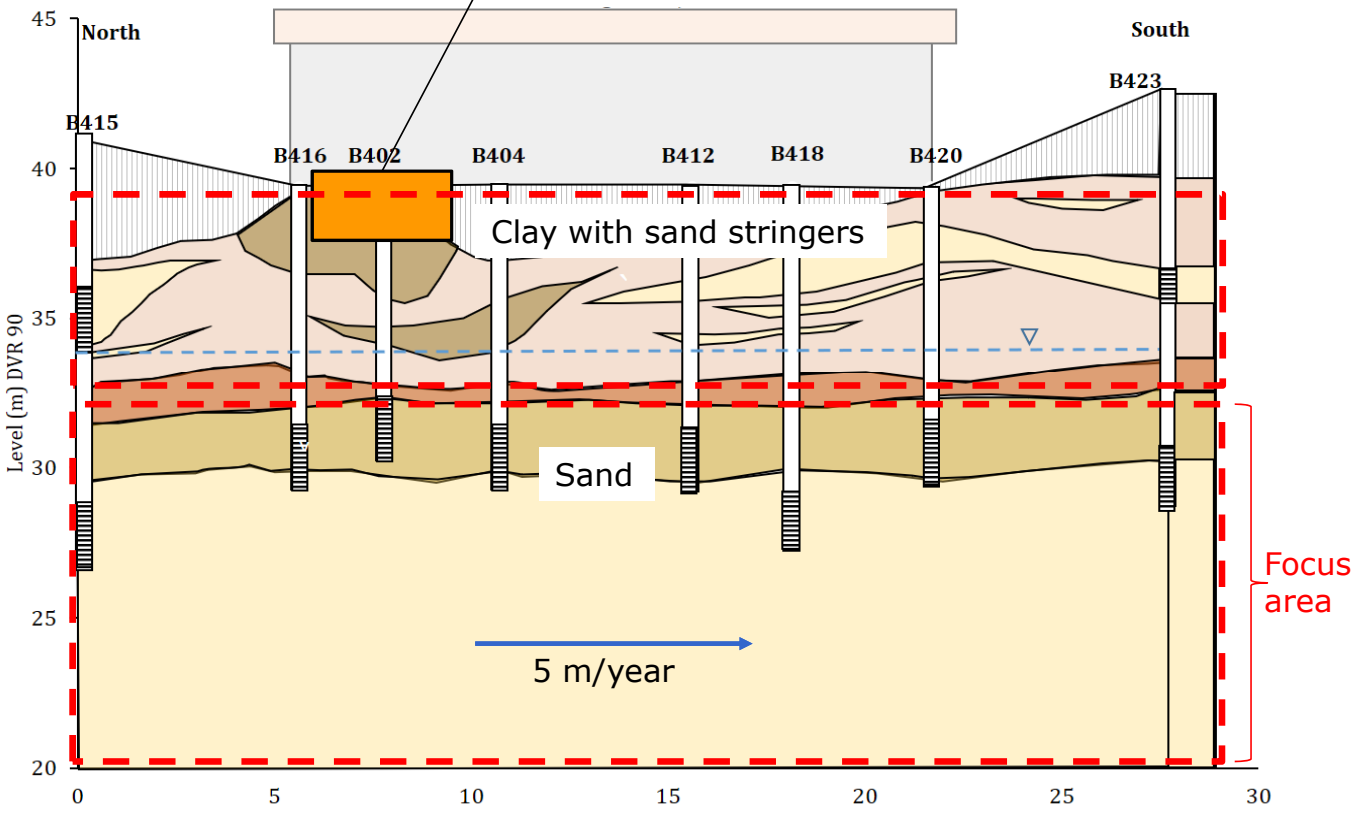

DTU Environment
Department of Environmental Engineering

# Site description

- A machine- and surface treatment company was situated at the site from 1982-2001. Applied TCE as degreaser from 1990-2001.

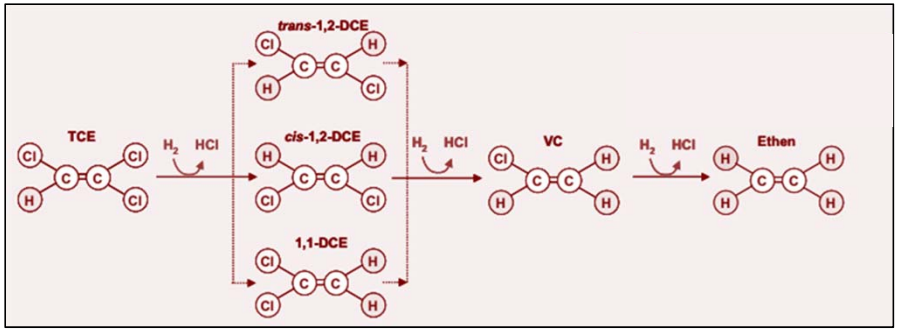
- 26 boreholes (several with two screens)



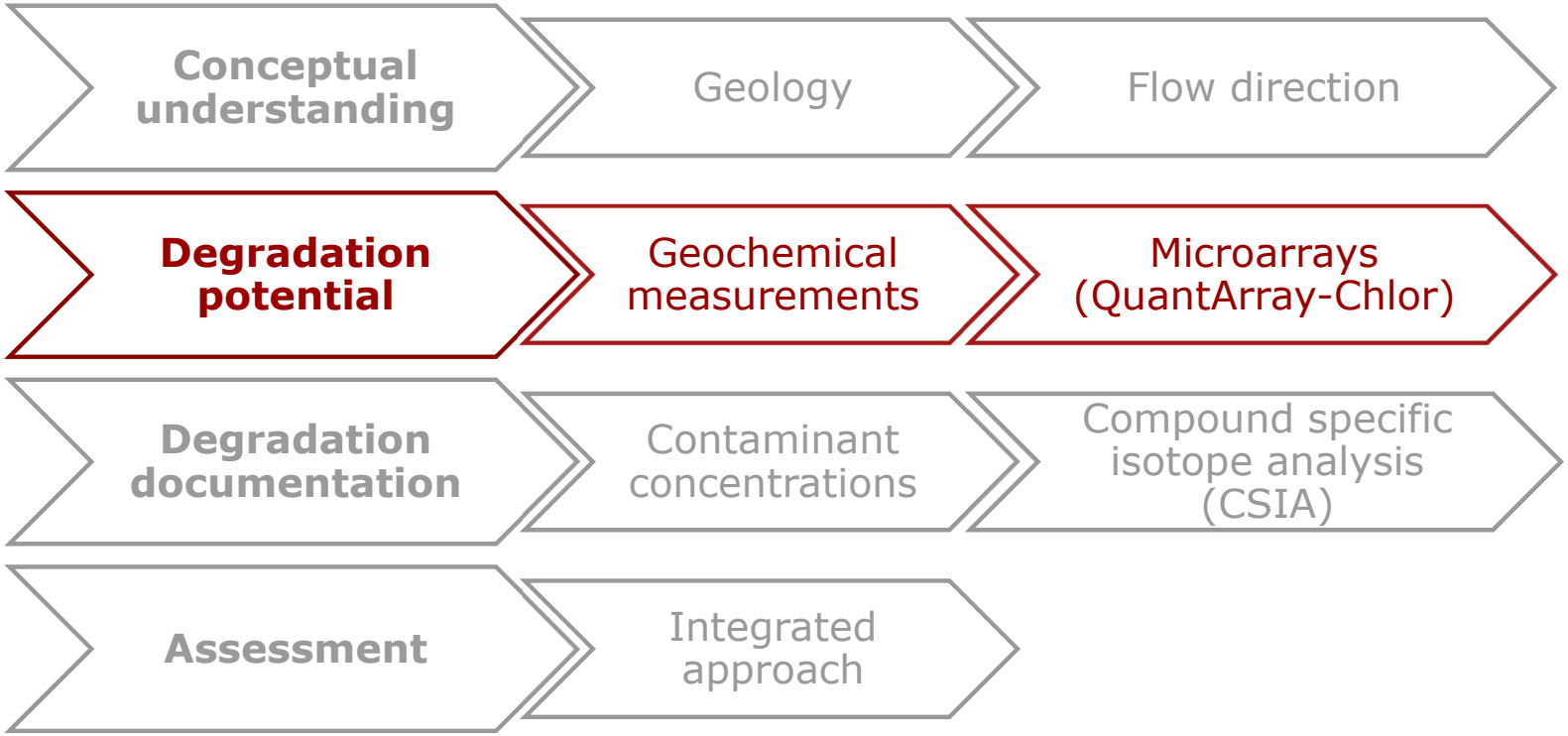



# Approach for integrated assessment

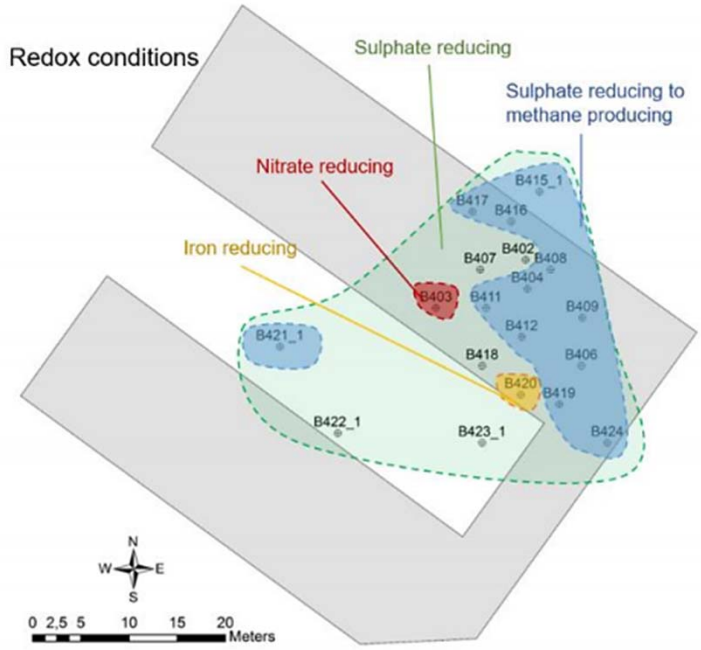
| | | |
|---|---|---|
| **Conceptual understanding** | Geology | Flow direction |
| **Degradation potential** | Geochemical measurements | Microarrays (QuantArray-Chlor) |
| **Degradation documentation** | Contaminant concentrations | Compound specific isotope analysis (CSIA) |
| **Assessment** | Integrated approach | |

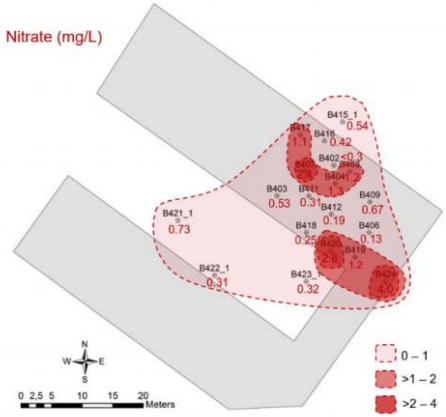


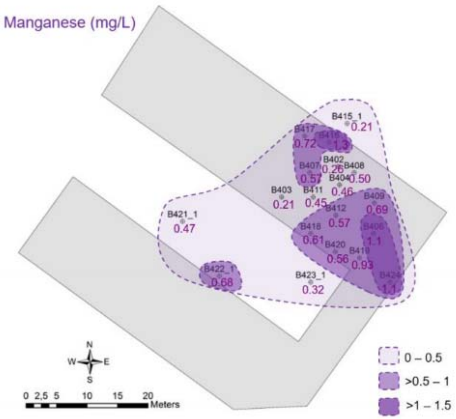
# Degradation potential

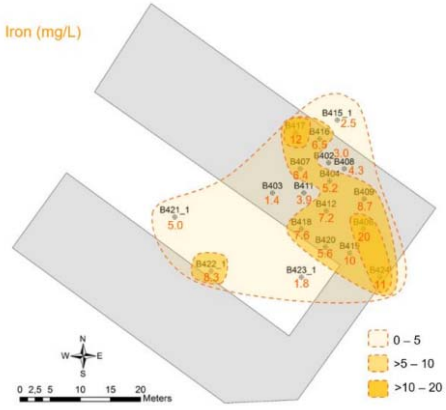


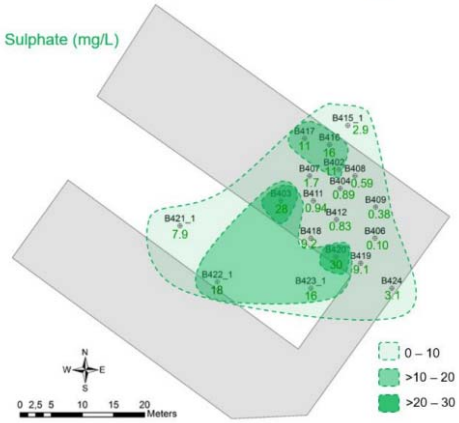
# Redox conditions

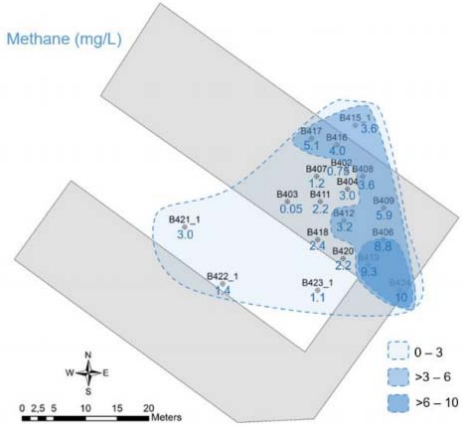


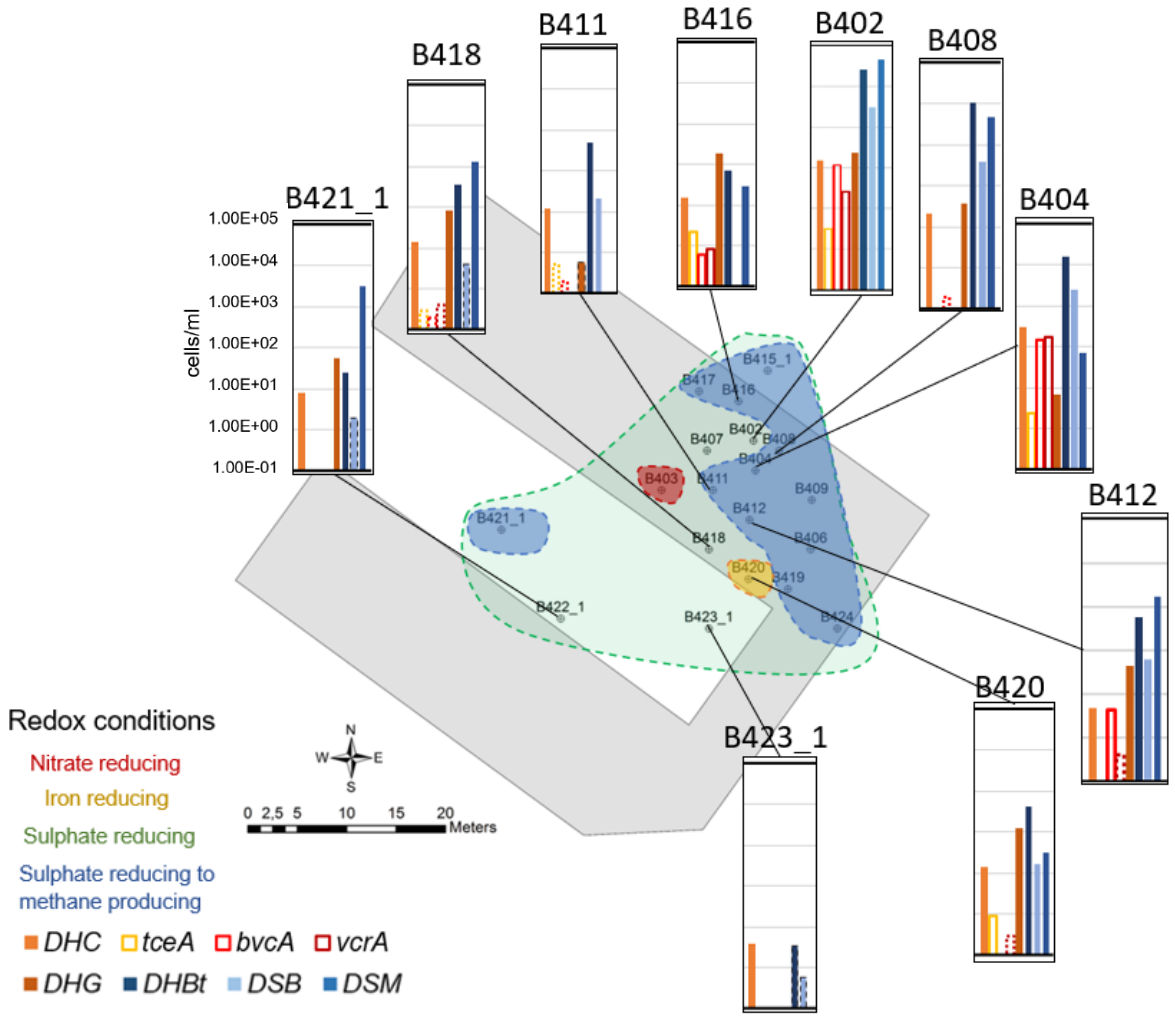



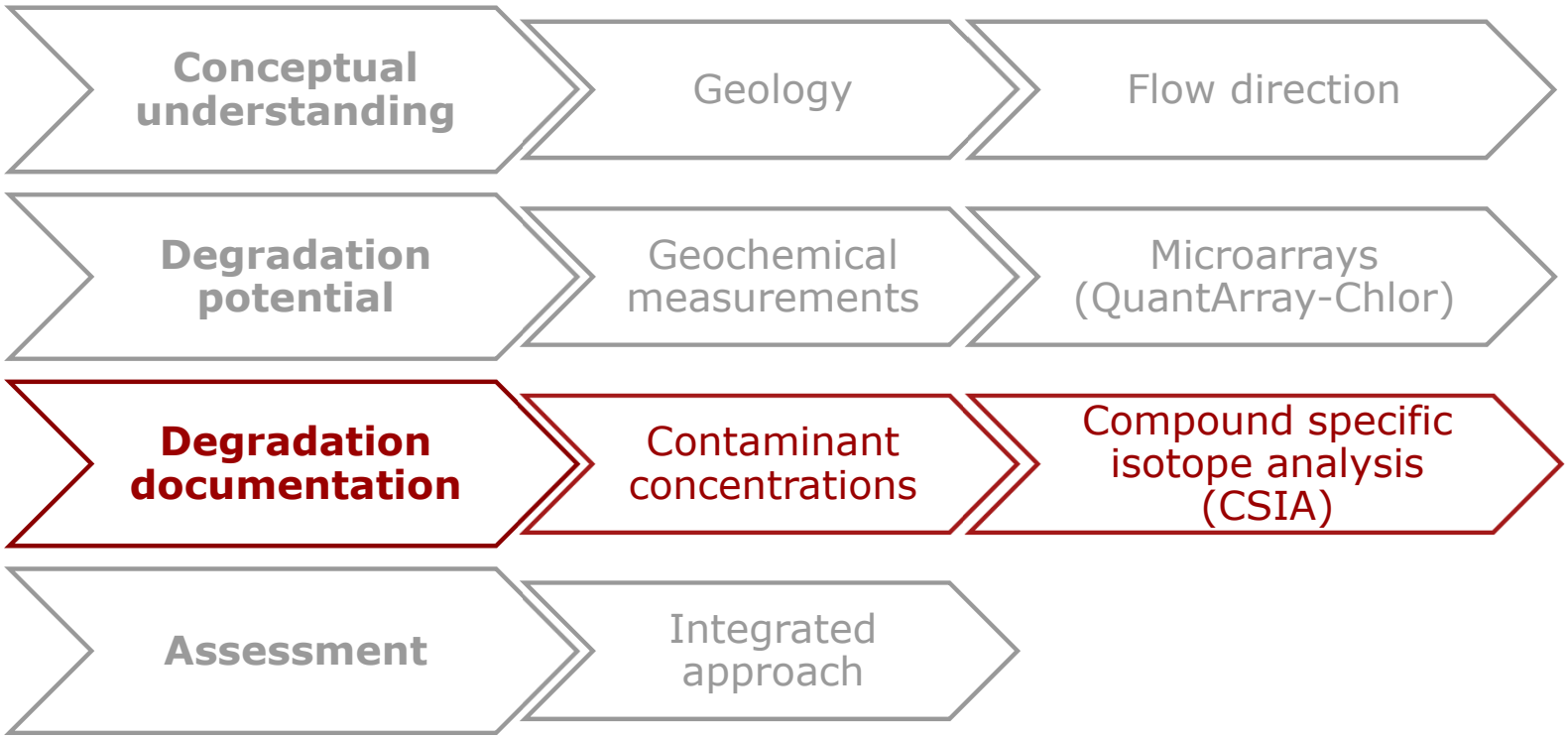



# Microbial analysis

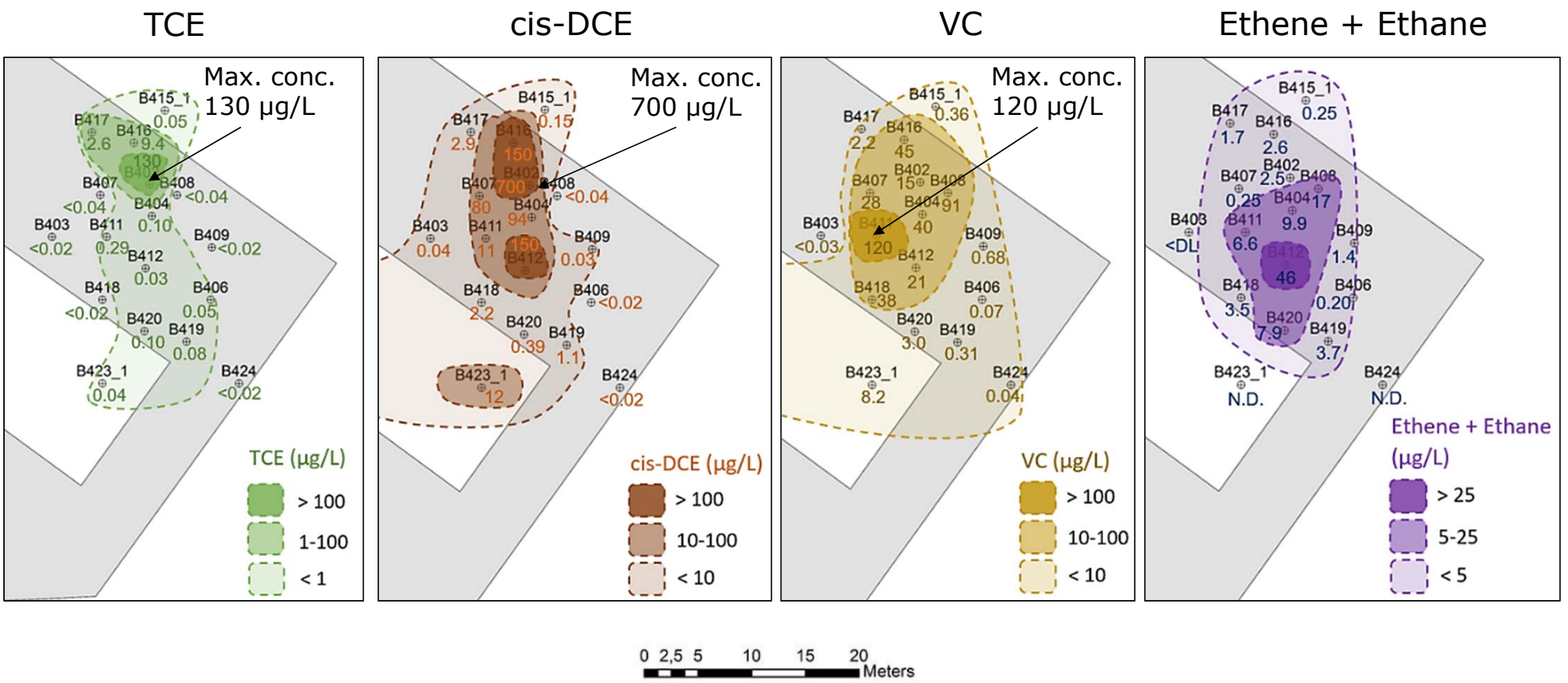



- Abundance of *DHC* and *bvcA* and *vcrA* genes highest in B404
- Functional genes are present in boreholes downstream source

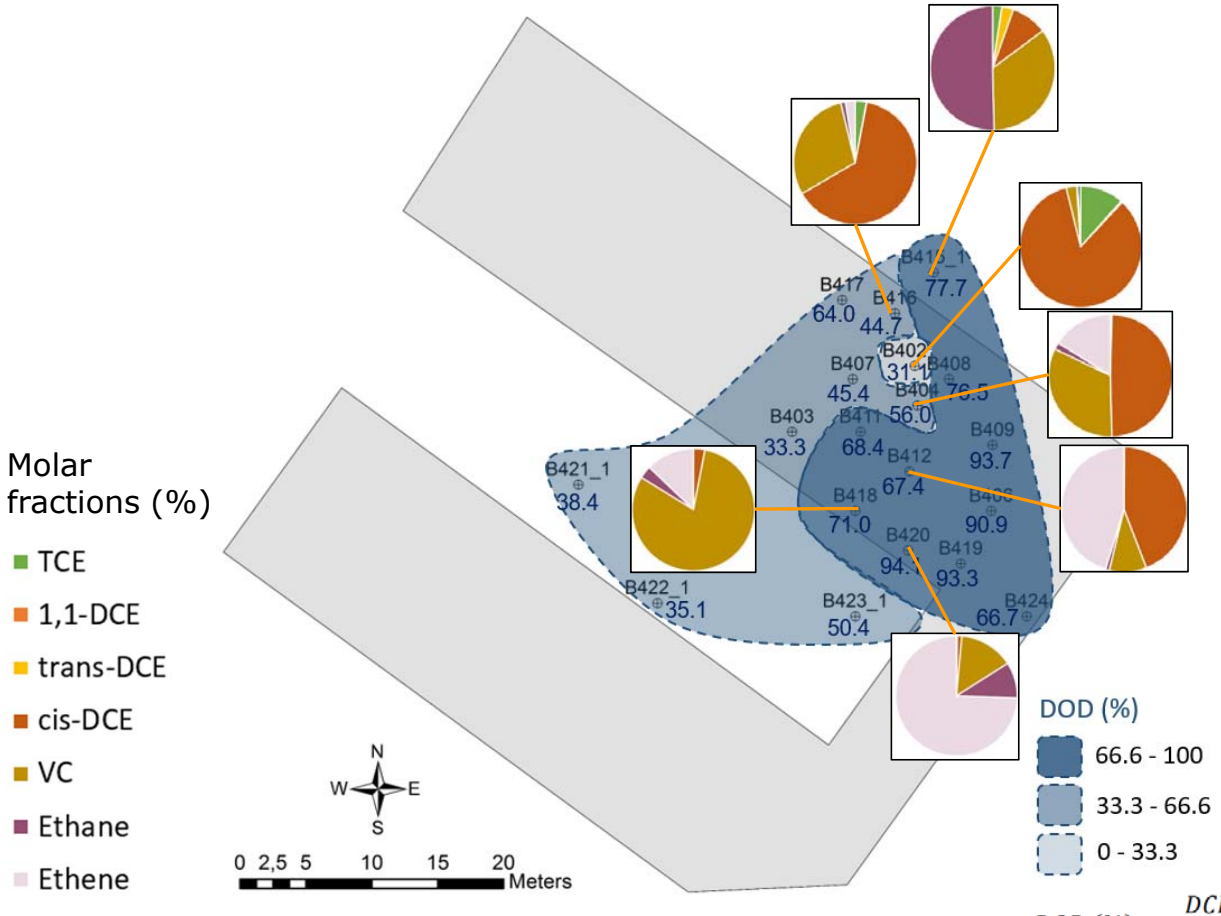
# Degradation documentation



# Contaminant concentrations



# Molar fractions and degree of dechlorination

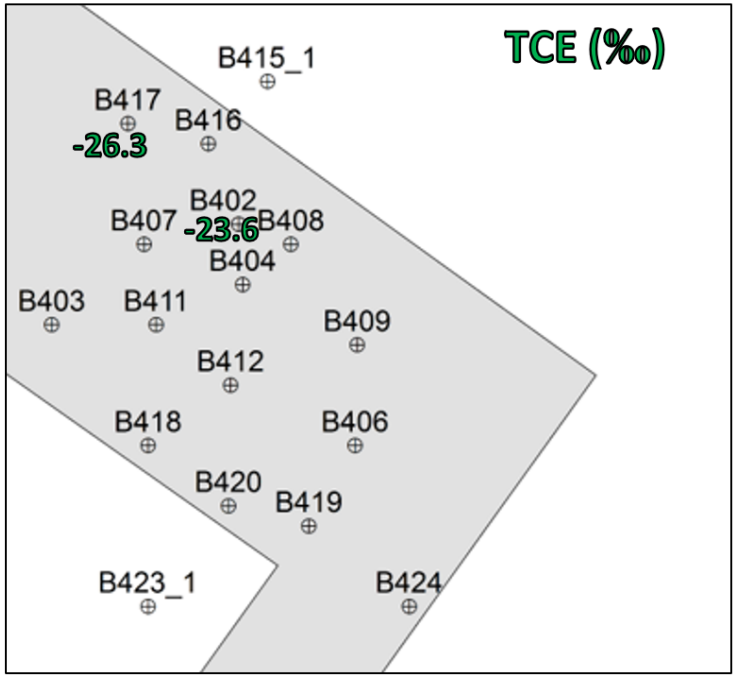



$$DOD\ (\%) = \frac{DCE + 2 \cdot VC + 3 \cdot Ethene + 3 \cdot Ethane}{3 \cdot (TCE + DCE + VC + Ethene + Ethane)} \cdot 100\%$$

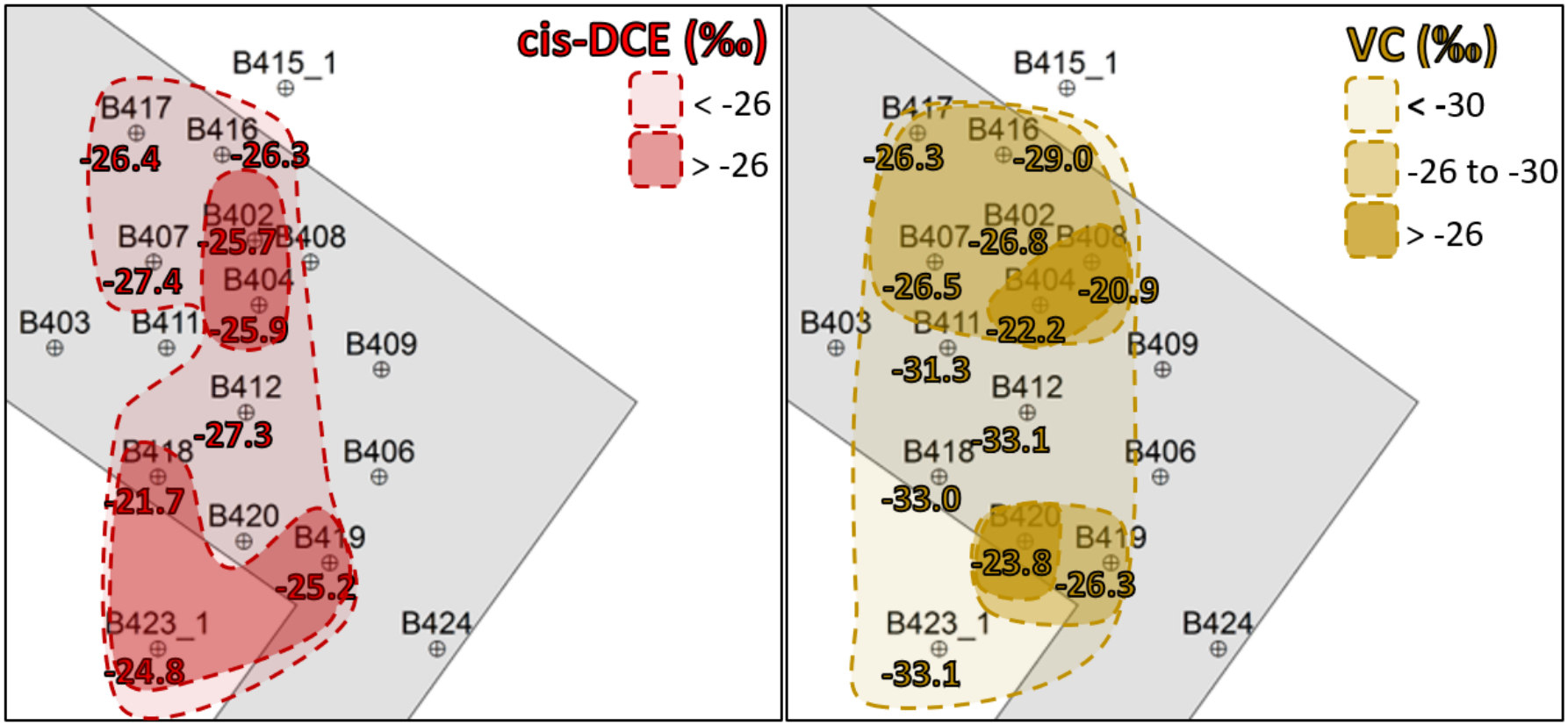
# $\delta^{13}C$ value of the mother compound

- Lowest observed $\delta^{13}C$ value of TCE is -26.3 ‰
- Calculated initial $\delta^{13}C$ value in source of -25.5 ‰

$$\delta^{13}C_{average} = \frac{[\mathrm{TCE}] \cdot \delta^{13}C_{\mathrm{TCE}} + [\mathrm{cisDCE}] \cdot \delta^{13}C_{\mathrm{cisDCE}} + [\mathrm{VC}] \cdot \delta^{13}C_{\mathrm{VC}}}{[TCE] + [cisDCE] + [VC]}$$

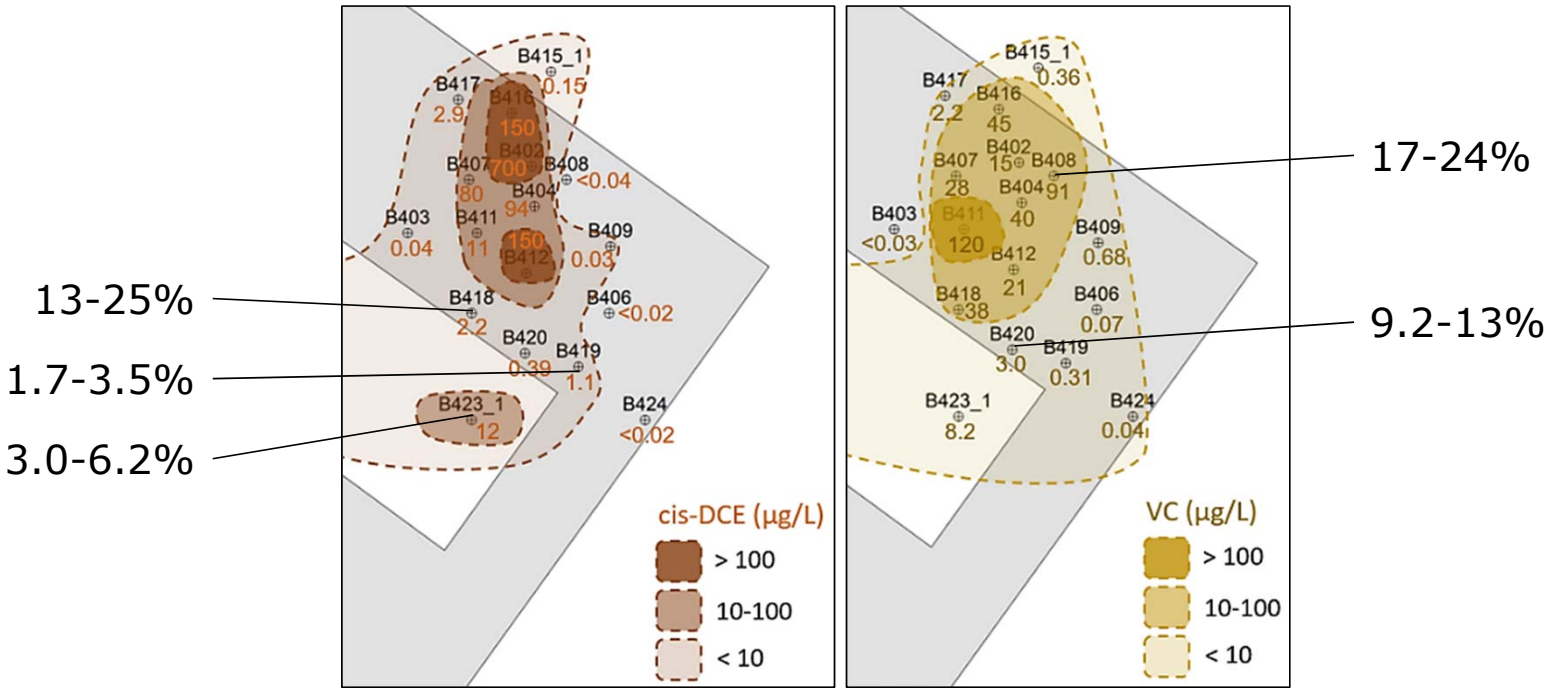


# $\delta^{13}C$ values of the degradation products



# Extent of degradation

Estimation of the degradation extent can be done by(*Badin et al. 2016*): $D = 1 - \exp\left(\frac{\Delta\delta^{13}C}{\varepsilon}\right)$



# Degradation rate

• Degradation rate (*Morrill et al. 2005*):

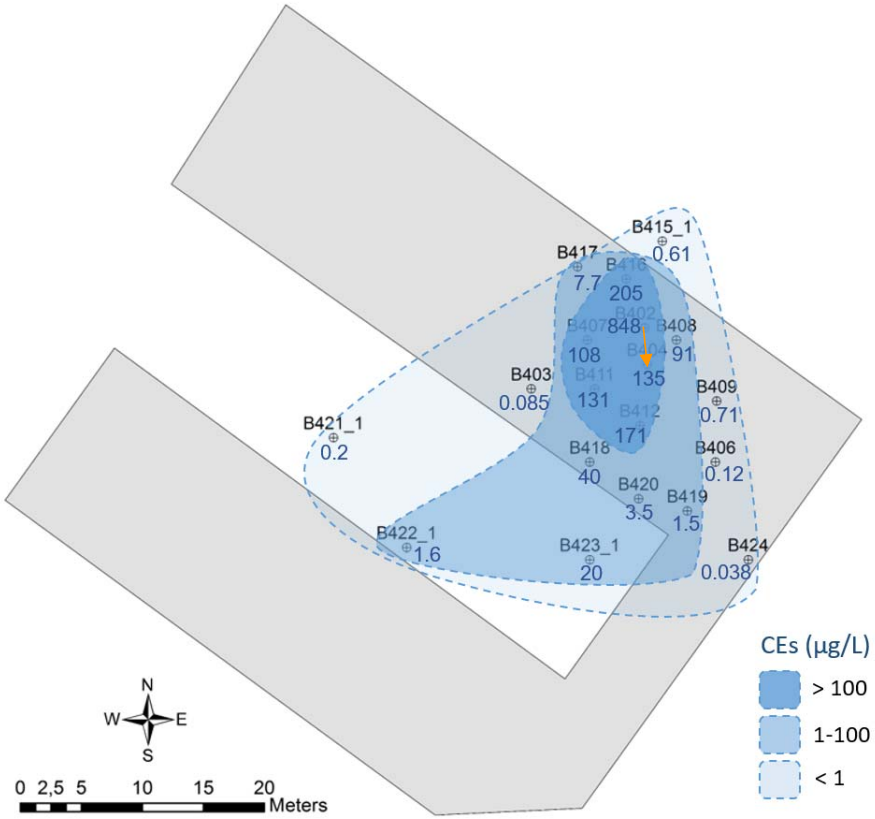
$$k_{12} = \frac{-(\frac{1000}{\varepsilon}) \cdot \ln(\frac{\delta^{13}C/1000 + 1}{\delta^{13}C_0/1000 + 1})}{t}$$

• Lumped enrichment factors (*Aeppli et al. 2010*):

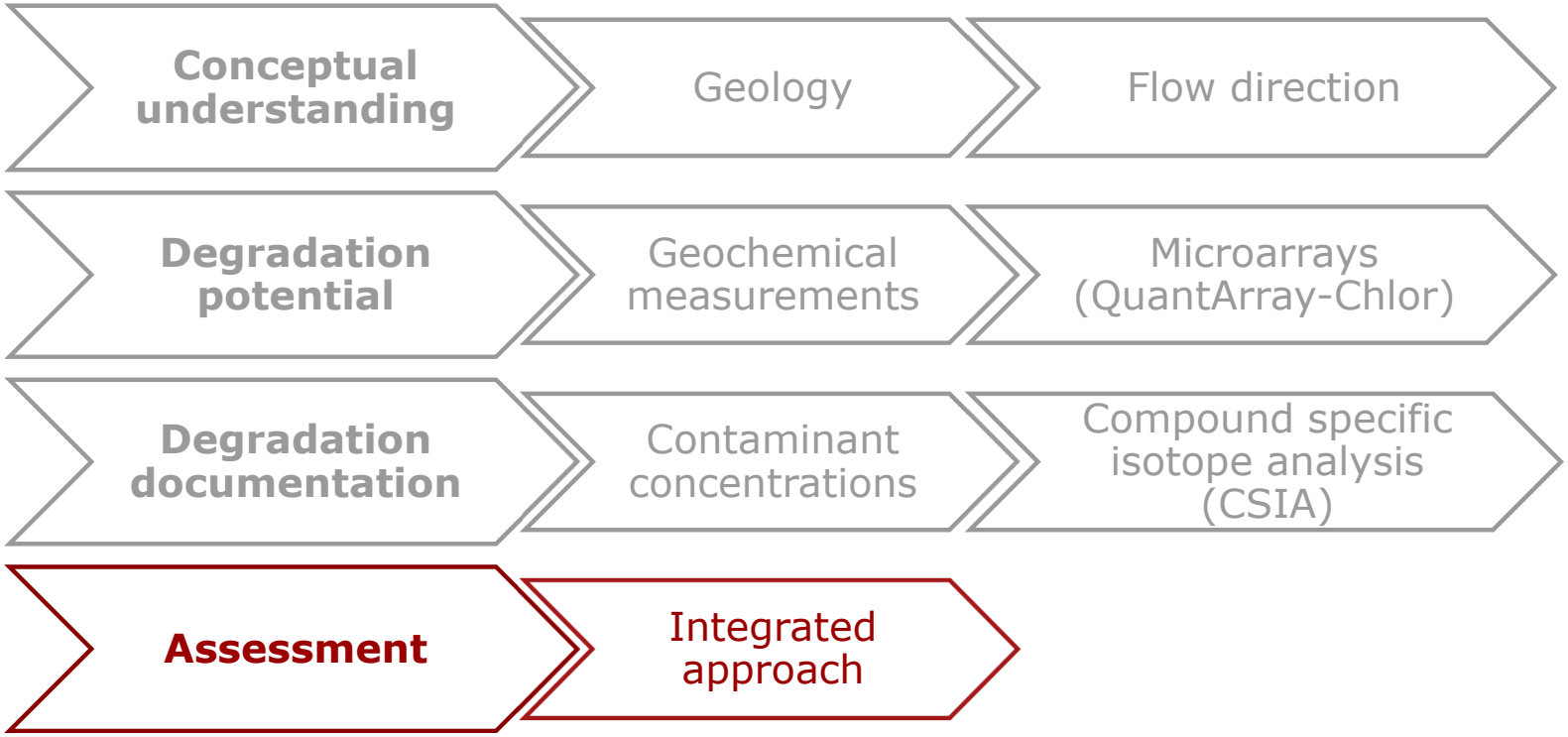
$$\varepsilon^{min}_{\sum(CE)} \approx \varepsilon_{TCE} + \varepsilon_{cis-DCE} + \varepsilon_{VC} \; and \; \varepsilon^{max}_{\sum(CE)} \approx \varepsilon_{VC}$$

• Lumped degradation (TCE → Ethene):

Conservative enrichment factors:
k(B404) = 0.021-0.052yr$^{-1}$ ($t_{½}$ = 33-13 years)
Non-conservative enrichment factors:
k(B404) = 0.042-0.075yr$^{-1}$ ($t_{½}$ = 16-9 years)



# Assessment based on integrated approach



# Assessment of degradation at the site

- **Presence of degradation products** documents degradation, however it does not document where the biodegradation occurs.

- The **biodegradation potential**, determined by the abundance of specific degraders and functional genes, was highest near the source zone and less abundant down-gradient.

- The highest enrichment in the **$\delta^{13}C$** value for cis-DCE at the front of the plume. For VC it was found near the source zone, indicating currently higher degradation near the source zone than in the past and less potential for further degradation down-gradient.

- Combination of **microbial analysis and CSIA** provide a more robust characterization of the biodegradation – where and when the degradation is occurring.

- Isotope mass balances and a **lumped variable enrichment factor** further facilitate the quantification of biodegradation.

- The **integrated approach** provided essential information for the evaluation of the occurrence, extent and rate of the natural biodegradation at the site.

# Comments on integrated approach in general

- Making a **conceptual model** is important.
- **No stand-alone method** exist to quantify and characterize degradation – you need to combine methods in order to be able to conclude anything. It is important to consider **which methods** you apply and when, also how they can be compared (spatially and temporally).
- For stable **carbon isotope** analysis it should be prioritized the highest to collect samples along the **flow line** from the source zone.
- Consider **which bacteria and genes** to look after for biodegradation potential.
- **Additional parameters** that could be included in the integrated approach:
  - Dual-isotope analysis
  - RNA analysis

# QUESTIONS?

# References

Aeppli, C., Hoftstetter, T. B., Amaral, H. I. F., Kipper, R., Schwarzenbach, R. P. and Berg, M. (2010). Quantifying in situ transformation rates of chlorinated ethenes by combining compound-specific stable isotope analysis, groundwater dating, and carbon isotope mass balances. *Environmental Science and Technology*, 44 (10), pp. 3705-3711.

Badin, A., Broholm, M. M., Jacobsen, C. S., Palau, J., Dennis, P. and Hunkeler, D. (2016). Identification of abiotic and biotic reductive dechlorination in a chlorinated ethene plume after thermal source remediation by means of isotopic and molecular biology tools. *Journal of Contaminant Hydrology*, 192, pp. 1-19.

Morrill, P. L., Lacrampe-Couloume, G., Slaterm G. F., Sleep, B. E., Edwards, E. A., McMaster, M. L., Major, D. W. and Lollar, B. S. (2005). Quantifying chlorinated ethene degradation during reductive dechlorination at Kelly AFB using stable carbon isotopes. *Journal of Contaminant Hydrology*, 76 (3-4), pp. 279-293.